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Preface

As global waste generation increases at a rapid rate, there is a dire need for waste management practices such as collection, disposal, and recycling to protect from environmental pollution. Improper disposal methods such as open-air burning and unsafe recycling have led to significant public and environmental health issues including respiratory disorders, resource depletion, and infant mortality. Adopting new waste management techniques is a necessity in order to preserve the health of the global community and ecosystem.

The field of waste management is evolving, especially as the world's population continues to grow and more solid and liquid waste are being generated by society. Staying informed of the most up-to-date research trends and findings is of the utmost importance. That is why IGI Global is pleased to offer this three-volume reference collection that will shed light on critical issues on the management of different types of wastes and new waste management technologies by providing both broad and detailed perspectives on cutting-edge theories and developments. This reference is designed to act as a single reference source on conceptual, methodological, and technical issues, as well as to provide insight into emerging trends and future opportunities within the field.

Waste Management: Concepts, Methodologies, Tools, and Applications is organized into seven distinct sections that provide comprehensive coverage of important topics. The sections are:

1. Fundamental Concepts and Theories;
2. Development and Design Methodologies;
3. Tools and Technologies;
4. Utilization and Applications;
5. Organizational and Social Implications;
6. Critical Issues and Challenges; and
7. Emerging Trends.

The following paragraphs provide a summary of what to expect from this invaluable reference tool.

Section 1, "Fundamental Concepts and Theories," serves as a foundation for this extensive reference tool by addressing crucial theories essential to the understanding of waste management. Introducing the book is "Introduction to Solid Waste and Its Management," by Prof. Hamidi Abdul Aziz (Universiti Sains Malaysia, Malaysia) and Prof. Salem S. Abu Amr (Universiti Sains Malaysia, Malaysia): a great foundation laying the groundwork for the basic concepts and theories that will be discussed throughout the rest of the book. Section 1 concludes and leads into the following portion of the book with a nice segue chapter, "A Review of Emerging Contaminants in Water: Classification, Sources, and Potential Risks," by Prof. Alexandros I. Stefanakis (University of Brighton, UK) and Prof. Julie A. Becker (University of the Sciences, USA).

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Section 2, "Development and Design Methodologies," presents in-depth coverage of the conceptual design and architecture of waste management. Opening the section is "Integrated Leachate Treatment Technology," by Prof. Zawawi Daud (Universiti Tun Hussein Onn Malaysia, Malaysia) and Prof. Halizah Awang (Universiti Tun Hussein Onn Malaysia, Malaysia). Through case studies, this section lays excellent groundwork for later sections that will get into present and future applications for waste management. The section concludes with an excellent work by Prof. David de la Varga (Sedaqua, Spain), Prof. Manuel Soto (University of A Coruña, Spain), Prof. Carlos Alberto Arias (Aarhus University, Denmark), Prof. Dion van Oirschot (Rietland bvba, Belgium), Prof. Rene Kilian (Kilian Water, Denmark), Prof. Ana Pascual (AIMEN, Spain), and Prof. Juan A. Álvarez (AIMEN, Spain), "Constructed Wetlands for Industrial Wastewater Treatment and Removal of Nutrients."

Section 3, "Tools and Technologies," presents extensive coverage of the various tools and technologies used in the implementation of waste management. The first chapter, "Economic Instruments for Sustainable Environmental Management," by Prof. Günay Kocasoy (Bogazici University, Turkey), lays a framework for the types of works that can be found in this section. The section concludes with "Scientific Insights Into Modified and Non-Modified Biomaterials for Sorption of Heavy Metals From Water," by Prof. Tawfik A. Saleh (Department of Chemistry, King Fahd University of Petroleum and Minerals, Saudi Arabia), Salawu Prof. Omobayo Adio (King Fahd University of Petroleum and Minerals, Saudi Arabia), Prof. Prakash Parthasarathy (Independent Researcher, India), and Prof. Gaddafi I. Danmaliki (King Fahd University of Petroleum and Minerals, Saudi Arabia). Where Section 3 described specific tools and technologies at the disposal of practitioners, Section 4 describes the use and applications of the tools and frameworks discussed in previous sections.

Section 4, "Utilization and Applications," describes how the broad range of waste management efforts has been utilized and offers insight on and important lessons for their applications and impact. The first chapter in the section is "Waste Disposal: Sustainable Waste Treatments and Facility Siting Concerns," written by Prof. Hossein Farraji (Universiti Sains Malaysia, Malaysia), Prof. Nastaein Qamaruz Zaman (Universiti Sains Malaysia, Malaysia), and Prof. Parsa Mohajeri (Universiti Sains Malaysia, Malaysia). This section includes the widest range of topics because it describes case studies, research, methodologies, frameworks, architectures, theory, analysis, and guides for implementation. The breadth of topics covered in this section is also reflected in the diversity of its authors, from countries all over the globe. The section concludes with "Bioremediation of Pharmaceutical Wastes," by Prof. Alka Bali (Panjab University, India), a great transition chapter into the next section.

Section 5, "Organizational and Social Implications," includes chapters discussing the organizational and social impact of waste management. The section opens with "Legislation for Solid Waste Management," by Prof. Azhar Abdul Halim (Universiti Kebangsaan Malaysia, Malaysia) and Prof. Siti Hafizan Hassan (Universiti Sains Malaysia, Malaysia). This section focuses exclusively on how these technologies affect human lives, either through the way they interact with each other or through how they affect behavioral/workplace situations. The section concludes with "Human Overpopulation and Water Pollution: Reduction of Microbial Pollution by Vertical Flow Constructed Wetland," by Prof. Gargi Sharma (Malviya National Institute of Technology, India) and Prof. Pravin Kumar Mutiyar (National Mission for Clean Ganga, India).

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Section 6, "Critical Issues and Challenges," presents coverage of academic and research perspectives on waste management tools and applications. The section contains the chapter "Nanotechnology for Filtration-Based Point-of-Use Water Treatment: A Review of Current Understanding," by Prof. Kathryn Gwenyth Nunnelley (University of Virginia, USA) and Prof. James A. Smith (University of Virginia, USA). The chapter in this section looks into theoretical approaches and offers alternatives to crucial questions on the subject waste management.

Section 7, "Emerging Trends," highlights areas for future research within the field of waste management, opening with "Novel Bioremediation Methods in Waste Management: Novel Bioremediation Methods," by Prof. Charu Gupta (Amity University, India) and Prof. Dhan Prakash (Amity University, India). This section contains chapters that look at what might happen in the coming years that can extend the already staggering amount of applications for waste management. The final chapter of the book looks at an emerging field within waste management, in the excellent contribution, "Reverse Logistics in the Electronics Waste Industry," by Prof. Berk Ayvaz (Istanbul Commerce University, Turkey) and Prof. Ali Görener (Istanbul Commerce University, Turkey).

Although the primary organization of the contents in this multi-volume work is based on its seven sections, offering a progression of coverage of the important concepts, methodologies, technologies, applications, social issues, and emerging trends, the reader can also identify specific contents by utilizing the extensive indexing system listed at the end of each volume. As a comprehensive collection of research on the latest findings related to using technology to providing various services, *Waste Management: Concepts, Methodologies, Tools, and Applications* provides researchers, scientists, environmentalists, engineers, policymakers, government officials, academicians, and all audiences with a complete understanding of the development of applications and concepts in the management of waste products. Given the vast number of issues concerning usage, failure, success, policies, strategies, and applications of protecting the environment through the effective disposal of waste products in countries around the world, *Waste Management: Concepts, Methodologies, Tools, and Applications* addresses the demand for a resource that encompasses the most pertinent research in technologies being employed to globally bolster the knowledge and applications of managing societal waste products.

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Section 1

Fundamental Concepts and Theories

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Chapter 1
Introduction to Solid Waste and Its Management

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ABSTRACT

Municipal Solid Waste (MSW) disposal has become an increasingly serious problem in many parts of the world. In general, greater economic prosperity and a higher percentage of urban population correspond to a greater amount of solid waste produced. However, less effort has been exerted in the proper management of solid wastes produced by urban dwellers, particularly in developing countries. This chapter introduces the basic MSW rules. MSW composition, production, and collection are also highlighted. Furthermore, the concept of landfilling and waste decomposition is discussed in this chapter.

INTRODUCTION

Growing population and industrial development have increased waste generated by urban areas. Municipal solid waste (MSW) can be defined as the wastes arising from domestic, commercial, industrial, and institutional activities in urban areas (Bartone 1990; Ravindra et al., 2015). In developing countries, MSW disposal has become an ever-increasing problem in many parts of the world, especially in the developing countries (Al-Khatib et al., 2014; Caniato et al., 2014). Generally, the greater the economic prosperity and the higher the percentage of urban population, the greater is the amount of solid waste produced. This tremendous increase in the amount of MSW generated is due to changing lifestyles, food habits and living standards of the urban population. Despite this growth, there has been less parallel effort to properly manage the solid wastes produced by the urban dwellers, especially in the developing countries.

MSW are defined by EPA as a waste consisting of everyday items "used and then thrown away, such as product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances, paint, and batteries," which come from homes, schools, hospitals, and businesses (US EPA, 2013).

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Gershman et al. (1986) described MSW as rubbish from residences, institutions, and commercial establishments and non-hazardous light industrial refuse. McBean et al. (1995) defined MSW as residential solid waste produced from the house, and outdoor activities of a single or multi-family house. Dixon and Jones (2005) defined MSW as a mixture of waste primarily originating from residential and commercial establishments. The Malaysian Solid Waste and Public Cleansing Management Act of 2007 (Act 672) defines MSW as any substance requiring disposal because it is broken, worn out, contaminated, or physically spoiled. The management of MSW that has already been generated can be roughly divided into four methods: recycling, composting, thermal treatment with energy recovery, and landfilling. However, the generation of wastes can be reduced by various means, such as a better design of products and packaging, and therefore "Reduction" is placed at the very top of the waste management hierarchy.

SOLID WASTE PRODUCTION

Solid waste generally refers to unused solid materials generated as a result of human activities. Many of these items can be considered as waste such as domestic rubbish, sewage sludge, wastes from manufacturing activities, packaging items, discarded cars, discarded electronic devices, garden waste, old paint containers etc. Accordingly, all human daily activities can give rise to a large variety of different wastes arising from different sources (Ngoc & Schnitzer, 2009). Based on their sources, solid waste can be classified into various types which include MSW, hazardous waste, agricultural waste and industrial waste (Tchobanoglous et al., 1993). In Malaysia; the generation of MSW has significantly increased in recent years, ranging between 0.5 - 2.5kg per capita per day (or a total of 25000 - 30000 tons per day). More than 70% of the generated wastes are collected using both curbside and communal centers with a collection frequency varying from daily to every two days (Johari et al., 2014).

MSW defined as a waste collected from households, in addition to the commercial waste collected by a municipality but it generally excludes hazardous wastes. Because urbanization and population growth have rapidly increased the rate of MSW production and disposal in many cities of the world, the management of MSW has emerged as a major concern around the world particularly the rapidly developing countries.

According to Tanaka (2006), the generation of solid waste is expected to increase steadily along with economic growth if we continue the lifestyle of mass production, mass consumption and mass disposal (Figure 1).

It has been reported by Chong et al. (2005) that solid waste is one of the biggest environmental problems in Malaysia and the generation rate of solid waste is expected to increase tremendously due to the rapid increase in population and economic growth in the country.

Table 1 illustrates the annual MW generation in tons by weight in South East and East Asian Countries. China has the highest waste generation in the region, followed by South Korea, Japan and Indonesia. Currently, there is no data on municipal waste generation at the national level for Cambodia and Mongolia. But in Phnom Penh, the capital of Cambodia, the amount of municipal waste is observed. Actual statistics of municipal waste generation is illustrated in countries like Brunei Darussalam, Phnom Penh - Cambodia, PR China, Indonesia, Republic of Korea, Lao PDR, Mandalay in Myanmar, Singapore, Thailand and Vietnam. Most of the member countries do not have the data and information on the actual municipal waste generation, so that estimated and/or projected amount of municipal waste generation

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Figure 1. Predicted solid waste generation (Tanaka, 2006)

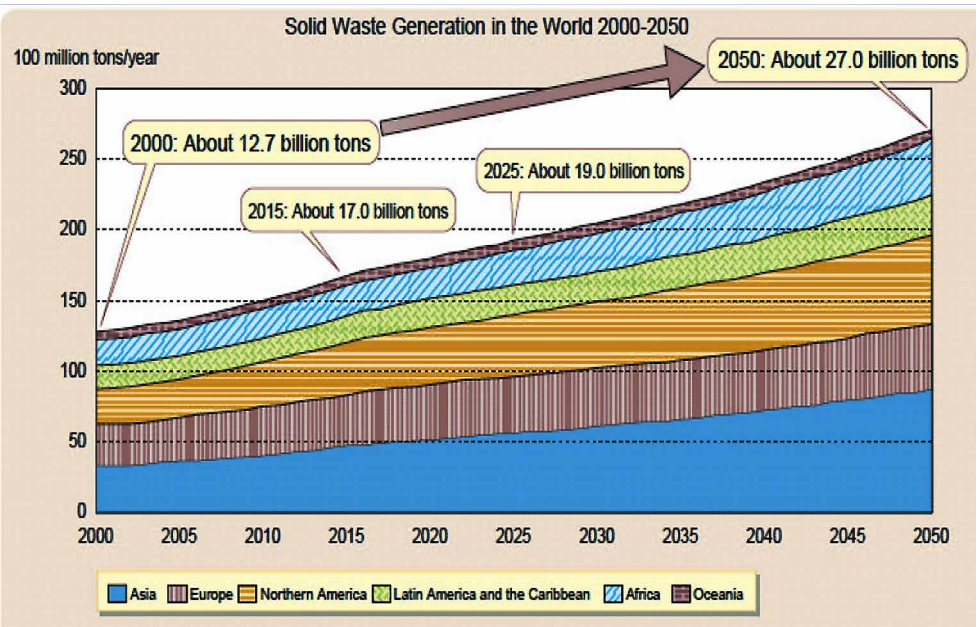

Table 1. Municipal Waste Generation and population in East, West, South and North Zone (Velumani et al., 2009)

Zone	Number of Houses	Population	MSW Generated in Tons / Day			
			Degradable	Recyclable	Inert	Total
East	63,355	2,87,553	102	7.2	22.4	131.6
West	59,838	2,66,717	114.4	7.9	21.4	143.7
South	46,509	2,38,571	120.4	8.1	19.1	147.6
North	59,007	3,01,047	109.4	7.8	23.9	141.1
Total	2,28,709	10,93,888	446.2	31.0	86.8	564.0

can be noticed. This is so in countries like Malaysia and Philippines' Metro Manila. The MW recycled is the highest in South Korea, followed by Singapore while other member countries do not have sufficient data on recycled MW.

The composition of the waste is a description of the contents of the waste. In addition to providing important information about the way to handle the waste, the composition tells us about the people who generated the waste. The composition of waste varies widely from place to place, especially country to country. Table 2 shows the average composition and amounts of waste for low, medium and high-income countries.

The most striking difference that can be seen is the difference in organic content which is much higher in the low income countries than the high income countries and the paper and plastic content which is much higher in higher income countries than low income countries. This shows the difference

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Table 2. Relative composition of household waste in low, medium and high-income countries (INTOSAI working group on environmental auditing, 2002)

	Parameter	Low-Income Countries	Medium-Income	High-Income Countries
Contents	Organic (putrecible), %	40 to 85	20 to 65	20 to 30
	Paper, %	1 to 10	15 to 30	15 to 40
	Plastics, %	1 to 5	2 to 6	2 to 10
	Metal, %	1 to 5	1 to 5	3 to 13
	Glass, %	1 to 10	1 to 10	4 to 10
	Rubber, leather, etc., %	1 to 5	1 to 5	2 to 10
	Other, %	15 to 60	15 to 50	2 to 10
Physical and chemical properties	Moisture content, %	40 to 80	40 to 60	5 to 20
	Specific weight, kg/m3	250 to 500	170 to 330	100 to 170
	Calorific value, kcal/kg	800 to 1100	1000 to 1300	1500 to 2700

in consumption pattern, cultural and educational differences. In higher income countries, the usage of disposable material, magazines and packaged food is used in higher quantity that results in a waste having higher calorific value, lower specific density, and lower moisture content. In case of lower income countries, the usage of fresh vegetables to packaged food is much higher and mostly materials that are reusable are used. This results in a waste composition that has high moisture content, high specific weight and low calorific value. This shows how waste statistics can be used to describe the life style of the people and also their income.

MUNICIPAL WASTE COMPOSITION

Composition is the term used to describe waste components that comprise a solid waste stream and its relative distribution, which is usually based on weight percentage. Waste components are significantly affected by social and economic factors, including population increase, consumption growth, changes in consumption patterns, and technological development of waste treatment systems (Buttol et al., 2007). Waste composition is influenced by factors such as culture, economic development, climate, and energy sources. Composition affects how often waste is collected and how it is disposed. In the MSW stream, waste is normally classified as organic and inorganic. Waste composition is categorized as organic, paper, plastic, glass, metal, and "others." These categories can be further refined. However, these six categories are often sufficient for general solid waste planning purposes. Table 3 describes the different types of waste and their sources.

An effective waste management and minimization strategy is practically impossible without reliable information on waste characteristics. Adequate information on waste characteristics is important to assess the effects of different waste types and to estimate the age of landfills. However, dependable information on MSW characteristics is difficult to achieve (Idris et al., 2004). MSW composition is provided in Table 3 and Figure 2.

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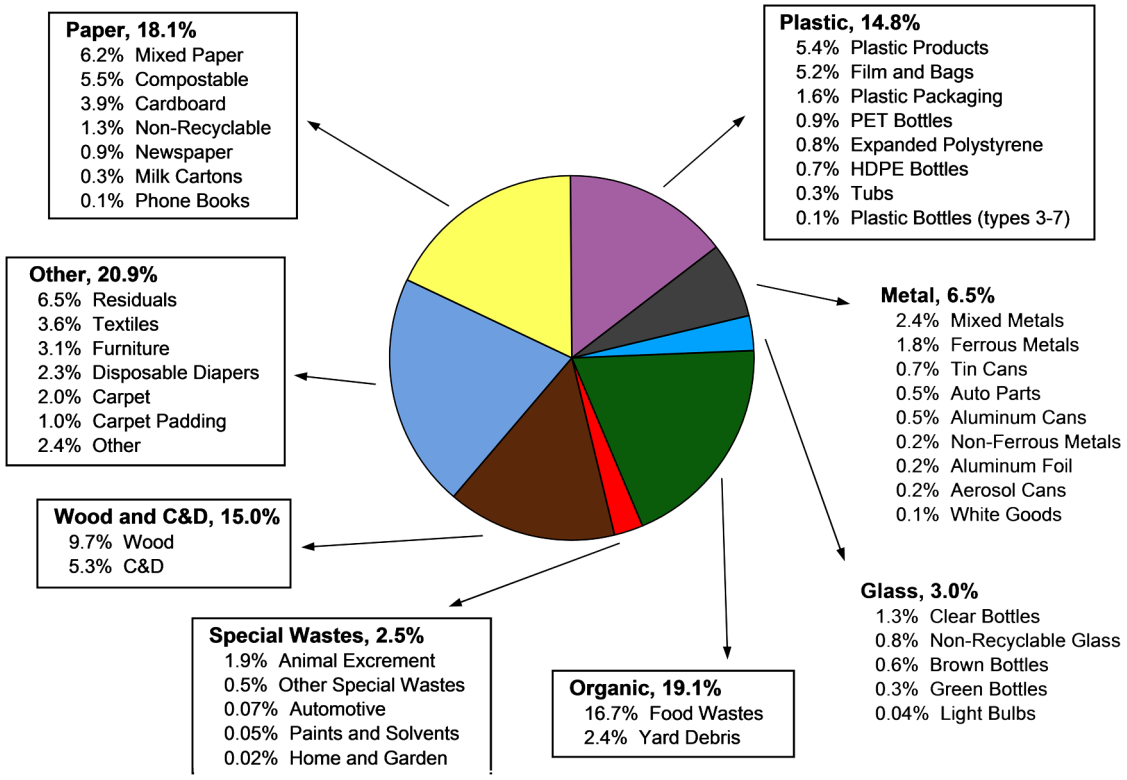
Table 3. Type and source of solid waste

Organic	Food scraps, yard (leaves, grass, brush) waste, wood, process residues
Paper	Paper scraps, cardboard, newspapers, magazines, bags, boxes, wrapping paper, telephone books, shredded paper, paper beverage cups. Strictly speaking paper is organic but unless it is contaminated by food residue, paper is not classified as organic
Plastic	Bottles, packaging, containers, bags, lids, cups
Glass	Bottles, broken glassware, light bulbs, colored glass
Metal	Cans, foil, tins, non-hazardous aerosol cans, appliances (white goods), railings, bicycles
others	Textiles, leather, rubber, multi-laminates, e-waste, appliances, ash, other inert materials

Figure 2. Waste composition in the world (Thurston county Waste composition study, 2009)



SOLID WASTE STORAGE, COLLECTION, AND TRANSFER

1. **Waste Collection:** Is a part of the waste management_process and involves the transfer of solid waste from the point of use and disposal to the point of treatment or landfill. Waste collection also includes the curbside collection of recyclable materials, which are technically not waste, as a part of a municipal landfill diversion program. A transfer station is a building or processing site that is used for the temporary deposition of waste. Transfer stations are often used as places where local waste collection vehicles will deposit their waste prior to loading into larger vehicles. These larger vehicles will transport waste for recycling or to the endpoint of disposal in an incinerator, landfill,

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or hazardous waste facility. The waste collection is a process that includes gathering solid wastes and recyclable materials and transporting these materials to either the processing facility, transfer facility, or disposal site. Several types of waste collection are presented as follows (Tchobanolous et al., 1993):

2. **Community Bins:** Bins are placed in convenient locations where community members can throw waste. This method is comparatively cheaper to implement than other methods and is the most widely adopted method in Western countries. For this method to be adopted, bins should be covered, aesthetically presentable, are attended regularly, kept clean, and easy to handle. Moreover, separate bins should be provided for recyclable, mixed, paper, and biodegradable waste materials.
3. **Door-to-Door Collection:** In this process, the waste is placed at the doorstep at a set time when the waste collector arrives. In this method, the waste collector is responsible for collecting the waste separately. This method is highly convenient for householders, although it requires homeowner cooperation and a scheduled service for homeowner cooperation.
4. **Block Collection:** Collection vehicles arrive at a particular place, day, and time to collect waste from households. Household members bring their waste containers and empty them directly into the vehicle. This method requires a higher homeowner cooperation and scheduled service for homeowner cooperation.
5. **Curbside Collection:** The homeowner is responsible for placing their garbage containers at the curb on the collection day and for returning the empty containers to their storage location until the next collection of transfer and transport

Waste materials are transferred from a small collection vehicle to larger transport vehicle. The subsequent transport of waste to a processing or disposal site often takes long distances. Thus, the transfer often takes place at a transfer station. Non-engineered disposal, which involves no controls or only slight or moderate controls, is the most common method of disposal in low-income countries. Waste materials tend to remain for a long time, thus increasing the risk for environmental degradation, including mosquito and rodent infestation, water pollution, and land degradation.

A sanitary landfill is a fully engineered disposal option that can avoid the harmful effects of uncontrolled dumping by spreading, compacting, and covering the engineered wasteland. The four minimum requirements for setting up a sanitary landfill are full or partial hydrological isolation, formal engineering preparation, permanent control, and planned waste placement and covering. Land filling relies on waste containment rather than waste treatment (for control). Appropriate liners for groundwater protection, leachate collection and treatment, well monitoring, and appropriate final cover design are integral components of an environmentally sound sanitary landfill.

In the future, transfer stations could be equipped with material recovery facilities and with localized mechanical biological treatment systems to remove recyclable items from waste streams.

SOLID WASTE DISPOSAL

Solid waste disposal is defined as the final placement of refuse that is not salvaged or recycled. The treatment and disposal of solid waste vary from one country to another and depend on various factors, such as waste type, composition, infrastructure, land availability, labor, economic aspects, recycling strategy, public awareness, and environmental impact. The objectives of waste disposal are to remove

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the solid waste from the community as soon as possible, reduce its quantity, stabilize it, and maintain the cleanliness. Landfilling is currently the only technology employed for solid waste disposal in Malaysia, and the majority of landfill sites are open dumping areas, which cause severe environmental and social risks (Manaf et al., 2009; Yunus & Kadir, 2003). The current volume of generated waste continues to increase because of the growing population and rapid development. Moreover, only less than 5% of waste is recycled. The rapid development and industrialization of Malaysia necessitate an efficient waste management plan (Fauziah et al., 2004). Despite the numerous advantages of landfilling, the resulting highly polluted leachate has been a cause of significant concern, particularly because landfilling is the most common technique of solid waste disposal (Ghafari et al., 2005). MSW disposal requires handling waste in a manner that does not cause problems to society or to the environment. Furthermore, solid waste can be processed to recover several components that can be used for useful purposes (Weiner and Matthews, 2003).

MSW disposal methods include open dumping, sanitary landfilling, composting, incineration, grinding and discharge to sewer, compaction, milling, hog feeding, dumping and burial at sea, reduction, and anaerobic digestion (Davis and Cornwell, 2008).

Landfilling

General Overview

A landfill is like a big rubbish bin (JICA, 2005). In the last few decades, the disposal of waste to land has become the most favored means of waste management (Chong et al., 2005). Open landfill sites are the most popular solid waste disposal method in Southeast Asian countries which is primarily due to their ability to deal with high quantities of solid waste generated each day (Ngoc & Schnitzer, 2009). Further, landfilling provides economical MSW disposal and it is also suitable for the type of wastes which constitute higher percentage of organic matter. However, landfills in many places in ASEAN are classically unsanitary open disposal sites without a leachate management system. Figure 3 illustrates the waste treatment methods used in ASEAN.

Robinson and Maris (1983) reported that the landfill is one of the most sustainable forms of solid waste disposal because adverse environmental effects and other risks and inconveniences are minimized, thereby allowing waste to decompose under controlled conditions until it eventually transforms into relatively inert and stabilized material. In fact there are no combinations of waste management practices that do not require landfilling.

Among other management alternatives, landfilling is the only management technique that is both necessary and sufficient. Several wastes are basically not recyclable and they finally reach a point where their intrinsic value is dissipated completely. Recycling also generates residuals that require ultimate disposal in a landfill (Messineo & Panno, 2008).

The challenge is to ensure that all operating landfills are properly designed and monitored after their closure. Currently, operating landfills do not continue to take hazardous wastes. In addition, they do not receive bulk liquids. They have gas control systems, liners, leachate collection and extensive groundwater monitoring systems (Theisen, 2002)

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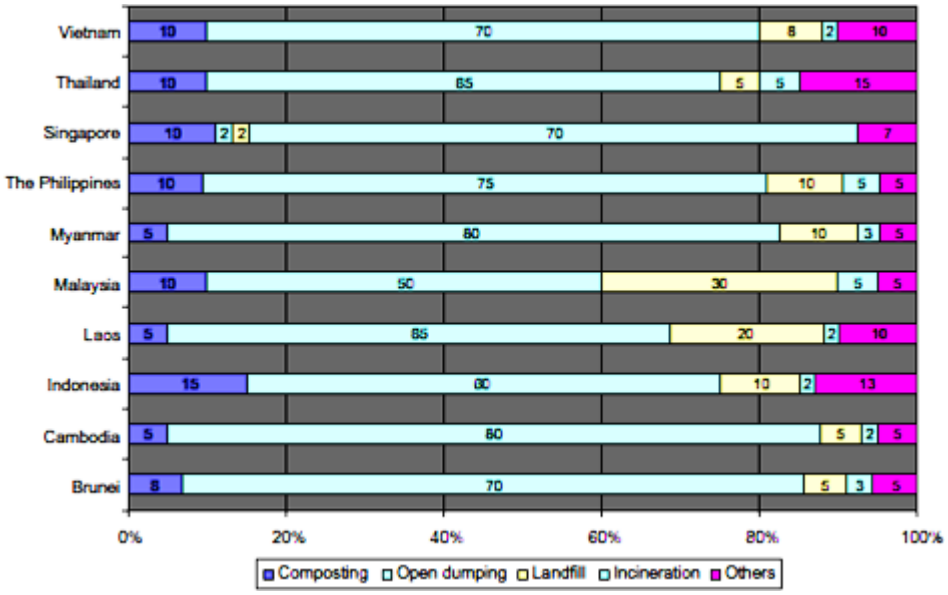
Figure 3. Solid waste treatment methods in ASEAN (%) (Ngoc and Schnitzer, 2009)



Landfilling Design, Operation and Challenges

Landfill Siting

Land selection for construction of landfill is one of the main problems of MSW landfilling because of the difficulty in locating the suitable site and in obtaining administrative clearance and public consensus. Public will generally oppose to the decision for the landfill situated near their neighbourhood. This is because they are driven by the fear of unknown and the distrust of the government in securing the safety of the landfill (Tammemagi, 1999). Thus, it is important to find a site which is technically suitable and at the same time safeguarding the interest of the community especially in relation to the health issue and compensation that they should be received.

Landfill Design

A proper designed landfill should incorporate different features according to sound engineering principles and environmental codes of practice (i.e (1) base liner and leachate collection system, (2) daily soil covering, (3) final top liner, (4) diversion of surface runoff system, (5) gas emission control system (6) and proper access roads to the site) in order to prevent and to minimize any negative environmental impacts during the waste degradation process. The materials of choice in landfill construction are limited and no more, so then the regulations requiring them for liner use for consideration. The biggest challenges of base liner system are to contain the waste so that the waste doesn't cause problems in the outside environment, particularly groundwater. The composite base liner consists of an upper geomembrane liner and a lower compacted soil. However, the lifespan of the landfill liner is yet to be sure and there is a high probability that the leachate could form and leach through the artificial liner as the liner deteriorates along time and the interaction with the chemical components in the landfill cell (Allen 2001).

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Allen et al., (2001) suggested that the landfill should be situated at land with natural hydrogeological characteristics which can contain and naturally attenuate contaminants to acceptable level instead of trying to contain the contaminants within the landfill by relying on artificial liners.

Landfill and Environmental Impacts

Disposal of waste in the landfill can cause serious environmental problems if the landfills are not properly designed and constructed. During the waste degradation process, the temperature within the landfill will increase. And with the high percentage of methane, this will cause fire hazard. Other environmental threats that posed by dumpsites and landfills including stench, water pollution, air pollution and potential health hazards.

Leachate Generation and Effect on Water Resources

One of the most significant disadvantages of landfill disposal methods is the generation of highly polluted liquid (i.e., landfill leachate). Landfill leachate is the liquid that seeps through solid waste in a landfill (Christensen et al., 2001). The amount of leachate produced depends on the amount of water that percolates through the landfill cell and mixes with waste. The more water content in the waste, the more leachate will be produced. This leachate will leach through the landfill either vertically or laterally. Numerous factors affect the quality and quantity of leachate, including seasonal weather variation, landfilling technique, waste type and composition, and landfill structure (Mohajeri, 2010; El-Fadel et al., 2002). Unfortunately, landfill leachate is rapidly generated in tropical countries, such as Malaysia, because rainfall generally exceeds the evaporation rate during the rainy season (Lema et al., 1988). Researchers have yet to determine an effective solution to this problem. The technology that can be used may differ according to the type of leachate produced. Unless returned to the environment in a carefully controlled manner, landfill leachate is a polluting liquid that may bring harmful effects on groundwater and surface water around a landfill site. The sequential migration of leachate away from landfills and its release into the environment pose serious environmental risks that threaten public health and safety (Read et al., 2001).

To protect groundwater from contamination, an impermeable liner system should be placed inside the landfill, and prober collection and drainage systems should be designed to allow rainfall to run off. EU waste management and legislation introduced this containment strategy to keep the pollutant and inert waste within the landfill (Allen, 2001). The belief is that the lining system can completely contain the leachate produced during the waste degradation process, thus preventing the pollution of water sources. However, Dr. Montague explained that landfill liners cannot hold leachate and toxic materials within the landfill site forever. The durability of the artificial liner system is still unknown, and waste degradation may take decades or even centuries to achieve its inert state; thus, leachate leakage problems have a high probability of occurring (Allen, 2001). On the basis of laboratory experiments, researchers determined that volatile organic chemicals, such as toluene and xylene, can eat through synthetic liners and leave the landfill unable to hold the leachate within it (Breen, 1990). Hence, the durability of the lining system is not guaranteed in the long term. Leachate and toxic materials may percolate and leach through the liners, thus causing ground water pollution. Modern sanitary landfills only postpone these effects to future generations. Thus, many environmental specialists have sought to develop efficient treatment methods for large quantities of polluted leachate.

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Gas Emission

When MSW is disposed of in a landfill, naturally occurring Microorganisms (bacteria) degrade the waste. The amount of water in and the temperature of the MSW control the rate of degradation. This process turns the organic portion of the waste into methane (a primary constituent of natural gas) and carbon dioxide in about equal proportions. Additionally, some organic compounds may be released directly into the gas from products contained in the waste, such as household cleaning materials. The non-methane organic compounds (NMOC) in the gas amount to less than one percent of the total gas created by waste degradation. Gas generated can threaten human health and the environment if it migrates off site or is not collected and destroyed. Landfill odors often prompt complaints from community members. People may also have concerns about health effects associated with these odors and other emissions coming from the landfill. Typical constituents found in MSW landfill gas is given in Table 4.

Landfill Operation and Maintenance

A safe design of landfill is barely enough to ensure the safety of the public and the environment protection; it requires a well-managed operation which should include the following: (1) the waste that is entering to landfill should be identified by Landfill operators to prevent hazardous waste from being delivered and co-disposed with other municipal solid waste at the landfill. They should be authorized to reject any waste until it is identified to be safe and acceptable at the landfill site, (2) daily cover should be used at the end of each working day operation or in a more frequent interim to control disease, vectors from breeding, scavenging activities by rodents, seagulls, crows, odors and windblown littering, (3) Run-on control to prevent water from outside the landfill from entering the landfill cell because the additional water will increase the leachate production, and runoff control to prevent the escape of contaminants from the landfill area, (4) protective equipment should be provided and safety operation should be implemented to the site workers in order to minimize the risks of operators and workers. Most of the existing solid waste landfill sites in developing countries are practicing either open dumping or unsanitary landfilling. Some are located at the upstream of water intakes or at sensitive groundwater catchment area. Most of these sites are simply dumping grounds without any environmental protection. This practice is very

Table 4. Typical constituents found in MSW landfill gas (Tchobanoglous et al., 1993)

Component	Percent (Dry Volume Basis)
Methane	45-60
Carbon dioxide	40-60
Nitrogen	2-5
Oxygen	0.1-1.0
Sulfides, disulfides, mercaptans, ect.	0-1.0
Ammonia	0.1-1.0
Hydrogen	0-0.2
Carbon monoxide	0-0.2
Trace constituents	0.01-0.6

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unsustainable and creates a lot of problems such as fires due to landfill gases, rodents, bad odours and leachate pollution. Proper sanitary landfill concepts and the usage of intermediate treatments such as incineration, pyrolysis, and recycles are not actively practiced to effectively remove the wastes in many countries. This is mostly due to technological and financial constraints.

CATEGORY OF MUNICIPAL LANDFILL SOLID WASTE

Landfill sites are generally classified into five: anaerobic, aerobic, anaerobic sanitary, improved anaerobic sanitary, and semi-aerobic. The use of these different landfills is generally based on environmental concerns and economic factors.

A. **In an Anaerobic Landfill:** Solid wastes are decomposed by a conventional municipal method (Matsufuji, 1990). However, this type of landfill poses many major environmental and health concerns because it produces toxic leachate. Hudgins and Harper (1999) reported that anaerobic landfills contain high concentrations of organic compounds and pathogens. The waste mass also slowly degrades, posing long-term risks (Figure 4a).
B. **In an Anaerobic Sanitary Landfill:** Solid waste is sandwiched by soil. The conditions of solid waste here are the same as in anaerobic landfills (Figure 4b).
C. **In an Improved Anaerobic Landfill:** the leachate collection system is installed at the bottom of the site. Other features are the same as in an anaerobic sanitary landfill. The conditions are still anaerobic, but moisture content is much lower than that in anaerobic sanitary landfills (Figure 4c).
D. **Semi-Aerobic Landfills:** Are designed with an underlying piping system that allows air to flow inside and outside the solid waste. This design enlarges the aerobic zone inside the landfill, creates active aerobic consortia, and increases the rate of waste decomposition (Figure 4d).

Technology used in aerobic landfills has been evaluated over the last few years. The aerobic landfill system adds air and re-circulates leachate to maintain air humidity and to provide nutrients to microorganisms in order to reduce methane gas, volatile organic compounds, and odor emissions and thereby eliminate site leachate treatment. The aerobic landfill process enhances the biodegradation of waste and speeds up the stabilization of the landfill (Figure 5e).

SEMI-AEROBIC LANDFILL (FUKUOKA METHOD)

This type of landfill was first tested at the Shin-Kamata landfill in Fukuoka, Japan in 1975 (Chong et al., 2005). The Fukuoka method is specially designed for temperate climate and has been adopted in Japan and in tropical countries, such as Malaysia, Indonesia, China, Sri Lanka, and Iran, since the 1980s. A schematic diagram of semi-aerobic (Fukuoka) landfills is shown in Figure 5. The mechanism of the semi-aerobic landfill system allows oxygen flows into the waste mass through leachate collection pipes by passive ventilation to accelerate aerobic microbial decomposition in the waste. One of the main advantages of this landfill system is that discharged leachate and gas are continuously used in the leachate collection and gas ventilation system, thereby improving leachate quality.

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Figure 4. Classification of landfill category structures: (a): Anaerobic landfill, (b), Anaerobic sanitary landfill, (c): Improved anaerobic sanitary landfill, (d): Semi-aerobic landfill with natural ventilation and leachate collection, (e): Aerobic landfill with forced aeration (Shimaoka et al., 2000)

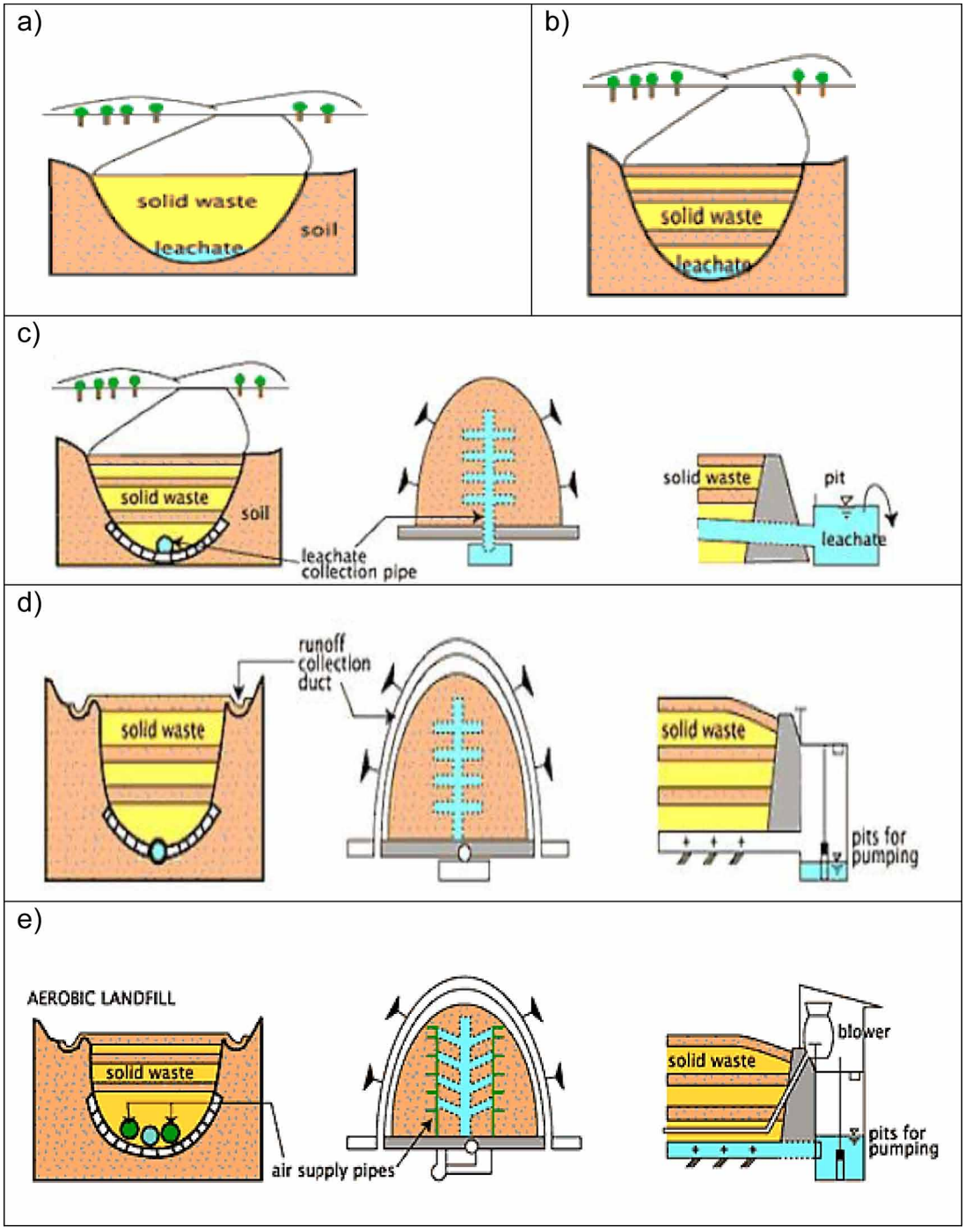

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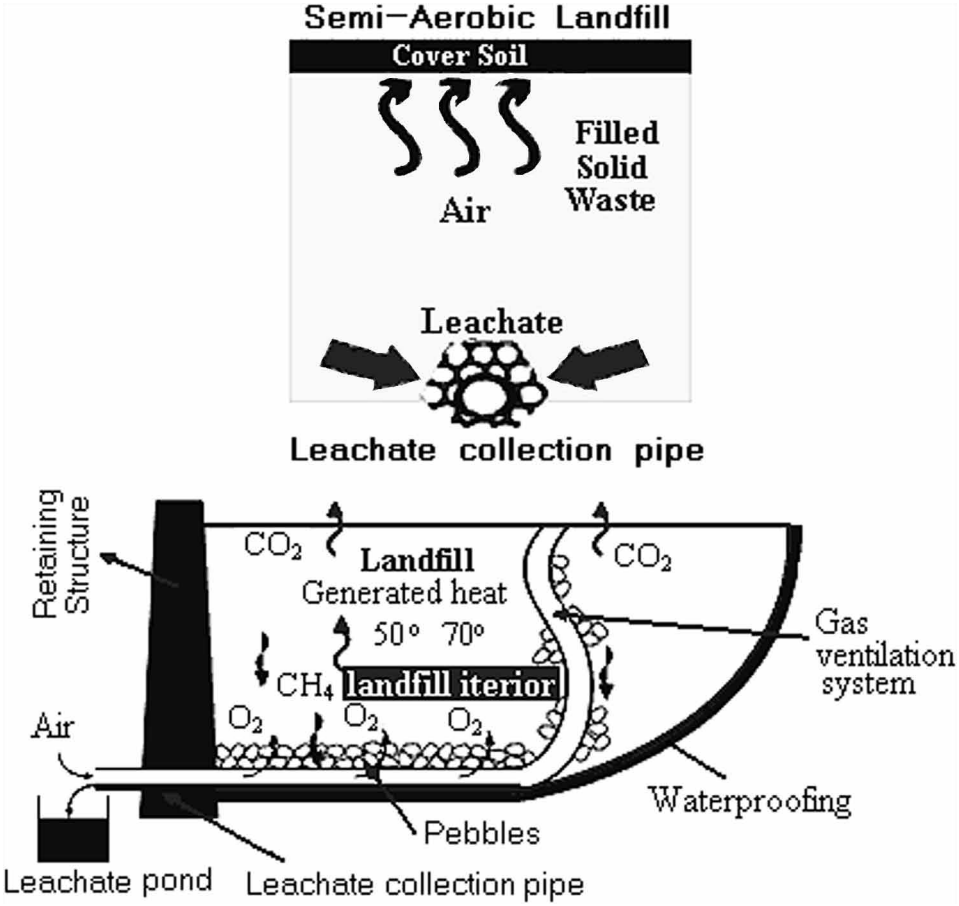
Figure 5. Schematic diagram of semi-aerobic landfill (Japan International Cooperation Agency, JICA, 2005)



PRINCIPLES OF DECOMPOSITION OF SOLID WASTE

A complex series of reactions occurs at the landfill when wastes are buried: physical, chemical, and biological decomposition reactions. Decomposition progress rates of solid waste largely depend on waste characteristics. Physical decomposition occurs during the operational management of solid waste landfill and includes segregation, mechanical size, and volume reduction. Chemical decomposition involves combustion, pyrolysis, and gasification. Biological decomposition includes aerobic and anaerobic degradation. Biodegradation generates highly contaminated hazardous leachate and gases (Matsufuji, 2007).

Biodegradation increases BOD levels in leachate and reduces the pH level, and then gasification generates gas from organic acids, thereby reducing BOD levels and increasing pH (Matsufuji, 2007). Decomposition in landfills is divided into five phases: initial adjustment (Phase I), transition (Phase II), acidification (Phase III), methane fermentation (Phase IV), and maturation (Phase V) (Tchobanoglous, 1993).

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Phase I: Initial Adjustment Phase

During this phase, aerobic conditions occur where organic biodegradable materials undergo microbial decomposition facilitated by air trapped within the landfill. Leachate generated from this phase is characterized by entrained particulate matter and small amounts of organic substances from aerobic degradation (McBean et al., 1995).

Phase II: Transition Phase

In this phase, biological decomposition of waste occurs. Transformation from aerobic to anaerobic environment occurs as the oxygen in waste cell decreases with more carbon dioxide being produced.

During the initial aerobic phase, oxygen present in landfill is rapidly consumed; resulting in the production of CO_2 and the leachate temperatures can be increased. The aerobic phase in a landfill lasts only a few days because oxygen is not replenished once the waste is covered and the pH in this early stage becomes neutral. When the condition turns anaerobic, the hydrolytic, fermentative, and acetogenic bacteria becomes dominant, resulting in an accumulation of carboxylic acids. Consequently, chemical oxygen demand (COD) and pH in the leachate are reduced by the end of this phase as more volatile organic acids and CO_2 are produced (Kjelsen et al., 2002).

Phase III: Acid Phase

This phase is also known as the acetogenic phase and is governed by acidogenic bacteria (acid formers). In this phase, oxygen in the landfill is consumed by aerobic bacteria. Development of organic acids and dissolved CO_2 reduces leachate pH to 5 or lower (Salem et al., 2008). Therefore, the heavy metals become soluble, and essential nutrients are removed from the leachate because of the decreasing pH. Ammonium and metal concentrations also rise, and complex molecules are degraded.

Phase IV: Methane Fermentation Phase

In this phase, methanogen conditions are established after several months or years, and leachate becomes neutral or slightly alkaline. Methanogenic bacteria consume acids and produce methane and carbon dioxide. Under stabilized methanogenic conditions, landfill gas is composed of approximately 55% to 60% methane and 40% to 45% carbon dioxide, with trace amounts of other gases (He et al., 2004). The pH in this phase increases to neutral values of 7 or 8.

Phase V: Maturation Phase

In this phase, nutrients and substrates become limited, and biological decomposition is less active. Aerobic conditions may return after conversion of biodegradable waste to carbon dioxide and methane gas. Landfill gas is depleted, and then the leachate stabilizes. Leachate often contains humic and fulvic acids, which are difficult to biodegrade. The slow degradation of these resistant organic materials may continue with the production of humic-like substances.

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Table 5. Physical parameters of the samples studied by (Janakiram and Sridevi 2010)

No.	Parameter	Sample 1		Sample 2		Sample 3	
		30 days	60 days	30 days	60 days	30 days	60 days
1.	Electrical conductivity, dsm-1	8.70	11.04	7.39	10.77	7.00	8.73
2.	Bulk density x 10-3 kg m-3	0.2196	0.2258	0.2411	0.2728	0.2418	0.2751
3.	Moisture content, %	15.65	18.82	12.30	16.43	12.31	16.35
4.	Water holding capacity, %	169.55	181.32	120.75	153.35	118.32	135.26

Table 6. Chemical parameters of the samples studied by (Janakiram and Sridevi 2010)

No.	Parameter	Sample 1		Sample 2		Sample 3	
		30 days	60 days	30 days	60 days	30 days	60 days
1.	pH	7.56	7.32	7.44	7.23	7.59	7.37
2.	Organic carbon, %	6.95	13.5	5.13	14.5	4.13	14.82
3.	Total nitrogen, %	0.81	1.26	0.61	1.50	0.53	1.22
4.	Total phosphorous, %	0.71	0.32	0.20	0.365	0.29	0.40
5.	Total potassium, %	1.53	1.70	1.66	1.80	1.61	1.78
6.	Total calcium, %	0.48	0.52	0.51	0.53	0.52	0.56
7.	Total magnesium, %	0.31	0.33	0.42	0.43	0.43	0.44
8.	Total sodium, %	0.26	0.27	0.26	0.28	0.28	0.30
9.	C / N ratio	8:1	11:1	8:1	10:1	7.5:1	12:1

Table 5 and 6 summarize the physical and chemical parameters of a composite sample for municipal solid waste in India. Bulk density is a measure of the weight per unit volume of a substance (kg /m^3). Materials with a high bulk density typically have very few air spaces with most of the fine pores filled with water. These conditions allow bacteria to grow in the absence of oxygen led to producing methane and other foul smelling gases. Mixing manures with low bulk density improves air exchange minimizing the need for artificial aeration. In the various samples used, the bulk density ranges from 219.6 to 275.1 kg m^3. Since these values are not high, so that the condition for the bacterial growth is prevented.

- **Water Holding Capacity:** Is the amount of water held into pores after gravitation loss for a specified time. This test is assessed to find the utilization of compost for growing media. This reveals that the amount of water held in pores increases with days of composting.
- **Moisture Content:** Is an important parameter for waste composting. Composting material with moisture content between 30% and 100% will be under aerobic condition. In practical aerobic composting, however, high moisture content must be avoided because water displaces air from the interstices between the particles causing anaerobic conditions. However, too low moisture content deprives organisms of water needed for their metabolism and inhibits their activity. Moisture content for satisfactory aerobic composting varies with material used.

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- **Calcium Content:** Has strong influence on ion absorption by soil particle and on the availability of other elements. Calcium is important in the formation of plant cell walls and in the layers between the cells is called middle lamella.
- **Magnesium:** Is closely related to calcium and is absorbed in the soil as anion. It involves in energy conversion and phosphorous metabolism. The percentages of calcium and magnesium for the various samples studied have been observed to increase as the time of composting increased. This shows that the composted material obtained when used for growing plants will have the capability to supply other elements for the solid and the ion absorption by soil particle will be enhanced (Mendoza.and Jamora 2008) . The composted material also helps in energy transfer and phosphorous metabolism.

Other elements such as nitrogen, phosphorous, sodium and potassium are playing a significant role if used in the form of fertilizer. Since composting finally leads to organic manure, it is worthwhile in estimating these elements in the composted material obtained after a period of 30 and 60 days. In the various samples of the solid wastes that have been studied, it is observed that as the days of decomposition increased, there is an increase in the percentage of nitrogen, phosphorous, sodium and potassium.

- **C/N Ratio:** Is an important parameter to determine the extent of composting and degree of compost maturity. The C/N ratio below 20 is considered suitable for compost maturity. The C/N ratio is used as an index for maturity of organic wastes. C/N ratio less than 20 indicates an advanced degree of organic matter stabilization and reflects a satisfactory degree of maturity of organic wastes (Janakiram & Sridevi 2010).
- **The Electrical Conductivity:** In matured aerobic compost increased as the days progressed which may be due to high microbial activity and mineralization, so that the soluble salt content is high.
- **pH:** Generally gives and approximate index of compost maturation. Manure composts tend to have near neutral pH values, while composts under maturation tend to be more acidic. Averagely, mature composts have pH between 6 and 8 and the composts prepared have pH in this range indicating maturity of the compost.

Municipal Solid Waste Management

MSW management is considered a public service, providing citizens with a scheme of disposing of their waste in an economically and environmentally friendly method (Beigl et al, 2008). It is one of the main concerns in most cities of the developing countries due to rapid modernization and urbanization that consequently lead to increased rate of MSW production and disposal (Zhang et al., 2010; Manaf et al., 2009). Additionally, Al-Khatib et al. (2010) stated that rapidly growing population, quick economic growth and improved community living standards have resulted in increased generation rate of MSW, the management of which is a great challenge for concerned authorities. MSW management is a significant feature of environmental hygiene in addition to planning, administration, organization, financial and legal aspects of different activities associated with generation, collection, transportation, and disposal processes (Figure 6). In other words, MSW management in an environmentally friendly way shall adopt principles of aesthetics, economy, conservation and energy (Pattnaik and Reddy, 2010; Hui et al., 2006). In order to establish an effective management of municipal solid waste, the following steps should be used (Figure 6).

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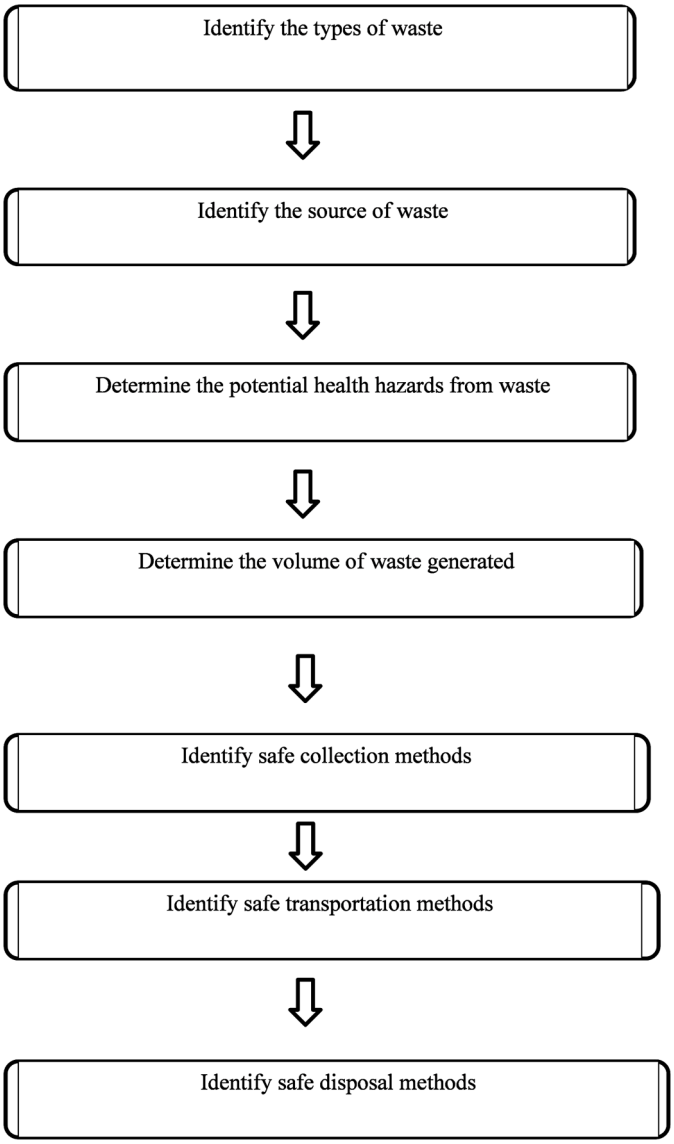
Figure 6. Initial steps for solid waste management



Integrated MSW Management and Waste Management Hierarchy

MSW management is strongly required in order to deal with the huge daily amounts of solid waste. Solid waste management involves the overall management of activities associated with waste such as generation, storage, collection, transportation, processing, reuse, recycling and disposal (Hamer, 2003; Khatib & Al-Khateeb, 2009). Normally, an integrated waste management approach is used to cover all these activities. Several types of solid waste management systems have been implemented in different countries. Most of the countries including Malaysia employ landfill as the most common method of MSW management. On the other hand some countries have adopted different waste management schemes such as incineration. In Japan, incineration is the most common method of MSW management (Beychok, 1987).

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Tchobanoglous et al. (1993) recognized integrated solid waste management as the selection and application of appropriate techniques, technologies and management programs to achieve specific waste management objectives. Solid waste management hierarchy classifies waste management strategies according to their desirability. As shown in Figure 8, the most common methods used for the management of MSW are waste prevention, minimization, reuse, recycle, energy recovery and landfill disposal.

Sustainable waste management simply means managing waste by prioritizing as per the waste hierarchy (Butt et al., 2008). A proper waste source separation is expected to improve the overall recycling process. The waste hierarchy prioritizes prevention and source reduction of waste followed by reuse, recycling and the optimization of ultimate disposal.

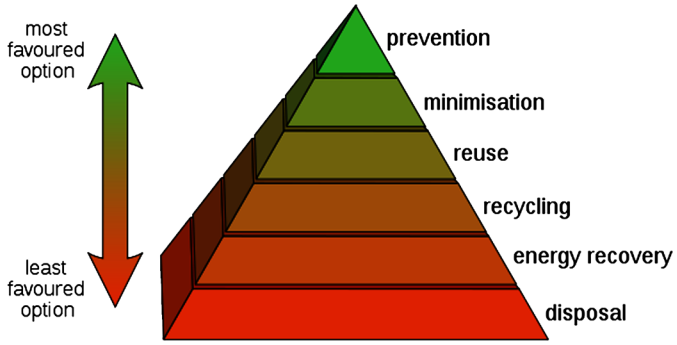
Waste Reduction and Minimization

MSW problems should be solved from various angles by using an integrated system with a combination of different techniques. The combination of methods should be complementing and not competing with one another. Furthermore, a solid waste management system should be tailored to suit local, regional, and national conditions (USEPA, 1988; Rylander, 1998). Therefore, regardless of the combination of methods being adopted, the following priorities should be followed (Figure 8):

1. Waste prevention
2. Waste reduction and reuse
3. Waste recycle and recovery
4. Final disposal

The first and most effective component of the waste hierarchy is reducing the waste produced. Waste minimization is defined as a process of elimination that involves reducing the amount of waste produced in society (US Environmental Protection Agency, 2012). The most environmentally resourceful, economically efficient, and cost-effective way to manage waste is to try to determine a suitable and applicable action to reduce waste in the first site of generation. Waste minimization should be considered a primary focus for most waste management strategies. Proper waste management can require a significant amount of time and resources; therefore, understanding the benefits of waste minimization is important, as well as how it can be implemented in all sectors of the economy, in an effective, safe, and sustainable manner (Davidson, 2011).

Figure 7. Solid waste management hierarchy (UNDP, 2008)



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Waste prevention means to reduce the amount of waste produced. Reuse means to use products and materials again for the same or different purpose. Recycling and composting seeks to recover resources from waste. Energy recovery involves recovering value by producing energy from waste. Disposal means waste should be disposed of only if none of the aforementioned methods offers an appropriate solution. Waste minimization involves efforts to minimize resource and energy use during manufacture. For the same commercial output, the less materials used corresponds to less waste produced. Waste minimization typically requires knowledge of the production process, cradle-to-grave analysis (the tracking of materials from their extraction to their return to earth), and detailed knowledge of waste composition. The zero waste concept has been recently introduced to confront waste problems (Zaman, 2014). The zero waste concept is being developed and implemented in various sectors, including waste management and treatment, mining, manufacturing, and urban development. This concept has been adopted by decision makers and professionals in solid waste management because it stimulates sustainable production and consumption, optimum recycling, and resource recovery. On the basis of critical review, zero waste programs are applied in many countries without any holistic zero waste strategy.

Reduction and Reuse

Waste reduction should be the top priority in the solid waste management hierarchy because this method reduces the amount and toxicity of waste before entering the municipal waste stream (Franklin Associates, 1999). Source reduction can be implemented in several ways, as shown in Table 7.

Figure 8. Waste minimization hierarchy holistic zero waste strategy

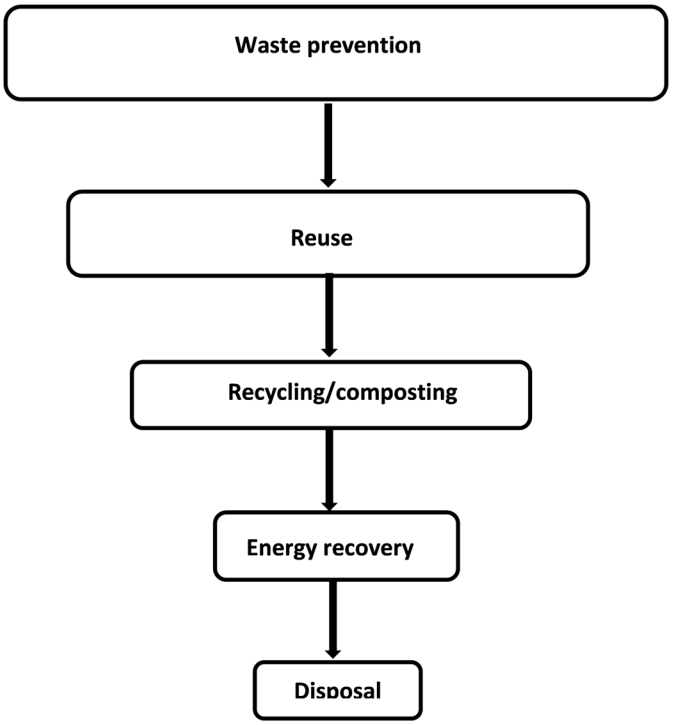

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Table 7. Some ways for waste reduction

Redesign	The producers should redesign the products and packages in order to reduce the quantity of materials and the toxicity of the materials used and lengthening the products life to delay for disposal
Reduce material used	Consumers should change their consumption behaviour to reduce wastegenerated such as buying in large quantity or in refillable package in order to reduce the packaging. Removing from commercial mailing list could also significantly reduce the paper waste.
Reuse of product and packages	Examples of reuse including using refillable containers, washable plates, glass instead of using disposable products. Durable goods such as furniture and appliances can be resold or donated to the needy family.

Source reduction is a prevention technique to reduce waste generation. The success of source reduction is significantly dependent on the attitude of producers and consumers, which involves legislation, social perception, and education, among others. Along with an increasing living standard, Malaysians are developing the "use and throw" consumption behavior, wherein disposable products are increasingly being consumed. This consumption pattern should be inverted to reduce waste from entering the waste stream. Furthermore, emphasis should be placed on producers because preventing waste from being generated must begin with the product and production process (Rylander, 1998). In Malaysia, source reduction has yet to be recognized as a major part of solid waste management. Thus, encouraging people to reuse products is imperative in the recycling program.

CONCLUSION

A sustainable waste management system requires full compliance to the waste management hierarchy in overall management systems, either in developed or developing countries. The waste reduction and minimization aspects are important factors for the successful management of MSW. As landfilling is widely accepted as a suitable method of solid municipal waste disposal worldwide, the implementation of a fully engineered semi-aerobic sanitary landfill is suggested in developing countries to achieve the goal of sustainable development.

Source reduction is rather a prevention technique to reduce the waste from being generated. The success of source reduction is very much depended on the attitude of producers and consumers which involves legislation, social perception, education and so on. Along with the increasing living standard, Malaysians are developing the "use and throw" consumption behaviour where there are more and more disposable products being consumed. This consumption pattern should be inverted in order to reduce the waste from entering the waste stream. On the other hand, emphasis should be placed on producers because preventing waste from being generated must begin with the product and the production process (Rylander, 1998). In Malaysia, there is yet any emphasis on source reduction as a major part of the solid waste management. It is imperial in the recycling program to encourage people to reuse products.

Sustainable waste management system requires full compliance to the waste management hierarchy in the overall management systems, either in developed or developing countries. Waste reduction and minimization aspect is an important key factor for successful management of MSW. As landfilling is widely accepted as a suitable method of solid municipal waste disposal worldwide, Implementation of a fully engineered semi-aerobic sanitary landfill is suggested in developing countries towards achieving the goal for sustainable development.

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Chapter 2
The Role of Waste Management in the Green Economy: An Empirical Analysis of Economic Data of the Business

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ABSTRACT

Green economy has become highly relevant over the last years. We are currently experiencing pollution issue and environmental decay that had its origin, however, in the previous centuries. The development of industrial economy inevitably entails the production of waste, in such a quantity that the environment is incapable of assimilating and transforming it naturally. Therefore, it is believed that one of the main green economy sectors is the waste retrieval and recycling, that means waste management. In the existing literature, this sector has not been deeply analyzed from a viewpoint of performance business analysis. Although a European legislation exists, every country manages this business by itself. After a historical introduction, this study, using the regression model, analyses the variables that influence the Italian business of waste retrieval and recycling, in the process establishing which of them has a deeper impact on performance.

INTRODUCTION

Environment and Human Beings: A Historical Background

Animal and vegetable organisms carry out their lives in the biosphere, i.e. in the environment surrounding them. Such physical and biological components have neither been designed not built by man.

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No doubt, the environment undergoes an ongoing evolution, and accordingly changes as years elapse by virtue of nature itself. Not only that. The activities engaged in by man have altered the terrestrial biosphere; thereby have occasioned changes in soil, air and water. Such transformations may result in environmental decay.

The natural environment changes by the action of endogenous or exogenous agents. These agents modify the earth demolishing a part and constituting another, to thereby maintain a balance.

Classical literature describes Germany as entirely covered by forests (Tacitus in *Germania)* and Egypt and Mauritania as the granaries of the Empire. In the first case, human settlements of Germanic tribes expanded the vital space by creating glades to locate the settlements and develop agriculture. In the second one natural events transform it in desert.

Human activity has often transformed the landscape through destructive actions, which have irreversibly compromised the environmental balance. At the beginning of agricultural activity that the human species started causing deep changes to the territory. Man has exploited the environment for the sake of his personal sustentation. Over time, this exploitation increased ever more, because it was related to the country development. The trend began to abuse the available resources, as if they were at no cost (which was, after all, the case from the perspective of sheer economic cost). The Earth was offering resources to man, and men were using them.

Through the cultural development, spread awareness that such resources were not "free of charge". One of the first environmental protection laws dated back to 1769, when it was decreed that forests on the island of Mauritius should be safeguarded. As Grove (1996) stated, the most important and innovative aspect of French's environmental protection in Mauritius, was the acknowledgment of a link between deforestation and local climatic changes. Deforestation, after all, is the work of man, implemented in order to set aside the soil for a different use than the preservation of forests, generally by using the soil first for agricultural purposes and then for industrial ones. Consciousness was thus undergoing a change. The development of industrial economy was deemed by many scientists to represent "a threat to mankind's survival". Well-known, among others, is Wilson's (1858) study on the drying up of the earth and the atmosphere, in which his concern surfaced: changes in the atmosphere are slowly drawing close to the state in which it will be impossible for man to live on the Earth. *This paper can be said to mark the onset of a truly international environmental debate in which processes operating at a global scale were being considered* (Grove, 1995, p. 159).

This realization burst forth in the 70s of the XX century. So a new branch of economic discipline, viz. "environmental economy", was born for the sake of picking up the interactions between environment and development, by setting a limit on the constant growth of production and on the use of resources, and by implementing the environment's ability, to receive the only product unable to transform itself, save across millennia: waste.

Environmental economy may be defined as the study of the regulation of polluting activities and the assessment of environmental beauties. Famous is the exemplification of the economy-environment relationship by the economist Kenneth Boulding (1966). He used the "metaphor of the space shuttle": the economy experienced up to this moment was compared to a cowboy who saw the far west as a «frontier» capable of being continuously shifted by acquiring new lands, and thus new resources to exploit. The economy, instead, should be considered as an astronaut aboard a space shuttle, who can solely enjoy a limited kit of resources, which he must try to save and recycle as much as possible.

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In this period, there was no way of severing the link between environment and economy. Politics began to adapt to these new ideas and realizations. Companies began to adapt to the policies and the new legislative provisions, until they arrived at a system where health and environmental integrity acquired an ever-increasing relevance.

Pollution

The term "environmental pollution" means the change in the biosphere composition caused by pollutants and emitted from many human activities. This change has a negative connotation; in fact, it interferes with the growth rate of the species and causes damage both to human health and territory.

The effect of the different agents depend on their own characteristics and on the quantity released.

There are different types of pollution categorized according to the polluted site. For each site the causes, sources and the effects are different. They are: air pollution that changes the composition of air; water pollution that changes the composition of the water; soil pollution that changes the composition of the territory; noise pollution that changes the sound in a given environment; electromagnetic pollution that alters the natural values of the electromagnetic field.

Pollution is a direct result of industrial development. Human activities, which are promoted for the economic development, produce most of the contaminants. The economic processes (mining, processing or manufacturing and consumption), generate necessarily waste that will inevitably come back to nature. This involves a biological change, damaging animals, plants, and then the ecosystem, i.e. a contamination that is defined pollution (Turner et al., 1993, p. 16). It has a direct effect on the economy. One of the first researcher in this field was Pigou (1920), who introduced the concept of "externalities": pollution causes external costs that result in a gap between private costs and social costs.

Sustainable Development and Waste

In order to fulfil human's needs, it is necessary to obtain goods and services. Their fulfilment is strictly linked to economic development, and in order to obtain goods and services, the use of energy is required. Yet its use inevitably entails repercussions on the environmental balance, such as "negative externalities".

Already Malthus (1798) had concerned himself with the limits, which he had termed absolute that existed in the relationship between population and economic resources.

The fact that the availability of resources was limited, gave rise the problem of a sustainable development; in other words, the tendency is to promote social-economic growth that might be sustained over time both by the natural environment and by society.

The best-known definition is the one given in the *Brundtland Report* 1987 (WECD): *the "Green Development"* (Adams, 2001) is *development that meets the needs of the present without compromising the ability of future generations to meet their own needs (Brundtland, 1987)*[1]. Companies simultaneously consider their financial, social, and environmental performance (Marshall & Brown, 2003, p.101), keeping services and quality of natural resources.

Inevitably, economy is linked also to natural resources: renewable and nonrenewable. Gray and Hotelling were the firsts who studied the relationship between economy and non-renewable resources.

By resorting to the manufacturing industry as a case study, they identify an optimal rate of exploitation of resources, so that the current extracting activity does not affect the future extraction quantity.

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In order to achieve that, they identify a value, and thus a cost of utilizing the non-renewable resource, which includes extraction and user cost (Gray, 1914). Nevertheless, user cost should increase over time based on the discount (Hotelling, 1931).

Two types of approach to sustainable development have been classified in accordance with the hypothetical replaceability scenario between natural capital and artificial (man-made) capital (Pippo, 2011): can be achieved the same level of well-being by replacing the natural capital with the artificial (man-made) one?

The "Strong substitutability current", believes that the artificial capital is not able to produce the same well-being given by natural capital, i.e. there is a very weak and limited compensation level. You need to preserve the natural capital because is irreplaceable by human activities. The risk of damaging environmental resources irreversibly must be minimized. According to this approach the economic growth should be slowed down or even stop in order to preserve the environmental capital integrity.

Instead, according to the "weak sustainability current", there is an almost perfect substitution between the two types of capital (environmental and human), since the satisfaction derived from human can easily equal or exceed that received by the natural capital. This approach believes in the possibility of decoupling between environmental growth and degradation. Technological progress allows more efficient use of resources and the reduction of human activities.

The objective of sustainable development is therefore to achieve simultaneously both socio economic growth and environmental care. Emerge the three pillars of the concept sustainability: economy, environment, society (Williamson, Lynch-Wood, & Ramsay, 2006). The link among these tree aspect is deeply developed in literature. Lounsbury et al. (2003) have found that industries are shaped by social structures of meanings and resources. Lounsbury et al., have explained that the waste management is strongly interconnected with the political, social, and cultural situation. The both social movement and political practices transform the extant socio-economic practices. Given this background the authors believe that a complete analysis of the Green Economy should include both environmental aspects (in this case the waste management), and economic aspects (in this case an analysis of a green business) through the study of economic performance using indicators such as EBITDA.

WASTE

Maybe one of the most relevant issue is to identify waste. The problem may seem trivial, but it is not. Economic operations such as produce, research and develop, create inevitably the existence of products or waste products. While there have always been, during the last two decades of the 1900s waste has started to be a great issue for States and policy. As a consequence of that, it was formed ad hoc legislation on waste management.

To define uniquely waste, here is used the legislative definition that is found in the Basel Convention: *Waste are substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law*[2].

At European level, the previously mentioned legislation is possibly the first and most exhaustive legislation in the waste field. The Basel Convention was signed in 1989 and came into force on 5 May 1992. It was born out of the need to contain the production of a wide range of waste categories and the possibility of handling and disposing of it as close to the place of production as possible, with a view to reducing the environmental risk associated with handling activities and combating transport towards developing Countries, a then frequent phenomenon (Marzetti, 2001).

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The Basel Convention made a change in the environmental situation, now unsustainable, that many developing countries or "economies of the transaction" were living. In fact, many large industries were using these countries for disposal of waste, as easy way, less "controlled" and certainly cheaper. In doing so, however, it is threatened not only the environment but also human health. Therefore, with the Convention of 1989 it was decided to establish a genuine system of checks in respect of both imports and exports, both disposal of hazardous and non-hazardous.

The Italian legislation, in article 184 of Legislative Decree No. 205/2010, regulates the classification of waste categories, which are differentiated according to their origin into urban and special waste, and according to their dangerous characteristics into dangerous and non-dangerous waste.

The function of waste classification is the prerogative of the producer (or holder), who bears the obligation and thus the responsibility to assess it carefully for purposes of allocating the CER code.

Such classification is important because indicates the type of waste involved and distinguishes between "waste" and "non-waste" (i.e. "end of waste"). **R**etrieval activity, as regulated by Legislative Decree 152/2006 in article 181, is the reuse, recycling and the other forms of recovery. The result is a departure[3] from the regulations in the field of waste of substances or objects in question.

Directive 2008/98/CE: Waste Management

Article 4 has a great relevance. It establishes a waste hierarchy as a priority order in waste prevention and management legislation and policy[4].

The hierarchical order, as established by the Directive is:

1. Prevention;
2. Preparing for re-use;
3. Recycling;
4. Other recovery, e.g. energy recovery;
5. Disposal.

Member States shall take measures to encourage the options that deliver the best overall environmental outcome. However, they must ensure that waste management does not jeopardize human health and does not affect the environment. When they are subjected to a salvage operation, they stop to be regarded as waste and therefore they are no longer subject to this law.

The Directive lays down measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use[5]

The said hierarchy sums up whatever has been asserted so far, namely, that all the activities pertaining to waste management are of equal environmental impact. Nay, the legislator, in his intent to promote an ecologically rational management of those substances or objects which must be necessarily disposed of, wanted to specify the fact that certain activities have a lesser impact on environment and health, and that they should be favoured over the others.

The legislation does not promote "the removal of existing waste", but first the prevention, and only subordinately, the waste management through the reuse or processing of waste, to cause the least possible.

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When it is not possible, it will be necessary to dispose waste in precisely demarcated places, equipped in conformity to the law. In this work, it is studied the economic performance of a green business: the waste business. Particularly retrieval and recycling business.

RECYCLING AND WASTE MANAGEMENT

The recycling process could be implemented in a very broad range of sectors and fields, through infinite methodologies and motivations. Accordingly, it becomes hard to find in the literature, a unique definition of waste recycling, without focusing on any specific sector or any specific type of recycling.

It is believed that, even in this instance, the broadest definition of recycling may be drawn from the legislation in force, Directive 2008/98/CE of the European Parliament and of the Council:

'Recycling' means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations[6].

Therefore, the very same European directive identifies the recycling activity as one of the main paths for a sustainable waste management.

As the authors were pointing out, the said specific activity is strictly interconnected with many sectors and thus with several subjects, such as health care, public administration, local legislation, education etc. Suffice it to think of the repercussions which inappropriately managed waste causes to the health of living beings and to the proper functioning of civilization.

An efficient waste retrieval system, in fact, must involve both the citizens and the companies. In other words, is necessary to pay heed both to the phase "at source", i.e. where the waste is produced, and the "end-of-pipe" phase, i.e. where the waste is managed. In such a system, efficiency is accordingly determined both by producers and by consumers. As regards the former, they may contribute from different viewpoints: by devising a "sustainable product", they may facilitate both a lesser waste of resources at the time of transforming the input into finished product and an easier retrieval of the utilized products. The consumers may instead contribute by efficiently managing the products capable of being retrieved (for instance through waste separation). Uncertainty concerning the quality of recycled materials and the incapacity of laying down a «common language» of dialogue between buyers and sellers may not only engender problems caused by asymmetrical information but also, more generally, give rise to significant transaction costs (D'Amato, 2008, p. 436).

Other research studied the "organizational citizenship behaviour", defined by Organ as *individual behavior that is discretionary, not directly or explicitly recognized by the formal reward system, and that in the aggregate promotes the effective functioning of the organization*'' (1988, p. 4). These researches suggest that such ''organizational citizenship behaviors for the environment'' are a distinct and important aspect of organizational behavior and there is a strong relation between citizenship behaviors and environmental performance (Organ, 1988; Boiral 2009; LePine and Erez 2002; Podsakoff et al. 2000; Boiral and Paille 2012; Daily et al. 2009).

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For example, in this field it has been carried out a research that presented a *case study of recycling at a large University, that does not have a formal organizational structure to address sustainability concerns*, and they *found that recycling behavior was influenced in important ways by the university context and by processes designed to promote recycling* (Weaver et al., 2015, p.427).

Companies have used recycling as a sustainable strategy. Many studies analyze the effects and reasons for the implementation of environmental strategies. It has been shown that more and more companies implement environmental strategies as a key success factors (Maas et al., 2014; Siegel, 2009; Aragon-Correa & Sharma, 2003; Sharma & Vredenburg, 1998; Gouldson, 2004; Ambec & Lanoie, 2008; Anderson & Anderson, 2009; Al-Najjar & Anfimiadou, 2012).

To the best of our knowledge, little attention has been devoted on recycling retrieval as core business and not only as an environmental strategy implemented to gain competitive advantage.

Having the aim to study the performance of the waste business, it seems that this study is not broadly connected to the research on environmental performance. It is significant, however, that some studies using environmental performance as variable, the percentage of total waste that is treated, recycled or recovered as a percentage of total waste generated (Dobler et al., 2014, p. 8)

The Italian Context

Already in the past years, studies on environmental issues have been conducted in our jurisprudential doctrine (A.A. V.V., 1998; Catturi, 1990; Ferrara, 1998; Matacena, 1984; Miolo Vitali, 1978).

Within the Italian background, researches have been carried out in the green economy field. More specifically, studies have been undertaken on social reporting (Campedelli, 2005; Secchi, 2006) as well as on the more specific environmental report (Noci, 2000), on Corporate Social Responsibility (Masini, 1970; Fiori et al., 2007), and on voluntary environmental disclosure (Quagli & Teodori, 2005; Andrei & Pesci 2009; Garzella et al., 2011).

To the best of our knowledge, neither at an Italian level nor at the level of other nations, have specific studies been conducted on the retrieval/recycling business.

This research has deliberately focused on a single country, given that business is undoubtedly influenced by national politics and culture. It is moreover undoubted, based on the different current episodes that a link exists between the said sector and mafia, at the Italian level as well as at the level of other countries.

Prior to developing the linear regression model, we deem it useful to provide some information of a general character about the Italian recycling business.

The Foundation for sustainable development (2014) has elaborated, based on the CONAI[7] data, a table setting out the amount of recycling of packages. As evinced by the following table, results have improved. This is no doubt due both to a higher "environmental consciousness" and to a better waste management.

REGRESSION ANALYSIS ON WASTE BUSINESS

Development of Hypotheses

Given the scant literature in the field of business analysis of retrieval and recycling companies, are used some variables utilized in the analyses of other businesses. The independent variables analyzed are deemed to be of a strategic nature. Regard was paid to two macro-categories: "where" and "what" determinants.

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Table 1. Recycling of packages, data in kt and %. Years 2011-2013

	2011		2012		2013		Variazione % delle quantità 2013/2012	Variazione % delle percentuali 2013/2012
	kt[8]	%	kt	%	kt	%	kt	%
Steel	353	73	332	76	320	74	-4	-2
Aluminum	41	59	41	61	44	65	8	4
Paper	3.526	80	3.594	84	3.531	86	-2	2
Wood	1.272	55	1.257	54	1.353	55	8	1
Plastic	749	36	770	38	789	39	2	1
Glass	1.570	69	1.568	71	1.596	73	2	2
Total	**7.511**	**65**	**7.562**	**67**	**7.633**	**68**	**1**	**1**

Source: Elaboration by the Foundation for Sustainable development upon CONAI data.

"Where" Determinants:

Localization

Waste is a European and world problem.

The Italian situation presents some peculiarities. In Italy, waste is mostly managed at regional level. For the purposes of this research, it is believed that the two macro areas distinction is sufficiently significant: the northern area and the central-southern area. This distinction is made because frequently, in the current news, come across several instances of mafia-like waste management and the legal or illegal trade in the same, mainly in the Centre-South area. Moreover, some reports by Italian companies (Amsa and Gruppo A2A, for instance) set out extremely positive data relate to northern Italy. As a consequence, the authors consider the retrieval and recycling companies performing in a different way, depending on their area: better in the north of Italy than the Centre-South, where companies have to manage higher waste levels and are obliged to interface with illegal organizations.

This work studies, first and foremost, the distribution of these companies in the North and Centre-South areas, in order to examine their performance level, in accordance with the following distribution:

- What is meant by north are the companies situated in the following regions: Emilia Romagna; Friuli Venezia Giulia; Liguria; Lombardia, Piemonte; trentino alto Adige, Valle d'Aosta e Veneto.
- What is meant by center are the companies situated in the following regions: Lazio; Marche; Toscana e Umbria.
- What is meant by south (and islands) are the companies situated in the following regions: Abruzzo; Basilicata; Calabria; Campania; Molise; Puglia; Sardegna e Sicilia.

The authors want to study, therefore, the relationship between the localization of retrieval and recycling companies and performance.

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H1: There is a positive relation between localization in the North area and the performance level of Italian retrieval and recycling companies.

"What" Determinants

Company Size

Another relationship that is studied in literature is the relationship between company size and performance. The number of employees is a variable frequently used to indicate company size. European Union considers this parameter, together with the total balance sheet, liabilities and the net turnover, in order to assess the company size. Even recently, Directive 2013/34/UE of the European Parliament and Council, dated 26 June 2013, has stipulated that, in order to fall within one of the three defined categories, the company must have *exceed the limits of at least two of the three following criteria (article 3):*

Based on previous literature, there is a positive relationship between profitability and company size. Many authors (Alexander 1949; Stekler, 1964; Hall and Weiss, 1967; Scherer, 1973; Ravenscraft & Scherer, 1987; Fiegenbaum & Karnani, 1991; Helfat et al., 2007; Jonsson, 2007 Bayyurt, 2007; Dogan, 2013) theoretically supported this link. Prior research confirms the existence of a positive relation.

H2: There is a positive relationship between the size of a retrieval and recycling company and performance.

Shareholders

A peculiarity of the recycling business, which is deemed as a "sustainable business", is that it is thoroughly interconnected with many different sectors. In fact, the environment care is interconnected with many different fields, healthcare, politics and business.

Regarding human health, the number of people who need medical attention and therapeutic treatment because of pollution is increasing, and it is going to continue to grow. This of course strains the whole system and increases the financial burden of health care providers, the state, and ultimately the individual. An "environmental culture" has been growing in many ways: by educating children at school, originating new university classes, new jobs specialized on environmental care, pollution prevention, green economy etc...

There is a patent link with the "public sector" and the extent to which it might be interested in a waste management system. Consequently, in order to conduct a deep analysis of this business, it indispensable to study the equity participation by public Authorities, State and Government and if exist a relationship

Table 2. Directive 2013/34/UE

	Micro Undertakings	Small Undertakings	Medium Undertakings	Large Undertakings
Balance sheet total (euro)	≤ 350.000	4.000.000 ≤	≤ 20.000.000	> 20.000.000
Net turnover (euro)	≤ 700.000	≤ 8.000.000	≤ 40.000.000	> 40.000.000
Average number of employees	≤ 10	≤ 50	≤ 250	> 250

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between this type of participation and the performance by retrieval/recycling companies. It is believed that, given the strong link between this business and various public sectors, the State is interested in intervening in the recycling business with a view to rendering it more efficient.

H3: There is a positive relation between participation by a public company in retrieval/recycling companies and performance.

Ageing

Undoubtedly, the recycling sector has been lively for a while. However, a substantial growth is being experienced by all the green economy sectors. No doubt, an increasingly greater number of companies have emerged in the recycling sector, by virtue also of the new legislative enactments, which enjoin a retrieval of waste. For this research the authors have considered only the companies which have drawn up the 2014 financial statement. Among the sample, the oldest company dates back to 1932, and it is a family business. From the 50s to the end of the 80s, have been founded 79 companies that are still active. 111 companies have been established in the 90s and the remaining 234 companies have come into being during the last 15 years.

These statistics evince that the business is certainly growing and that it is gaining considerable importance. Moreover, the specific legislation in the field of managing the retrieval and recycling of waste has become ever stricter, while technologies are more state-of-the-art.

Given that it is a very modern sector, the authors believe that, the most recent companies may attain a higher level of efficiency. In fact, they possess state-of-the-art equipment and technologies and, having been born in an age where the problem of the environment and in particular that of waste management, they are more capable of confronting the current situation.

H4: There is a positive relation between the age of retrieval/recycling companies and performance.

Presentation of the Sample

Using Aida database, 811 Italian companies have been identified (the main economic activity of which consists in the retrieval and preparation for recycling of solid urban, industrial and biomass waste). More specifically, this activity comprises the following:

- Crushing, cleaning and sorting of glass;
- Crushing, cleaning and sorting of other kinds of waste, such as demolition waste (rubble), in order to obtain secondary raw materials;
- Transformation of cooking oils and fats into secondary raw materials;
- Transformation of other types of waste relating to food, drinks, tobacco and residual substances in secondary raw materials.

Aida is a database produced by Bureau Van Dijk Electronic Publishing, which groups together financial, personal data and commercial information on Italian joint-stock companies.

In order to contextualize the selected sample, it is necessary to set out some general characteristics.

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The total number of employees amounts to 8.263 units that means an average of ten employees per company.

Out of n.811, n.425 companies, i.e. 52.4%, have lodged their financial statements in 2014.

In this sector, only three companies out of 811 are registered under the Company Registry's special section as innovative Start-ups. They draw up financial statements in abbreviated form. In 2014, one of these start-ups has not lodged its financial statement. The other two, instead, have recorded negative results at EBITDA level. This obviously entails a negative net income, a loss for the financial year, and negative profitability ratios (ROE and ROI). These data indicate that the analysed sector has no special interest in developing along this new company characteristic.

As for the economic performance of the sector, we may observe that 124 companies record a negative ROE (i.e. 29.18%), with a ROE in excess of 3% (that is, a level indicating a par condition) as regards 235 companies, i.e. 55.29%. These initial remarks point to a rather positive business result, especially if we contextualize it within the current period of crisis.

Among the 811 companies, it was our intention to focus the research on those companies that had lodged their financial statements in 2014, in order to make them comparable in accordance with the latest available data. We excluded, instead, those companies that did not record the other variables analysed by us, such as the region of the registered office or the year of foundation.

Our sample, therefore, analyses 386 companies, i.e. 48% of total companies in the business, a sample felt to be undoubtedly representative.

Variables and the Model

Dependent Variable

Because the aim of this empirical analysis is to study the economic performance of a "green business", we have used **EBITDA** as performance indicator. It is believed that this data might highlight income based on the characteristic management (Saita, 2015), thereby excluding interest, taxes, depreciation and amortization.

No account was taken of sales, inasmuch as these companies may deal with extremely different types of waste. The company dealing with food waste, of course, will have a lower turnover than another company managing the same amount in ferrous waste or companies from which, for instance, one might extract substances with a high monetary value (such as copper, zinc, etc.).

Likewise, no regard was paid, as a business performance indicator, to the Net Income. As we deem it better not to consider some components, such as taxes and amortizations, that might impact differently depending on the type of company involved (possibly one with public shareholding) or on the localization of the same in a region, possibly one governed by a Special Act.

EBITDA it is a good variable for cash earnings. Depreciation and amortization are non-cash expenses. So, EBITDA is a good way to know how much cash a company is generating – cash that can be used to pay dividends or reinvest in the company EBITDA is the preferred metric. Furthermore, EBITDA mitigates the distortions to operating income caused by arbitrary asset depreciation schedules (Becker-Blease, et al., 2010).

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Independent Variables

Localization

As previously explained, Italy is divided into 20 regions. Account has been taken of the region where the registered office is situated rather than the operational headquarters, given that this data was not always available. Having classified every region based on the area, the companies analysed in this database are equally apportioned between the two areas, as set out in the following table.

The area variable has been turned into a dummy variable, by assigning a value of 1 to companies in the northern area, and a value of 0 to those having their registered offices in the central-southern area.

The central-southern region with the largest number of retrieval and recycling companies is Campania (54); the northern region is instead Lombardy with 89 companies.

Company Size

The company size has been studied by paying regard to the number of employees. This choice has been made for two main reasons: the existing literature and the characteristics of the recycling business.

The number of employees is a parameter widely used as a size indicator in the literature as well (Cavusgil & Nevin, 1981; Bilkey & Tesar, 1997; Burton & Schlegelmilch, 1987; Kaynak & Kothari 1984; Mugler & Miesenbock, 1986; Bonaccorsi, 1992; Cavusgil & Naor, 1987; Holzmuller & Kasper, 1991). The existence of a relationship between size and profitability has been proven in multiple sectors, such as the hotel one (Israeli 2002; Pine & Phillips 2005; Claver-Cortés et al. 2006; Ruggero & d'Angella 2011; Santoro, 2015).

The retrieval and recycling companies are considered as a service companies. In this kind of companies, the number of employees is seen as the most significant size parameter (Saita, 2012, p. 23)

Moreover, the analysed companies deal with different kinds of waste. It is thus inevitable that those which handle urban waste, for instance, will boast a mostly lower turnover or profit, and not just negligibly so, than other companies that deal with other types of waste, such as industrial waste. The number of employees is accordingly deemed to be a fair index of company size in this sector.

In the analysed sample, most are micro-companies, which thing is absolutely in line with the Italian structure (Saita, 2015, p. 21).

Table 3. Localization variable

	Independent Variable	No. of Companies	% Companies Across Whole of Italy
Where - localization	**Area**		
	North	192	49,74%
	Centre - South	194	50,26%
	Total for Italy	386	100%

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Table 4. Company size variable

	Independent Variable		N. Companies	% Companies in Italy
where	**Company Size**			
	Micro	x<10	257	66.67%
	Small	10<x<50	114	29,45%
	Medium	50<x<250	13	3,36%
	Large	x>250	2	0,52%
	Total Italy		386	100%

Shareholding

In the sample, the shareholders of more than half of the companies consist in physical persons or families. This data, too, is in line with the Italian business structure. Other reference shareholders are represented by "industrial companies", which hold shares in more than 34% of the sample businesses. Relatively few, instead, are the companies in which holdings are in the hands of "public authorities, the State or Government" (Public shareholding), nearly 2%. In order to study the relationship between public shareholding and performance level, the variable has been turned into a Dummy, by assigning a value of 1 to all the companies in which shareholding is in the hands of a public authority (including as a minority shareholder), and and a value of 0 to companies where shares are not held by pubic bodies, the State or Government.

Ageing

For the sake of a comprehensive business analysis, it is important to study the seniorities operating there.

As indicated by the previously mentioned data, the business of retrieval and recycling companies mostly consist in companies born in the 2000s. No doubt, the know how acquired over time is an important element, but in this specific business it is believed that to be in the forefront when it comes to systems and structure is a highly relevant factor.

In the literature, the age variable has often been paid heed to when assessing a business (Campa and Kedia, 2002; Villalonga, 2004; Radipere and Dhliwayo, 2014).

Other Controls

Other variables have been taken into account:

1. Total asset
2. Equity
3. Current asset
4. Sales
5. ROE (Return on equity)
6. Net income

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These variables are deemed to be of great significance when conducting a business analysis. Just to give an example, among the selected control variables, total assets and sales are (besides the number of employees) the other two standards adopted by the European Union to measure company size. By contrast, is sufficiently independent from performance and is an index of stability. Current assets is an index of solvency, and points therefore to the capacity of duly meeting one's obligations. In order to avoid problems of multi-collinearity, the current asset, total asset, equity and sales variables have been clustered together in the Stability variable, as we are going to specify hereunder. In other words, a variable called "Stability", which groups together total asset, current asset, equity and sales variables, has been created.

As we may discern in the under-mentioned table, among the variables there are no problems of correlation, save to a slight degree between size and the variable by us established, i.e. stability. This correlation, however, is not particularly high, and the variables forming part of the Stability variable prove essential to the effectiveness of the model, indicated by the Rsquare.

As proven by the earlier literature, multi-collinearity has been studied through two tests: the Variance Inflation Factor (VIF) and the Condition Index. It should be noted that, apart from the "stability" variable, the maximum value of the VIF is less than 3, i.e. the threshold suggested by Hair et al. (2005). The variable reaches a value of 3, and is thus deemed thoroughly acceptable by the literature (Myers, 1990).

Model and Results

The gathered data relate to the year 2014.

The independent variables refer to the previously described what and where sizes.

Table 5. Pearson correlation table

		Company size	**Area**	**shareholding**	**Aiging**	**Stability**	**ROE %**	**Net income €**
Company size	Pearson Correlation	1	-,043	,441**	-,048	,615**	,011	-,320**
	Sign.		,400	,000	,351	,000	,826	,000
Area	Pearson Correlation	-,043	1	,040	-,185**	-,016	-,002	,064
	Sign.	,400		,432	,000	,747	,974	,210
Shareholding	Pearson Correlation	,441**	,040	1	,038	,232**	,026	,016
	Sign.	,000	,432		,453	,000	,614	,750
Aging	Pearson Correlation	-,048	-,185**	,038	1	-,093	,001	-,072
	Sign.	,351	,000	,453		,069	,990	,155
Stability	Pearson Correlation	,615**	-,016	,232**	-,093	1	-,035	-,716**
	Sign.	,000	,747	,000	,069		,489	,000
ROE %	Pearson Correlation	,011	-,002	,026	,001	-,035	1	,125*
	Sign.	,826	,974	,614	,990	,489		,014
Net income €	Pearson Correlation	-,320**	,064	,016	-,072	-,716**	,125*	1
	Sign.	,000	,210	,750	,155	,000	,014	
**p < 0,01; * p < 0,05. (2-tailed).								

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Table 6. Descriptive statistics

	Mean	SD	N
Company size	12,79	37,522	386
Area	,49	,500	386
Shareholding	,02	,143	386
Aging	36533,51	4159,287	386
Stability	3184649,2923	9039109,39601	386
ROE %	2,2318	35,42813	386
Net income €	12513,42	987663,072	386

The model utilized for the analysis of these variables is a model of multiple linear regression:

$$yi = \beta 0 + \beta 1X1i + \beta 2X2i + \cdots \beta nXni + \varepsilon i$$

Where

- *Yi* = Dependent variable, i.e. the performance of Italian retrieval and recycling companies;
- *X1…Xn* = Independent variables;
- *β1… βn* = Regression coefficients;
- $\mathcal{E}$ = Stochastic error.

Empirical Results

For purposes of this research, after having studied the correlation between independent and control variables of the model, and after having detected some rather high correlations between total assets, current assets, equity and sales, the "Stability" variable was created through the "mean" operation in order to avoid problems of multi-collinearity. In conclusion, therefore, the model takes into account the relationship between the dependent performance variable, by resorting to EBITDA (Earnings Before Interest, Taxes, Depreciation and Amortization) as performance indicator, and the independent variables:

- *Company size,* by utilizing as indicator the number of employees;
- *Area,* by utilizing as indicator the region of the registered office;
- *Shareholding,* by distinguishing whether or not, among shareholders, there are public Authorities, the State or Government;
- *Ageing* of companies, by paying regard to the year of their foundation;
- *Stability,* which takes into account the total asset, current asset, equity and sales;
- *Net income,* i.e. the result for the 2014 financial year;
- *ROE,* i.e. the return on equity.

If we analyse the correlations more specifically, the Beta columns indicate the sign of the relationship between the dependent variable and the independent variables. We may observe how size and seniority

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Table 7. Coefficients

Coefficients(a)								
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sign.	Collinearity Statistics	
		T	Std. Error	Beta			Tolerance	VIF
1	(Constant)	14125,765	151904,106		,093	,926		
	Company size	-3761,501	585,103	-,188	-6,429	,000	,516	1,939
	Area	71597,051	32219,715	,048	2,222	,027	,956	1,046
	Shareholding	148935,902	127077,466	,028	1,172	,242	,756	1,322
	Ageing	-,945	3,982	-,005	-,237	,813	,906	1,104
	Stability	,110	,003	1,320	34,581	,000	,302	3,314
	Net income €	,932	,025	1,225	37,531	,000	,413	2,422
	ROE %	462,122	450,130	,022	1,027	,305	,977	1,023
a. Dependent Variable: EBITDA €								

are negatively linked to performance. This entails that the more recent the company, the worse is the performance result, and also that the bigger the company, the worse is its performance. Conversely, the higher the total assets, current assets, equity, sales, net income and return on equity (ROE), the better will be the company performance.

It is nevertheless important to observe that not all the variables have significant causal relationships with performance, in particular those variables that show p-value > 0.05. The variables indicating the type of shareholder, the age and the percentage ROE do not explain the performance variation. Despite that, the model is altogether thoroughly valid, as will be elucidated by the Table hereunder.

Among the other variables, instead, size, stability and net income have a higher impact on the level of company performance, given that they show a value of Sign. < 0,000. The where variable, too, proves to have an impact on performance.

By virtue of what has been asserted, the H3 and H4 hypotheses are refuted, in that the type of shareholder found in the companies and the age thereof do not impact at all on performance. The H1 hypothesis is accepted, whereas hypothesis H2 evinces the fact that size negatively impacts on the company performance.

In order to assess the effectiveness of the model, we should bear in mind the value of the RSquare. In the model implemented by us, the RSquare equals .831, which represents a pretty satisfactory value, hence the model of the aforesaid seven variables proves to be significant and accordingly capable of explaining the 83% performance variance in the waste sector.

Analysis of Results

As shown by the model summary, the totality of utilized variables proves to be especially significant when trying to explain the performance trend of companies active in this waste business. That is further confirmed by the value 2 of the Durbin-Watson statistic indicating the absence of self-correlation in regression.

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Table 8. Model summary

Model Summary[b]					
Model	**R**	**R square**	**Adjusted R Square**	**Std. Error of the Estimate**	**Durbin-Watson**
1	,913[a]	,834	,831	309325,475	2,005
a. Predictors (constant), ROE %, Ageing, Shareholding, Net income€, Area, Company size, Stability					
b. Dependent variable: EBITDA €					

Relationships Between the Independent Variables

If we embark on an in-depth analysis of the relationships between control variables and independent ones (by breaking up the stability variable into the four variables it consists of), we will note that *current asset* is the item with a stronger correlation with control variables: net income, sales, total asset, equity and company size variable as well. This data is quite easy to deduce, in that current assets is an index of solvency, and thus of stability as well. As confirmed by the Pearson Correlation, as current asset increase the total activities, sales, equity and number of employees all increase. These data may be explained on the basis that companies with available liquidity generally have a wide turnover (hence large Sales), but at the same time need also to provide guarantees to their own customers and creditors (equity).

More singular is instead the significant and negative relationship (-0.66) with the fiscal year result. This may be explained if one pays regard to the items making up current assets in the Italian budget. Current assets consists of inventories, receivables, and financial assets other than fixed assets and cash. If, accordingly, some of these items, such as receivables and inventories, increase, there will be a simultaneous increase in financial need. Since, in fact, companies are small in size and with scant capital, they have to resort to market financing (we should not forget, moreover, that these companies have a limited self-financing capacity), save in the case of exceptions arising from the leverage (where investments are obviously made only until profitability exceeds the investment cost). The same explanation holds true for the negative relationship between the net profit and the stability variables. After all, if we analyse the correlation between net income and four variables grouped together under Stability, we may discern a negative link with each one of them.

The age of the companies, by contrast, is not specifically linked to any variable (the Pearson Correlation always shows values not exceeding 0.185). This indicates the fact that the year of foundation of the company does not impact on such fundamental budgetary variables as equity and net income or even on the company size.

The number of employees, hence the company **size** as well, besides showing a positive link with current assets and turnover, discloses a positive link (weak and yet existing) with the type of shareholder. We may infer from it that public shareholding in recycling/retrieval companies mostly occurs in medium- to large-size companies. That fact is confirmed by the data retrieved by the database, which indicate that 50% of companies with shares held by public authorities, State and Government, fall under the “medium- to large-size” category, which in turn represents only 3.63% of the total companies of the sample. This means that public bodies, State and Government hold shares especially in medium- to large-size companies.

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Relationships between the Dependent Variable and the Independent Ones

Once the significant relationships have been clarified, we will now proceed to analyse the hypotheses that have not been accepted by virtue of the statistical results, given the lack of any correlation. The performance proves to be correlated neither with the company's seniority nor with the presence of public shareholders.

As far as the first relationship is concerned, different explanations might be put forward. Despite being a new sector, it does not means that companies established on a more recent date should record a higher level of performance. The new companies, in fact, must locate themselves in the most favourable areas, acquire sufficient know how to offer a good service, invest in state-of-the-art structures and in marketing operations, and thus establish a new customer base. Less recent companies must instead face problems of modernization and implementation of new structures and operations. On the other hand, however, they already boast good market shares and experience in the sector. Accordingly, a relationship between the company's seniority and its performance cannot be established, since the factors impact on the two variables in a radically different manner. Earlier, we had also discussed the presence of innovative start-ups in the Italian retrieval and recycling sector. Given the very negligible presence (3 companies out of 811) and the invariably negative result, account being taken of both EBITDA and the net income, we might assert that these innovative companies do not find in the Italian recycling and retrieval business a good sector wherein to operate and make profits.

The second unconfirmed hypothesis concerns the positive relationship between performance and the presence of public authorities, State and Government in the shareholding structures of Italian retrieval and recycling companies. The subject has been actually studied to an ample extent in other works as well as in various disciplines. In this sector, too, it is not possible to assert a better performance level in either public or private companies. This study indicates that performance is independent of the type of shareholding. This is an extremely significant element. It has in fact been explained that this business, and thus a sustainable waste management, is strictly linked to a Country's level of civilization and health care. The authors hold the view that a public presence in most of the sector companies might serve as an incentive to improve the performance level and standardize the sectorial management towards a more efficient and sustainable economy. Studies tackling economics often contend that, in Italy, public intervention, understood as public authorities, State and Government, most of the times does not entail efficient results. In the retrieval and recycling sector, however, it is believed, due to the abovementioned reasons, that the State has a specific interest in intervening in an efficient and constant fashion.

CONCLUSION

An analysis was conducted on a representative sample of the Italian retrieval and recycling sector, a sector of undoubtedly high relevance and importance within the green economy context. The analysed companies' record positive results altogether.

The companies are equally distributed between the Centre-South and Northern areas; the size thereof is in line with the Italian structure, and most of them have been set up during the last 15 years. We may notice that the most significant variables to explain the company performance are obviously represented by net profit and stability. Among the initially postulated hypotheses, the existence of a link between performance and size has been confirmed. The zero level of significance indicates in fact that the com-

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pany size impacts on performance. The Beta value, however, indicates that this link is negative, hence as company size increases the performance level decreases. This data may be explained by the fact that the difficulty in organizing large-size companies and the inability to exploit economies of scale created thanks to the company's size expansion do not only entail the fact that an improvement in the performance level cannot be attained, but also an actual worsening thereof.

The authors may accept the second hypothesis, and thus the fact that performance is better in companies having their registered offices in Northern Italy. The economic growth gaps between the two areas are well known (Daniele and Malanina, 2007). This data, too, is in line with the Italian situation, which generally records better performances in the northernmost Italian region.

Limitation

The study suffers from a few limitations: 1) the analysis has been conducted by analysing solely the Italian retrieval and recycling companies which have lodged their financial statements in the last year; 2) reliance was placed exclusively on results from one year, the 2014 financial year; 3) The current market crisis, which has been already going on for several years, has undoubtedly impacted on company performances in general, hence those of the analysed companies as well; 4) exclusive reliance was placed on the data available from the Aida database; 5) since any reference to other studies in the recycling sector was lacking, studies from different sectors were taken into account.

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ENDNOTES

1. Released in 1987 by the World Commission on Environment and Development (WCED). It introduces the concept of sustainable development.
2. Basel Convention, Article 2.
3. Directive 2008/98/CE of the European Parliament and of the Council of 19 November 2008, on waste and repealing certain Directives, art.6, "End-of-waste status": the substance or object is commonly used for specific purposes; a market or demand exists for such a substance or object; the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; and the use of the substance or object will not lead to overall adverse environmental or human health impacts.
4. Directive 2008/98/CE of the European Parliament and of the Council of 19 November 2008, on waste and repealing certain Directives, art.4, "Waste hierarchy".
5. Directive 2008/98/CE of the European Parliament and of the Council of 19 November 2008, on waste and repealing certain Directives, Art 1, "Subject matter and scope".
6. Directive 2008/98/CE of the European Parliament and of the Council of 19 November 2008, on waste and repealing certain Directives, Art 3.17, "Definitions".
7. CONAI, National Packageing Consortium, is a private non-profit Consortium and is a system which represents the answer to private companies and to a problem of collective interest, such as the environmental one, in due compliance with the guidelines and objectives laid down by the political system . More than 1.000.000 of companies producing and utilizing packages affiliate to the Consortium System. http://www.conai.org
8. Kiloton.

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Chapter 3
Effective Waste Water Treatment and its Management

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ABSTRACT

Worldwide there is an increasing industrialization leads to increased disposal of uncontrolled waste products into the environment which made the environment more pollute and creates hazards. Industrial wastewater is having a major role in the environmental pollution. The major physical, chemical and biological products of the wastewater are solid content, organic matter, in-organic compounds, detergents, soap, cleaning products, metals, gases, volatile compounds, numerous pathogenic microorganisms, nutrients and toxic compounds. Untreated wastewater can cause various environment pollutions problems such as eutrophication or oxygen depletion in the environment. Hence a effective wastewater treatment process and its management is necessary to reduce the contaminants in the permissible levels in the treated waste streams. The final outcome of an effective wastewater treatment and its management is to ensure and provide an appropriate environment protection to the living things and public human beings in the world.

INTRODUCTION

Wastewater is a combination of water and water-carried wastes originating from homes, commercial, industrial facilities and from various institutions. Untreated wastewater generally contains more than 99% of water, but the remainder contains high levels of organic material, small amounts of inorganic ions, numerous pathogenic microorganisms, nutrients and toxic compounds leads to environmental pollution and health hazards.

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Wastewater treatment is becomes a critical one due to its water resources, disposal costs, regulations which reduces the wastewater contaminant levels in the disposal waste water streams. The critical goal of waste water treatment and its management is to protect the environment, public health and at last the socio-economic concerns (Tchobanoglous & Burton 1991).

Hence, waste water must be treated suitably to meet the required standard before it is getting disposed to protect the environment from the pollution and prevent the health hazards of the human beings.

Choosing an appropriate waste water treatment technology is depends upon the nature of the contents in the waste water.

Selecting a suitable waste water treatment process is depends upon:

- How clean the final water effluent from our plant must be.
- The quantities and nature of the influent water we need to treat.
- The physical and chemical properties of the pollutants we need to remove or render to neutral in the effluent water.
- The physical, chemical and thermodynamic properties of the solid wastes generated from treating water. (Cheremisinff, 2002)

Treatment of Wastewater

Generally wastewater treatment is carried out in four stages. They are:

1. Preliminary treatment
2. Primary treatment
3. Secondary treatment
4. Tertiary treatment (Bozkurt et al., 2015; Kalbar et al., 2012; Garrido et al., 2011; Al-Rekabi et al., 2007)

VARIOUS TREATMENT PROCEDURES

Preliminary Treatment

Solids and oil with grease are combined to form sludge. Preliminary treatment is the first process which makes the effluent suitable for further process by reducing the non-favourable wastewater characteristics like large solids and rags, abrasive grit, odours and in certain cases, unacceptably high peak hydraulic or organic loadings.

Preliminary treatment processes consist of screening/filtration as physical unit operation which removes the coarse suspended matter and flotation for the removal of oil and grease. Other preliminary treatment operations are comminution, removal of greases and oils, flow equalization, equalization and neutralization of acid wastes and alkaline wastes.

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1. Screening

The screening of is one of the old technique used to remove the solids, gross pollutants from the waste water through the use of a porous medium by downstream equipment process. The porous shape may be of any shape, but in general circular or rectangular shape is used. In screening process various larger suspended and floating materials such as fibres, paper, rags, string substances and other materials are removed, before entering into the primary settling tanks.

Conventional screening process is carried in two stages. In first stage coarse screens such as metal bars or heavy wires spaced 25 to 50 mm apart is used in the waste water flow channel to remove the coarse/denser materials. Bar screens consist of vertical or inclined steel bars distributed equally across a channel through which wastewater flows.

In the second stage 0.8 to 6.0 mm fine screen size opening is used to remove the finer particles. Fine screens consist of various types of screen media, including slotted perforated plates, wire mesh, woven wire cloth and wedge-shaped wire.

The accumulated solid waste materials are frequently removed by screening process to avoid the clogging/choking of the screen filters. Various screen categories with its size of openings and its applications in preliminary treatment process are given in ***Table 1*** (Davis, 2013; Waste-water treatment technologies: A general review. United Nation, NY, 2003).

2. Comminution

Comminutors are used to pulverize large floating material into small one in the waste flow, where the screening technique is impractical. Generally comminutors are installed between the grit chamber and the primary settling tanks to remove the pulverized materials, which reduces odours, flies and unsightliness.

Table 1. Different screening technique in wastewater treatment

Screen Category	Size of Openings (mm)	Application	Types of Screens
Coarse Screen	≥ 6	Remove large solids, rags, and debris.	Manually cleaned bar screens/trash racks Mechanically cleaned bar screens/trash racks Chain or cable driven with front or back cleaning Reciprocating rake screens Catenary screens Continuous self-cleaning screens
Fine Screen	1.5-6	Reduce suspended solids to primary treatment levels	Rotary-drum screens Rotary-drum screens with outward or inward flow Rotary-vertical-disk screens Inclined revolving disc screens Travelling water screens Endless band screen Vibrating screens
Very fine screen	0.2-5	Reduce suspended solids to primary treatment levels	---
Micro fine screen	0.001-0.3	Upgrade secondary effluent to tertiary standards	---

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Two types of comminutors are used in the comminution process, such as Rotating cutter comminutor and Oscillating cutter comminutor (Waste-water treatment technologies: A general review. United Nation, NY, 2003).

3. Removal of Greases and Oils

In primary treatment the water is left to stand so that oil and grease can form an insoluble layer on the surface of the water. Grease traps can be removed from the surface of the water, whereas gravity or simple skimming methods can also be used to remove the grease and oil (Abd El-Gawad, 2014).

4. Flow Equalization

Flow equalization is a technique used to improve the effectiveness of secondary and advanced wastewater treatment processes by leveling out operation parameters such as flow, pollutant levels and temperature to achieve constant flow to minimizing the downstream effects during the treatment process.

There are four type of flow equalization processes are available.

1. Alternating flow diversion
2. Intermittent flow diversion
3. Completely mixed, combined flow
4. Completely mixed, mixed flow

In waste water treatment process flow equalization can be applied in various locations in the treatment plants. The locations are

- Near the head end of the treatment works
- Prior to discharge into a water body
- Prior to advanced waste treatment operations

5. Equalisation

Different properties of waste materials may be produced and discharged into the waste water stream at different intervals in an industry, hence waste water might having different characteristic properties from time to time. So, uniform treatment can't be possible to treat the waste water, unless the waste water has uniform properties. The receiving or initial treatment tanks of a facility often serve as equalization tanks. To attain the uniform properties wastes need to equalize in waste treatment facilities by holding waste streams in a tank for a certain time period to attain uniform properties which provides easier to the treatment. Introducing uniform waste stream to the treatment system controls the treatment operations resulting to produce more predictable and uniform treatment results. Operation parameters of waste water treatment processes are to improve its effectiveness which is based on the equalization technique, a leveling out operation by checking the flow, pH, BOD and pollutant levels. During equalisation process solids present in the waste will settle along with heavy metals. The size, shape and its dimension of equalisation tanks vary depends upon the quantity of waste and mode of discharge of the waste materials. The equalisation tank should have a capacity to hold the volume of waste produced up to the completion

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of a cycle of operations. Usually equalization tanks are equipped with agitators or aerators for mixing are preferred to prevent the settling of suspended solids to the bottom of the tank and to provide uniform effluent for the effective treatment. The agitators are normally placed at the centre line of the length of the tank spaced equidistantly, whereas aeration prevents settling of solids at the bottom of the tank. Systematic diagram of equalization tank is shown in ***Figure 1***.

Uniform effluent can be obtained by proper mixing in the equalization tank by:

1. Appropriate distribution and baffling
2. Mechanical agitation
3. Aeration

6. Neutralisation of Acid Wastes and Alkaline Wastes

Wastewater might have a wide range of pH depends upon the type of waste added into the waste water stream. Neutralization is required in the untreated waste waters to eliminate either high or low pH values prior to such as biological treatment. Generally chemical treatment process such as chemical precipitation is utilized along with the neutralization to adjust the pH of the waste water. Various chemical precipitating agents includes lime, sodium hydroxide (caustic), soda ash, sodium sulfide, and ferrous sulfate. Neutralization is performed by adding acids such as sulfuric acid or hydrochloric acid, to reduce pH, and alkalies, such as sodium hydroxides, to raise pH values. Neutralization may be performed in a holding tank, rapid mix tank, or an equalization tank to control the pH of the discharge between 6 and 9 (Waste-water treatment technologies: A general review. United Nation, NY, 2003; Cheremisinff, 1995; Spellman, 2004; Wastewater treatment technologies; Sincero, & Sincero, 2003; Drinan, & Whiting, 2001; Subramanyam, 2005). Systematic neutralization tank is shown in *Figure 2*.

Figure 1. Systematic diagram of equalization tank

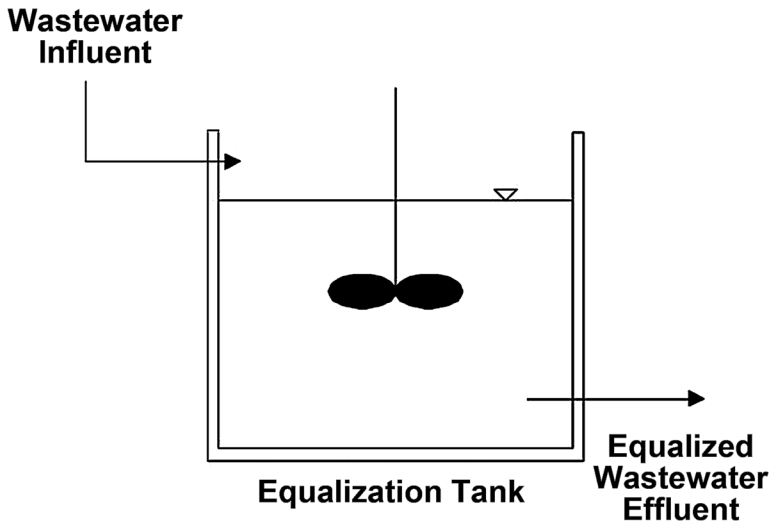

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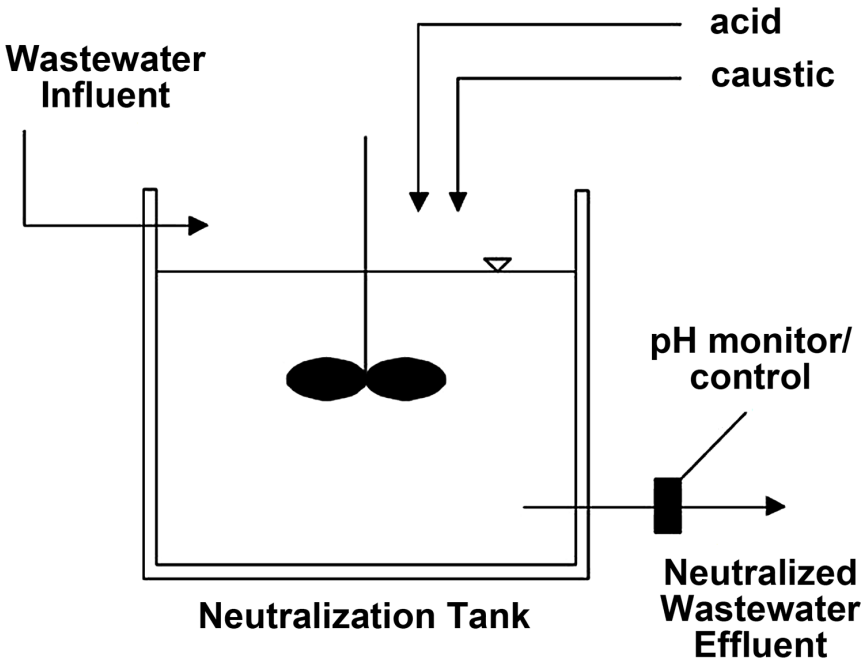
Figure 2. Systematic diagram of Neutralization tank



PRIMARY TREATMENT

Primary treatment acts as a precursor for secondary treatment which makes the effluent suitable for further downstream biological treatment by separating the solids as sludge. In primary treatment solids are removed as sludge by the physical operations such as screening and sedimentation, but doesn't remove or degrade the dissolved organic matter. Some circumstance depends upon the nature of the effluent pre-aeration or mechanical flocculation with chemical additions can be used to enhance primary treatment.

1. Sedimentation

Sedimentation is one of the unit operation in wastewater treatment involves settling of solid particles based on gravitational force in a suspended mixture. In this way the gritty particles, particulate and biological substances in the sludge, and chemical precipitates are removed. Sedimentation takes place in a settling tank, also referred to as a clarifier. There are three main designs, namely, horizontal flow, solids contact and inclined surface (Sperling, 2007).

2. Flocculation/Coagulation

Flocculation is a process of stirring or agitation of chemically-treated water to induce coagulation. Both flocculation and coagulation process are interchangeable one. In general "coagulation" is the reduction of the net electrical repulsive forces at particle surfaces by addition of coagulating chemicals, whereas "flocculation" is the agglomeration of the destabilized particles by chemical joining and bridging.

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Flocculation usually consists of a rapid mix tank which enhances the sedimentation or filtration treatment processes results increased settling rates. Coagulating agents are added in the waste water to initiate the coagulation. Once coagulation over, the coagulated wastewater flows into a flocculation basin where slow mixing of the waste occurs, which allows the flocs to absorb and entrap the particles and other suspended materials to agglomerate into heavier, more settleable/filterable solids by bring them down.

Generally three types of chemicals are used in the coagulation/flocculation treatment processes. They are inorganic electrolytes, natural organic polymers and synthetic polyelectrolytes.

Commonly employed coagulating agents in the waste water treatment process are:

1. Alum (Aluminium sulphate)
2. Ferric sulphate
3. Chlorinated copper
4. Ferric chloride

Among these, alum is the most popular coagulant used in the wastewater treatment (Waste-water treatment technologies: A general review. United Nation, NY, 2003; Wastewater treatment technologies; O'Melia, 1972; Amirthanrajah, & Mills, 1982; Davis, 2013).

3. Flotation

Flotation is a unit operation used to remove solid or liquid particles from a liquid phase by introducing a fine gas, usually air bubbles. The gas bubbles either adhere to the liquid or are trapped in the particle structure of the suspended solids, raising the buoyant force of the combined particle and gas bubbles.

Flotation is the process of introducing fine bubbles into the tank to encourage suspended particles to rise to the surface of the tank. When gas bubbles are introduced into the wastewater, gas bubbles either adhere to the liquid or are trapped in the particle structure of the suspended solids, thereby reducing their specific gravity and causing them to float. Flotation process is used to remove the suspended solids and oil and grease from oily wastewater by reducing the sedimentation times of suspended particles; which have a specific gravity closer to that of water (solids particles which has the specific gravity slightly greater than water whereas the oil/grease particles have specific gravity slightly less than water. Various components of a flotation process include a centrifugal pump, a retention tank, an air compressor, and a flotation tank. When the air introduced into fine bubbles, the bubbles are trapped inside the liquids or solids to form sludge flocs, which raises the buoyant force of the combined particle and gas bubbles and then floating them to the surface. The float is continuously swept from the tank surface. Flotation is mainly used to remove suspended matter and to concentrate biological sludge. Various flotation methods utilized in the waste water treatment process are dissolved air-flotation, air-flotation, vacuum flotation and chemical additives.

The mechanism involved in the formation of sludge flocs includes:

1. Attachment of the bubbles on the particle surface
2. Collision between a bubble and a particle
3. Agglomeration of individual particles or a floc structure as the bubbles rise

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4. Absorption of the bubbles into a floc structure as it forms (Waste-water treatment technologies: A general review. United Nation, NY, 2003; Wastewater treatment technologies; Spellman, 2010 & 2001; Qasim, 1999)

SECONDARY TREATMENT

Secondary treatment acts as a precursor for tertiary treatment which makes the processes are used to convert the finely divided and dissolved organic matter in wastewater into flocculent settle able organic and inorganic solids by chemical decomposition catalyzed by microorganisms. The untreated and escaped soluble, colloidal organics and suspended solids from the primary treatment are further treated in secondary treatment to reduce the Biological oxygen demand (BOD) and chemical oxygen demand (COD) through biological process.

In the secondary treatment process, micro-organisms, particularly bacteria, convert the colloidal and dissolved carbonaceous organic matter largely converted to 'biogas', a mixture of CH_4 and CO_2. Secondary treatment process operation involves trickling filtration, activated sludge process, oxidation ditch and oxidation ponds.

1. Activated Sludge Process

The activated sludge process is an aerobic biological treatment process employs suspended-growth aerobic microorganisms to biodegrade organic contaminants. This activated sludge process is one of the most valuable biological processes to treat the industrial wastes. A suspension of aerobic microorganism is utilized by mechanical mixing or turbulence induced in an aeration basin by diffused aerators in the waste water to mix the contents. In this process, industrial waste or sewage is continuously exposed and subjected to biological degradation. A series of biochemical reactions takes place in the aeration basins, which degrades the organic matters and generate new biomass. Microbial mass of bacteria, fungi, protozoa, rotifers and nematodes are used in the activated sludge process. They include carbon oxidizers, nitrogen oxidisers, floc formers but primarily gram-negative in strain. The nature of organic matter in the waste is the determining factor to identify exact type and species of bacteria or other microorganisms in the slimes.

Microorganisms oxidize the soluble and suspended organic materials into carbon dioxide and water using the available supplied oxygen. Oxygen is an important one to oxidize the organic materials. For effective oxidation atleast a residual of 0.5mg/l of oxygen should be present at all times which can be supplied either by mechanical or diffused aeration systems.

The amount of Oxygen requirements are based on the amount required for biodegradation of organic matter and for endogenous respiration of the microorganisms. The turbid effluents due to the growth of filamentious bacteria than the other required bacteria and protozoa when anaerobic conditions developed due the reduced supply of oxygen. The retarding of floc compaction and settling is observed in filamentous bacterial growth.

After the specific time duration, the treated mixture is passed to a settling tank, where the microorganisms are separated from the treated water. A portion of the settled sludge is recycled to the aeration basin to maintain a required concentration of microorganisms in the process. The remaining settled solids is collected as waste and discorded. For effective oxidation process the microorganisms should

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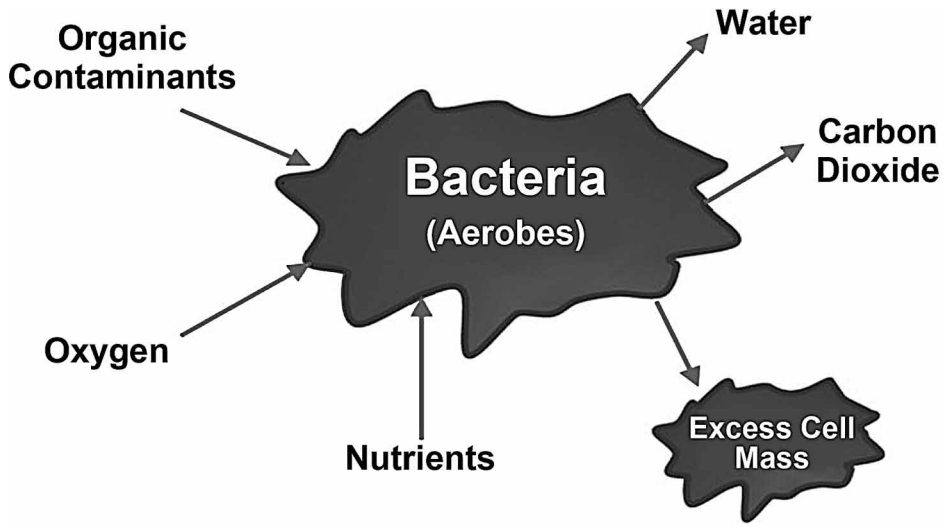
supply with adequate nutrient (nitrogen and phosphors) levels must be available to the biomass. Lack of these nutrients can impair biological activity and result in reduced removal efficiencies. Nitrogen and phosphorus are supplied by the addition of either urea or mono ammonium or diammonium hydrogen phosphate. Other than nitrogen and phosphorous various nutrient elements such as potassium, calcium, magnesium are usually present in the waste. Inorganic substances such as iron, molybdenum and cobalt are also required in trace quantities. Temperature, pH and oxidation-reduction potential are the other factors having important role in the activated sludge process. The optimum pH range for the activated sludge process is between 6.5 and 9.0; if the pH value is below 6.5 fungi will compete with the bacteria. Hence, for effective oxidation of the organic matters by bacteria, pH measurement must be made at regular intervals in the aeration tank.

Various operating variable have a role on the effectiveness of the activated sludge process, such as organic loading, sludge retention time, hydraulic or aeration detention time, oxygen requirements levels in the aeration tanks, Regulation of the amount of returning activated sludge and Control of the waste activated sludge. Role of bacteria in the activated sludge process is shown in *Figure 3.*

2. Aerated Lagoons

Aerated lagoons are large holding tanks used to oxidize the dissolved organics by mechanical aeration by surface, turbine or diffused aeration technique. Generally floating aerator technique is used to supply the required quantity of oxygen and mixing power. Aerated lagoons, the internal surface is lined with cement or butyl rubber or polythene used. In this process the waste materials are treated for 2 to 6 days depends upon the contaminant present in the effluent. During this time duration, around 90% of biological oxygen demand is removed by oxidation of organic matter and to form a denser flocculent sludge. This flocculent sludge is removed in a settling basin before final effluent discharge. After complete process, bacteria might be present in the final effluent, hence further biological purification is required.

Figure 3. Role of bacteria in the Activated Sludge process



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3. Trickling Filtration

Trickling filtration is an aerobic fixed-film biological treatment process for the removal of organic matters from the wastewater. In this process consists of a structure of highly packed with inert permeable such as rock, wood, or plastic. The treated wastewater is spread/sprinkled over the upper surface of the medium by moving sprinklers using either a fixed spray nozzle system or a rotating distribution system. The inert medium develops a biological slime layer, that absorbs and biodegrades organic pollutants by percolation. Air flows through the filter by convection, thereby providing the oxygen needed to maintain aerobic conditions. The microbial slimes formed on the bottom of the bed oxidize the wastewater. The thickness of the slime layer increases due to microbial growth. During this process, a gelatinous film of the microbial growth is formed on the whole surface of the bed which absorbs the dissolved and colloidal organic matter and degrades the organic matters. In trickling filtration process, organic concentration, temperature of the waste, size of the bed stone, microbial surface area, depth of the filter, retention time and oxygen transfer are having the important role in the removal of organic matters. The microbial layer formed at the bottom of the bed is very sensitive to temperature, and the metabolic activities are directly proportional to the temperature of the waste passing through the filter. A flow diagram of trickling filter is shown in *Figure 4*.

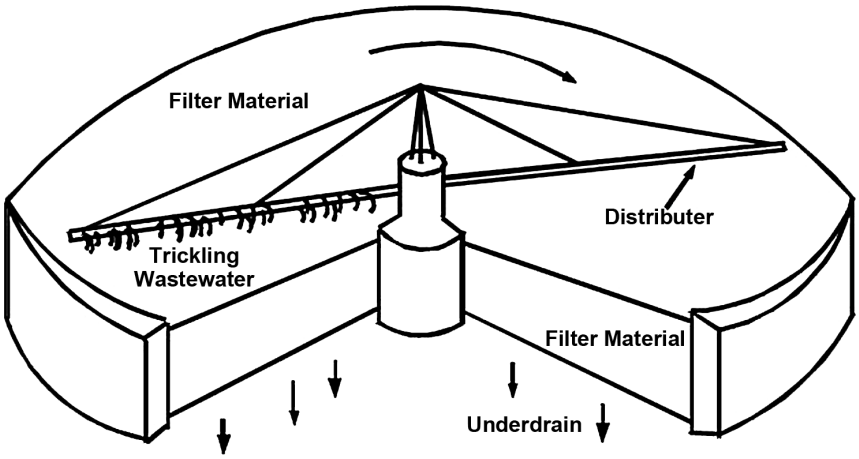
Trickling filters are classified depending upon the organic loading. They are:

Low-rate: In this the filters has a media bed depth of 1.5 to 3 meters
High-rate: In this the filters may have a bed depth from 1 to 9 meters.

4. Oxidation Ditch

Oxidation Ditch is a modified Activated Sludge process, which consists of a ring- or oval-shaped channel and is equipped with mechanical aeration devices. In this aeration is done by using an aeration system and mixing done by using brush rotors placed across a race-track-shaped basin. Filtered waste-water enters the ditch at one end, is aerated by rotors and circulates. Oxidation ditches normally operate in prolonged aeration mode with longer detention and solids retention time are provided.

Figure 4. Flow diagram of Trickling filter



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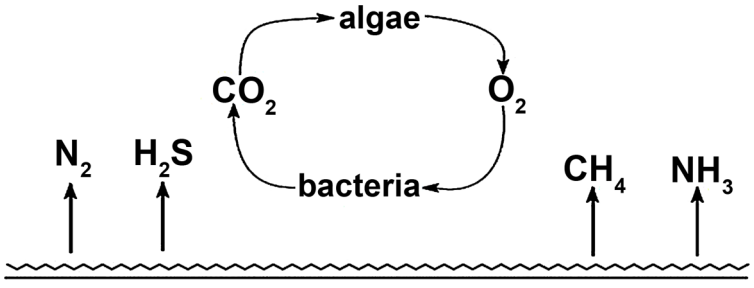
5. Oxidation Ponds

The liquid is treated by bacteria which break down the organic matter remaining in solution and then it is sent to oxidation ponds. Oxidation pond treatment is a very economical secondary treatment process. The effluent entering the ponds is a mixture of primary and secondary treated effluent. Oxidation pond is a large shallow pond in which wastes are added at one end where heterotrophic bacteria continue the breakdown of the organics in which the required oxygen is supplied by the algae for its metabolism. The composition of the effluent is varies during the year. In summer generally primary treated effluent, whereas in winter more secondary treated effluent is used. The carbon dioxide that is released by bacteria will be utilized by algae for the photosynthesis reaction. High penetrative photosynthesis of algae, powerful mixing and natural aeration are needed in effective treatment of wastes. These aerobic and anaerobic processes enable the purification of waste water.

Solids present in the waste are getting settled at the bottom of the pond. In this oxygen bond solid layer acts as anaerobic phase whereas the top liquid layer acts as aerobic phase. In the pond, algae use solar energy to produce oxygen from carbon dioxide and water, and bacteria use oxygen to break down the remaining organics to simple molecules such as carbon dioxide and ammonia.

The rate of purification is depends upon the amount of the algae present in the pond due to the release of more amount of oxygen released by the algae. The growth of algae is enhanced by the nutrients present in the waste. After the treatment the effluent is removed at another end. During this process maximum amount of BOD is reduced and no longer is BOD treatment required for the effluent. If there is any lacking of oxygen in the pond, the anaerobic conditions is created in the ponds leads to breakdown of waste and produce foul odour in the pond (Technology Transfer Manual of Industrial Wastewater Treatment, Overseas Environmental Cooperation Center, Japan, March 2003; Biological wastewater treatment; Boari, et al., 1997; Wastewater treatment technology and application in Industrial facilities; Hoffmann, 1998; Wang, et al., 2009; Melin, et al., 2006; Henze, et al., 2008; Van Haandel, & Van der Lubbe, 2012; Kalbar, et al., 2012; Sewage treatment; Verbyla, & Mihelcic, 2015; Mara, & Johnson, 2007; Muga, & Mihelcic, 2008'; Mahajan, 2007). The chemical reaction taken place in oxidation ponds is shown in *Figure 5*.

Figure 5. Chemical reaction of Oxidation Ponds



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TERTIARY TREATMENT

Tertiary treatment is the final treatment process in the waste water treatment to remove significant amounts of nitrogen, phosphorus, heavy metals, biodegradable organics, bacteria and viruses for further. This treatment process is also to remove the dissolved inorganic solids, bacteria and traces of organics. Removal of bacteria especially of faecal origin is achieved by keeping the effluents from secondary biological treatment units in maturation ponds for specified periods. If the final effluent still contains enough bacteria, then it is chlorinated. The tertiary treatment process operation involves chemical coagulation, flocculation and sedimentation, followed by filtration and activated carbon. Ion exchange and reverse osmosis for specific ion removal or for dissolved solids reduction are less frequently used. Inorganic dissolved solids are removed by the following methods.

1. Evaporation

It is a process utilized only when the recovered solids or concentrations solutions are reused. This process is specifically useful for the concentration of radioactive waste and other wastes of smaller volume. In this process waste effluent is evaporated by boiling and vaporising the water phase. The degree of evaporation is greatly dependent upon climatic conditions. This process is generally available only to those facilities located in arid regions (Waste-water treatment technologies: A general review. United Nation, NY, 2003; Wastewater treatment technologies; Evaporation - A Wastewater Treatment Alternative).

2. Reverse Osmosis

Reverse osmosis (RO) is a process for separating dissolved solids and metals from water, and it is useful only when the solute molecules are same size as the solvent molecule. Osmosis is the process of diffusion of a solvent (such as water) across a semi-permeable membrane from lower concentrated solution into higher concentrated solution. Whereas in the reverse osmosis process, pressure is applied which is greater than the normal osmotic pressure is applied in the higher concentration region to force the purified water pass through the membrane and into the lesser concentrated solution through permeation. The effluent liquid waste containing dissolved solids is passed over the surface of a semi permeable membrane and at a pressure, which leaves the concentrated liquor on the surface of the semi permeable members. In RO the low molecular-weight solutes such as salts, surfactants do not pass through the membrane, which are called as concentrate. These concentrates are recirculate through the membrane until the flow of permeate drops.

Various factors such as dissolved solids concentration and temperature of the feed stream, the applied pressure, and the type of membrane selected having the important role in the separation of solids in RO. Selectivity for water over ions, permeation rate and durability are the other factors need to be considered while selecting the semi-permeable membrane in the RO. Generally Cellulose acetate and polyamide-hydrazide membranes are used for the effective separation (Matsuura, 1993; Cruver, & Nusbaum, 1974; Xiao, et al., 2014).

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3. Membrane Separation

Various membrane separation processes such as reverse osmosis, ultrafiltration, dialysis, piezodialysis and electrodialysis are used; whereas dialysis and piezodialysis techniques are not having any significant role in the waste water treatment. In the dialysis technique separation of solutes from the solution is based on the difference in the rates of diffusion. In electrodialysis gradient electrical potential is used as driving force and an ion exchange membrane as discriminating barrier. Electrodialysis technique is used to remove the ionic constituent in the wastewater treatment process (Davis, 2013; Water Environment Federation, 2005).

4. Chemical Precipitation

Chemical precipitation technique is used to remove metal compounds from wastewater by forming a chemical precipitation of soluble metallic ions into insoluble form as precipitated product. Coagulation/ flocculation processes are used in conjunction with chemical precipitation to enhance the removal of suspended and colloidal materials by forming an agglomeration and convent into more readily settle able flocs and removed by liquid filtration or by clarification technique.

Commonly the metal ions are present as hydroxides, sulfides or carbonate forms. Commonly most of the heavy metals are precipitated as hydroxide at elevated pH. Chemical precipitation process taken place in two steps.

1. Addition of chemical precipitating agents: Precipitating agents are added into the wastewater and mixed by means of mechanical mixture to induce the formation of insoluble metal precipitants.
2. Filtration or clarification: The metal precipitates are removed from the wastewater through filtration or clarification technique. If clarification technique is used, a flocculent is sometimes added to aid the settling process. The degree of clarification in the separation of the precipitates is depends on the quantity of chemicals used.

Various chemicals are used as precipitants, but selection of suitable precipitants is based on performance, reliability and cost. Commonly used precipitants in the wastewater treatment are lime, sodium hydroxide (caustic), soda ash, sodium sulfide, and ferrous sulfate. Lime is the cheapest and effective precipitating agent. Chemicals such as sulfuric acid and phosphoric acid are used for the pH adjustment, whereas polyelectrolytes are used as flocculation aids in the wastewater treatment. Various factors such as chemical interactions, temperature, pH, solubility of waste contaminants, and mixing effects have an important in the formation of chemical precipitation.

There are two type of precipitation technique such as Hydroxide precipitation and sulfide precipitation are used in wastewater treatment process, often combination technique is used to remove the optimal metal.

Hydroxide precipitation: This technique is used to remove the metals like antimony, arsenic, chromium, copper, lead, mercury, nickel and zinc.

Sulfide precipitation: This technique is used to remove the metals like lead, copper, silver, cadmium, zinc, mercury, nickel, thallium, arsenic, antimony and vanadium (Waste-water treatment technologies: A general review. United Nation, NY, 2003; Wastewater treatment technologies; Davis, 2013).

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5. Ion Exchange

It is general technique used to remove the heavy metals from the low–concentration waste streams, such as electroplating wastewater, is ion exchange. This process is used only when the metal contaminants and exchanged salts are recovered and reused. In this technique, the waste water stream is passed through a bed of resin (cationic or anionic or mixed) containing ionic charge on its surface; which are used for exchange of same charge of ions in the wastewater. Selection of ion exchange technique in waste water treatment is dependent upon the contaminant to be removed and for water softening. Often, individual resin beds containing different resins are arranged in series, in specific treatment purpose mixed bed system is used. Generally polystyrene copolymerized with divinylbenzene resin is used for the treatment.

Ion exchange process is taken place in four steps.

1. **Treatment:** Wastewater is passed through the resin bed and ions are exchanged until pollutant breakthrough occurs.
2. **Backwash:** Backwash the bed to remove the suspended solids on the surface.
3. **Regeneration:** The resin bed is treated with higher concentrated acidic or alkaline solution to charge the resin originally present in the resin bed.
4. **Rinsing:** The resin bed is rinsed to remove the residual regeneration solution present in the surface of the resin (Gregory & Dhond, 1972).

ANALYTICAL TECHNIQUES

After the tertiary treatment wastewater can have different elements. The amount of elements such as phosphorous, nitrogen, dissolved oxygen, nitrite, nitrate, sulphide, might be present in the treated wastewater, and it's needed to be quantified. Various analytical techniques are available to detect the residuals in the treated waste water. The chosen analytical technique should be very specific to determine the residual present in the treated waste water even in very low levels to ensure the effluent purity and provide the assistance to the other stages for the treatment process.

Various instruments are used in the determination of residues in the treated waste water. They are:

1. Atomic absorption spectroscopy (AA)
2. Gas Chromatography (GC)
3. Inductively coupled plasma (ICP)

Atomic Absorption Spectroscopy (AAS)

AAS is used principally for the quantitative determination of metal elements in aqueous and solid samples. AAS deals with the absorption of specific wavelength of radiation by neutral atoms in the ground state. In the Atomic absorption spectroscopy, solution of metallic salt sample is atomising to form fine droplets. Due to thermal energy the solvent in the droplet evaporates leaving fine residues, which are converted into neutral atoms. These neutral atoms absorbs the light passing through the atoms present in the vapour stage and measure the amount of light absorbed by the atoms. The amount of light absorbed depending on the amount of element present in the vapour. Various lamps are used which are depends upon

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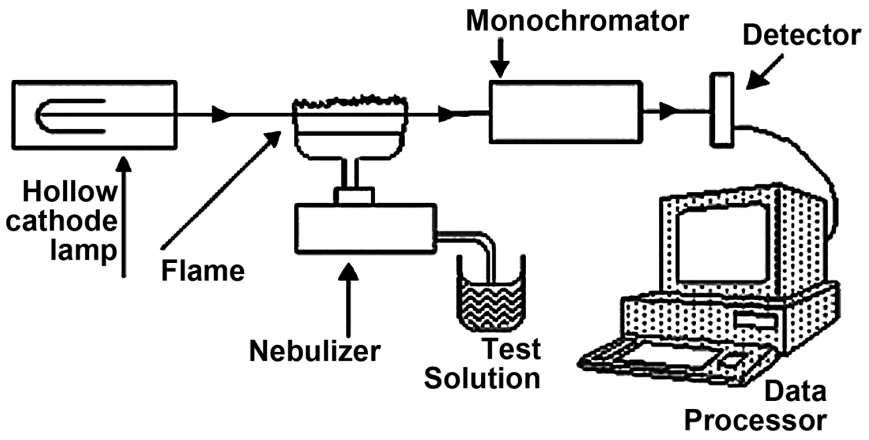
Figure 6. Schematic diagram of Atomic Absorption Spectroscopy



the element to be determined in the treated waste water. This technique is used for detecting cadmium, chromium, copper, lead, silver and zinc (Willard, et al., 1989). Schematic diagram of Atomic absorption spectroscopy is shown in *Figure 6*.

Gas Chromatography

Gas Chromatography consists of Gas solid chromatography (GSC) and Gas liquid chromatography (GLC). In GSC the principle of separation is adsorption, whereas in GLC the principle of separation is partition. In GLC, gas is used as mobile phase and liquid which is coated onto a solid support is used as stationary phase. In GLC, sample is converted into vapour and mixed with gaseous mobile phase. The components are separated based on their partition coefficient. The component which is less soluble in the stationary phase, travels faster and eluted out first and the components which is having more soluble will be eluted later (Willard, et al., 1989). Schematic diagram of Gas chromatography is shown in *Figure 7*.

Inductively Coupled Plasma (ICP)

ICP is one of the commonly used instruments for the determination of various metal elements such as arsenic, cadmium, chromium, copper, lead, silver and zinc. In this technique the sample is atomized and injected in a chamber packed with argon plasma, to convert the sample solution into an aerosol and pass into central channel to vaporize the sample. The vaporized sample liberates the atoms, due to collision excitation, atoms are promoted to higher energy excited states. The excited atomic and ionic excited species return to the ground state with the light emission of a photon, this photons have a characteristic energies that can be measured. The total number of the proton is directed proportional to the concentration of the element present in the sample. The intensity of the emission band is compared with the previously measured intensities of the known concentration of the elements, by interpolation in the calibration curve we can able to measure the concentration of the given sample. Thus the wavelength of the photons from the element has a characteristic emission band which can be used to identify the elements in the treated waste water (Hou, & Jones, 2000; Stefansson, et al., 2007). Schematic diagram of inductively coupled plasma is shown in ***Figure 8***.

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Figure 7. Schematic diagram of Gas Chromatography

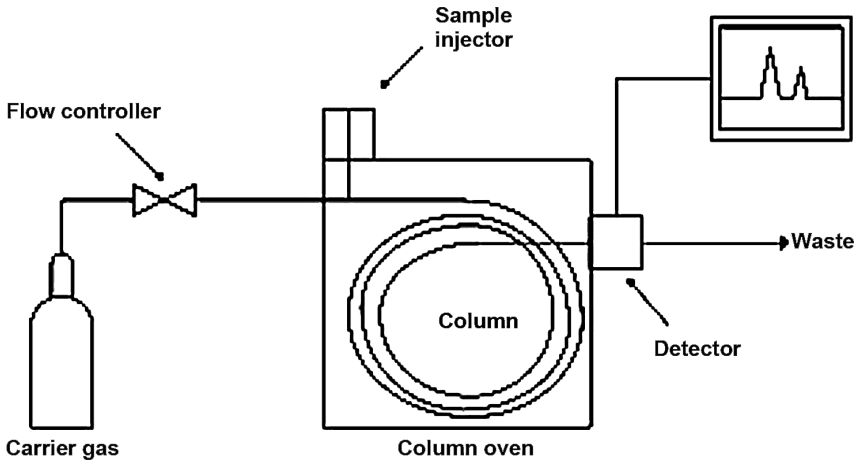
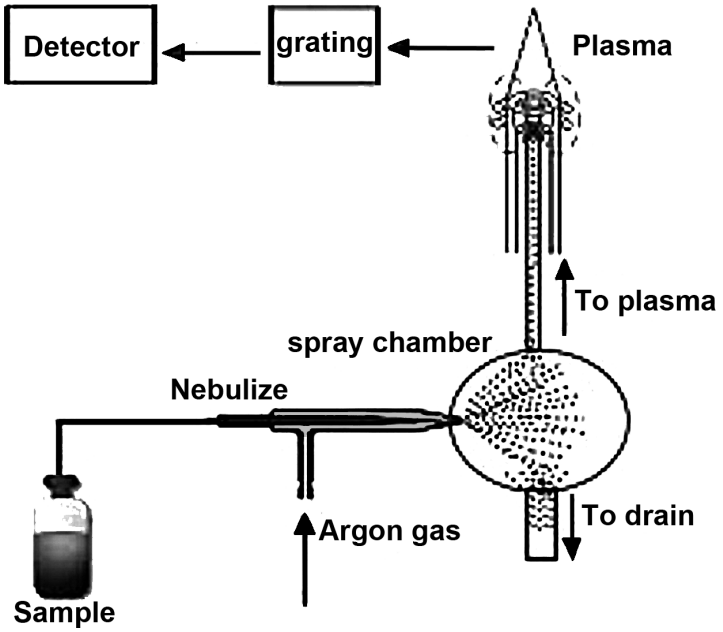


Figure 8. Systematic diagram of inductively coupled plasma



Total Phosphorous

Normally phosphorous is occurs in the fifth oxidation level. In wastewater phosphorous is present as phosphates, whereas the phosphorous atom combined with four oxygen atoms (PO_4^{-3}). Phosphorous is the limiting nutrient for the plant growth. Generally phosphates are originate from various sources such as cleaning solutions, fertilizers and biological wastes. If concentration of phosphate in high level persists, algae and other aquatic life will grow by decreasing the amount of dissolved oxygen by increasing the decay of organic matter.

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The amount of phosphorous in the treated wastewater can be determined by colorimetric method. The determination of phosphorous is done in three steps:

1. Oxidise the phosphate into orthophosphate using the mixture of sulphuric acid and nitric acid.
2. Formation of yellow complex by the reaction between the orthophosate with ammonium molybdate and potassium antimonyl tartrate in presence of acid.
3. Reduction of yellow complex with ascorbic acid to molybedenum blue.

The intensity of the blue colour is directed proportional to the concentration of the element present in the sample. The concentration of the phosphorous as phosphate present in the treated waste water can be determined from the standard curve.

Total Organic Nitrogen

In surface and ground water various concentrations of Organic nitrogen is present from free amino acids and ammonia. Presence of ammonia in the waste water is an indication of sanitary pollution. Ammonia is readily oxidized by bacteria and converts into nitrite and nitrate. Nitrogen present in the treated wastewater can be determined by heating the sample in acid using copper sulphate as catalyst. The reaction is continued until the complete conversion of nitrogen into NH4 + ions and then converted into ammonia by treating with a base. The amount of ammonia can be determined by using an autoanalyser with colorimetric detection.

Dissolved Oxygen

Oxygen enters into the water by diffusion from the atmosphere and dissolved oxygen is a vital one for various aquatic living things. The solubility of the oxygen in the water is directly proportional to the partial pressure in the gas phase, to salt concentration and temperature. The amount of dissolved oxygen in the water is affected by various factors such as temperature, flow (velocity of water flowing in a stream), presence of aquatic plants, altitude and dissolved or suspended solids. The amount of dissolved oxygen in the treated waste water can be determined by:

1. Oxygen selective electrode method
2. Redox reaction

Nitrite (NO_2)

Biological breakdown of organic nitrogen (oxidation of ammonia or reduction of nitrate) produces nitrites as an intermediate product in the water. Amount of nitrite in the wastewater is an indicative of the pollution. Amount of nitrite in the treated wastewater can be determined by reacting the nitrite with sulphanilamide to form diazonium compound (Griess-Ilosvay's method). This diazonium compound is reacts with N-(1-napthyl)ethylenediamine to form a colored azo dye, which can be measured spectrophotometrically.

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Nitrates

Nitrates are produced as end product in the water when biological breakdown of organic nitrogen occurs. When water shows presence of excess amount of nitrates, it indicates the poor quality of water. The quantity of nitrite present in the sample illustrates the amount of nitrate present in the treated wastewater. By measure the difference of nitrite present on successful treatment gives the quantity of nitrate present in treated waste water.

Hydrogen Sulfide

Sulfide as hydrogen sulphide which inhibits the aerobic respiration, muscle contractions, including breathing, and promotes excess breakdown of glucose. Hydrogen sulfide level in the treated wastewater increases when sulfate-reducing bacteria grow up in the anaerobic sludge of a pond. The amount of sulphide present in the treated wastewater can be determined by reacting the H_2S and N,N-dimethyl-*p*-phenylene diamine to form methylene blue (a strongly coloured complex) in the presence of $FeCl_{3.}$

Total Solids

Total solids include both the suspended and dissolved solids in the wastewater. These solids have an important role in the conductivity and turbidity of the sample. The amount of the total solid present in the treated wastewater can be measured by place a specific quantity of the sample in a previously weighed dish in a drying oven at the temperature between 103°C and 105°C to evaporate the water. The dish is weighed frequently until get the constant weight, the difference between the initial and final weight of the dish gives the total weight of the solid present in the sample.

pH

pH is defined as the negative logarithm of the hydrogen ion concentration. The pH value indicates the amount of hydrogen ion present in the sample and to categorise the sample into acidic, basic or neutral of the treated wastewater. pH of the treated wastewater can be measured by using an ion-sensitive electrode known as a glass electrode.

Alkalinity

The alkalinity of the sample is mainly due to bicarbonate, carbonate and hydroxide ions in the water, which increases the pH of the water above 4.5. Alkalinity of the sample indicates the buffering capacity of water and its ability to resist a change in pH. Alkalinity is differs from pH, and it can be measured by simple acid-base titration (amount of acid required to neutralize the sample) using a suitable color indicator.

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Five Day Biological Oxygen Demand (BOD5)

Biological Oxygen Demand measures the amount of oxygen utilized by organisms in the biochemical oxidation of organic matter in a wastewater sample in a specified time (usually 5 days), and at a specified temperature. BOD measurements are used as a measure of the organic strength of the water.

BOD of the sample can be determined by diluting the sample to get concentration of 2 mgL^{-1} O_2 (approximately) and incubating the sample in a sterile condition at the temperature of $20 \pm 1°C$ for five days (allyl thiourea is added to the incubating material to prevent the oxidation of these compounds); measure the dissolved oxygen content which gives the BOD value.

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand measures the total quantity of oxidisable materials (organic and inorganic matters) present in the sample. COD of the sample can be determined by oxidation reaction (using strong oxidant like potassium dichromate). The amount of oxidant utilized for the oxidation of the sample gives the value of COD (Janben, https://www.ecn.nl/docs/society/horizontal/hor16_nutrient.pdf; Elser, et al., 2007; Lapa, et al., 2000; Park, & Noguera, 2004; Posadas, et al., 2015; Barker, et al., 1999; Ma, et al., 2001; Interpreting Results From Additional Water Tests; Water quality parameters).

STANDARDS AND GUIDELINES

Globally various standards for the treated wastewater has been developed to ensure it's physical and chemical quality. Each country they have a standards for the treated wastewater, whereas the limits of the elements are reviewed and updated to meet the global needs for the protection of ambient waters.

Various regulatory agencies mandate the control of water pollution. They also establish secondary treatment standards, the agency which controls are United States Environmental Protection Agency (USEPA) and National Pollutant Discharge Elimination System (NPDES). Table 2 shows limitations in secondary waste water treatment plants and European Community Environmental Directive Requirements (EC EDR) for discharges from urban waste water treatment (United States Environmental Protection Agency, 2007; Eaton, & Franson, 2005). Various organizations of wastewater treatment standards are given in *Table 2*.

Table 2. NPDES and EC EDR for Discharges from Wastewater Treatment Plants

Parameter	NPDES			EC EDR WD	
	30-Day Average Concentration	7-Day Average Concentration	Percentage of Removal	Concentration (mg/L)	Percentage of Removal
BOD	30mg/L	45mg/L	85	25	70-90
TSS	30mg/L	45mg/L	85	35-60	70-90
pH	6-9	--	--	--	--
COD	--	--	--	125	75
Total Nitrogen	--	--	--	10-15	70-80
Total Phosphorous	--	--	--	12	80

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CONCLUSION

The effluent from the various industries contains various matters such as organic material, numerous pathogenic microorganisms, nutrients and toxic compounds which leads to environmental pollution and hazards of health community of various living things. An optimized wastewater treatment process and plant design needs to be developed to support the effective treatment process. The critical role of the wastewater treatment process is to ensure that the effluent leaves the treatment plant should meet the limitation of the environmental standard.

Hence, the treated effluent must ensure the safety, efficacy, quality of the treated wastewater and regulatory requirements to protect the public health from the various effluent environmental pollutions.

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Chapter 4
The Fundamentals of Water and Natural Waters

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ABSTRACT

This chapter provides information on the fundamental concepts needed to understand water and water pollution, enabling better comprehension of the subsequent material. Examining the molecular structure of water provides context for understanding its most important properties. The reader explores the various types of natural waters and learns how they are tied together in the global water cycle. An examination of the contents of natural waters reveals the presence of dissolved solids, liquids and gases and the intimate relationship between these substances and the community of life that dwells in aquatic systems. The chapter introduces basic concepts of the chemistry of water and discusses the action and distribution of pollutants. Readers also learn about the basic interaction between various pollutants and the aquatic food chain.

INTRODUCTION

This book is about the complex relationship between people, water and health. It will explore how the health of humans is intimately tied to the health of natural water systems. The first chapter will prepare the reader for a fuller understanding of the topics covered in the rest of the book. The objective of this chapter is to examine the fundamental properties of water beginning with molecules and finishing with the ocean. Life, water, and the atmosphere of Earth function together in a highly interdependent way. One cannot understand one single component without having some appreciation for the entire system. So this chapter is organized in a holistic way, with topics often blending together in order to give a fuller understanding.

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BACKGROUND

When viewed from a spacecraft, the Earth appears as a shining blue and white orb. The blue light is reflected from the water of the ocean and the white light from the condensed water vapor of the clouds. Water is the dominant and defining feature of our planet. Not surprisingly, water is also one of the defining features of life.

The Earth formed some 4.5 billion years ago. The ocean appeared about 1 billion years later (Stanley, 2009). From that primordial sea evolved the first forms of life about a half a billion years later. So for most of its existence Earth has been wet and alive. Water shaped the forms of life that evolved in the sea and eventually invaded the land. And as life developed it reshaped the nature of the ocean and atmosphere above. About three billion years ago the process of photosynthesis developed in certain bacteria and algae. This new type of metabolism used energy from sunlight to fuel these early plant-like creatures. To access the energy in sunlight, photosynthesis splits water molecules resulting in the release of free oxygen as a waste product. That oxygen changed the chemistry of the sea and the air. The splitting of water also produces high-energy electrons and protons that are used in photosynthesis to do the work of

Figure 1. View of Earth from space taken by Apollo astronauts on December 7, 1972.
http://en.wikipedia.org/wiki/The_Blue_Marble#mediaviewer/File:Apollo17WorldReversed.jpg

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the cell, including building sugars from atmospheric carbon dioxide (Garrison, 2001). Algae use sugars made in photosynthesis as the basis to create a huge variety of organic compounds. Those organic molecules fuel the rest of the ocean food chain, and a portion of them is buried in the ocean sediments. Over time those buried organic molecules transform into petroleum and natural gas that now fuel much of our economy. Indeed, it is the burning of millions of years' worth of fossil fuels over the last two centuries that is once again changing the atmosphere and the global climate (Miller & Spoolman, 2014).

THE STRUCTURE OF WATER AND ITS CHEMESTRY

Water is a wondrous substance. Its special structure gives rise to a variety of important properties the reader will need to understand in order to appreciate subsequent chapters. Water is a molecule made up of two different kinds of atoms, oxygen and hydrogen. Mostly water appears as H_2O, one larger oxygen molecule sharing electrons with two smaller hydrogen atoms. The sharing of electrons by the oxygen and hydrogen atoms results in what are called covalent bonds (Becker & Wentworth, 1973).

The oxygen molecule contains in its nucleus eight protons and eight neutrons. By comparison hydrogen atoms are much smaller, each containing only one proton and one neutron in its nucleus. The eight positively charged protons in the oxygen nucleus attract the negatively charged electrons away from the single protons of the hydrogen nuclei. Oxygen is said to be more electronegative than hydrogen due to its superior attractiveness for electrons. As such, the electrons from the hydrogen atoms in the molecule spend most of the time near the oxygen end of the structure. This makes the oxygen end carry a charge of -2, and each hydrogen on the other end carry a charge of +1. The overall charge of each water molecule is neutral, with -2 on the oxygen end and +2 on the hydrogen end. This distribution of charge makes the water molecule polar meaning that is it has a negative and a positive end (Armstrong, 1983).

That water is a polar molecule leads to its numerous special properties. First, the polarity causes water molecules to arrange themselves in a particular way. The negatively charged oxygen end of one molecule will be attracted to the positively charged hydrogen sections of an adjacent water molecule. Since it has a charge of -2, each oxygen end attracts two different +1 hydrogen ends. The resulting arrangement is a liquid crystal in which each water molecule is bonded with four other water molecules. The attraction between the positive H ends of one molecule and the negative O end of another results in what is called a hydrogen bond. Unlike the strong covalent bonds that hold a single water molecule together, the hydrogen bonds formed between different water molecules are rather weak. Yet, there are so many of these weak hydrogen bonds, four times the number of water molecules in a container, that they become very important (Armstrong, 1983).

The numerous hydrogen bonds of water hold together the molecules with surprisingly great strength. One can see this by laying a straight pin on its side on the surface of water in a cup. It remains on top of the water supported by the surface tension created by hydrogen bonds joining the water molecules cradling the pin. A gentle push on the pin is sufficient to break those H-bonds long enough for the pin to quickly sink.

The temperature of the water determines the distance between each water molecule. If heated, the energy imparted to the water will cause the hydrogen bonds to expand and as such makes the water expand, the same number of molecules now occupying a greater volume. The warmed water becomes less dense. Conversely, cooler water is denser than warmer water, but only down to the temperature of 4° C. As water cools further the liquid crystal again expands. At 0° C and with the removal of some more heat, the water turns to low-density ice and it floats on the surface (Wetzel, 1983).

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Figure 2. Water molecule showing distribution of charge. Note that the oxygen end carries an effective charge of -2 and that that each hydrogen atom caries a charge of +1.
http://upload.wikimedia.org/wikipedia/commons/0/05/H2O_molecule_scheme_of_dipole.png by Oz Nahum

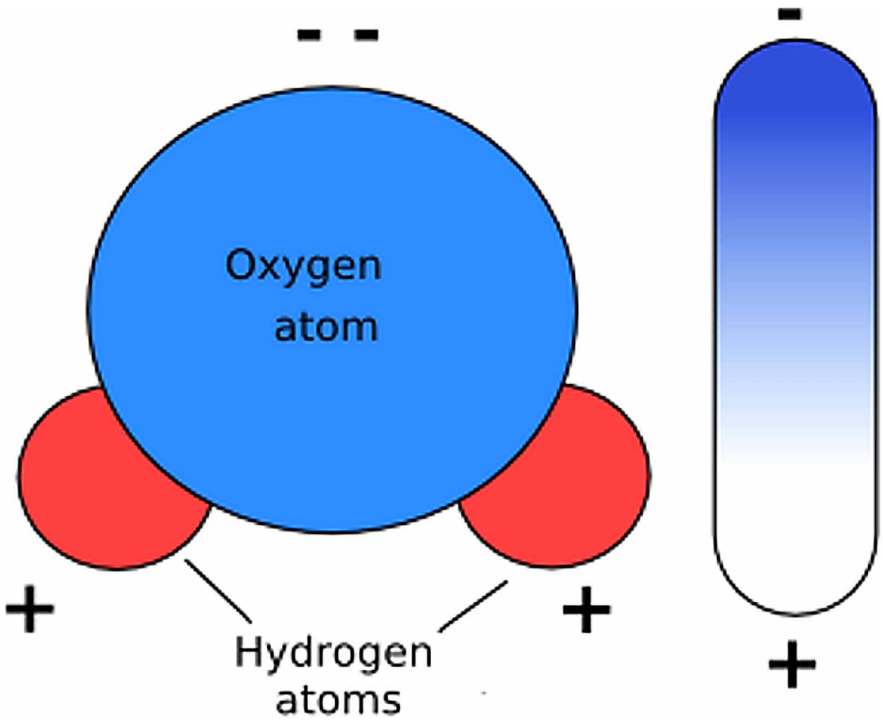
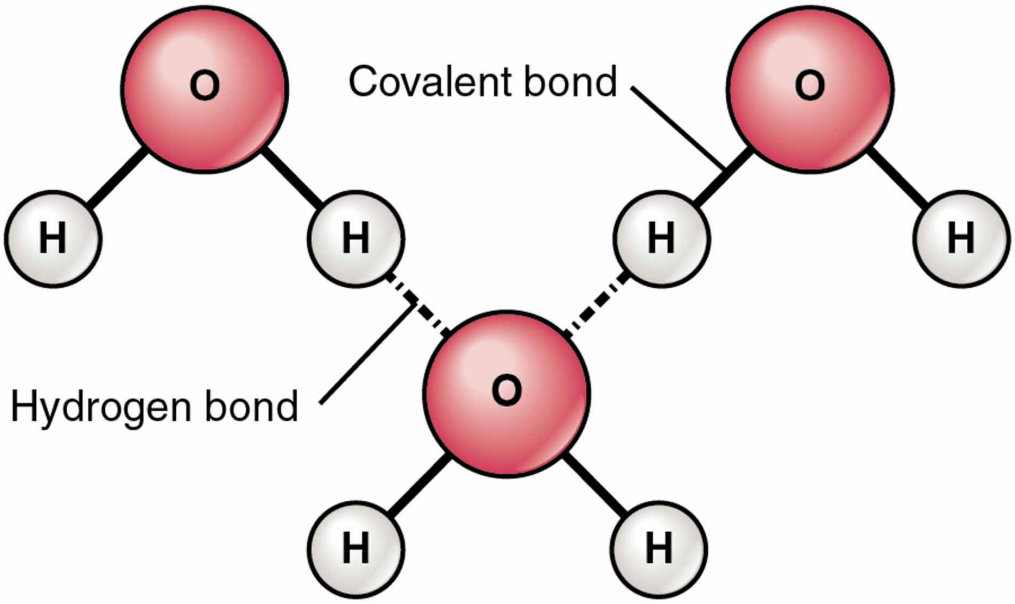


Figure 3. Water molecules in a matrix showing hydrogen bonds. Each water molecule can form hydrogen bonds with up to four other water molecules.
http://upload.wikimedia.org/wikipedia/commons/0/0f/210_Hydrogen_Bonds_Between_Water_Molecules-01.jpg by OpenStax College, from Anatomy & Physiology, Connections http://cnx.org/content/col11496/1.6/



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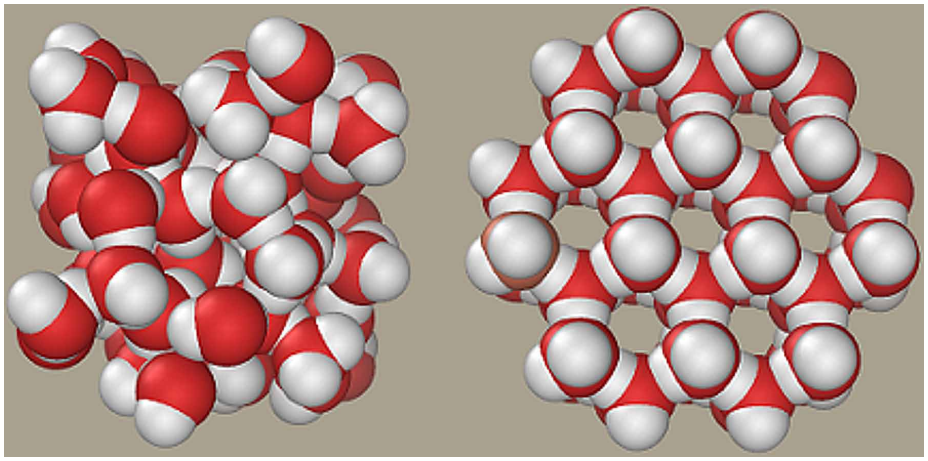
The global warming of recent decades means increasingly warmer ocean waters. The warmed seawater expands, submerging low-lying coastal lands. Expanding ocean waters coupled with drainage from melting glaciers leads to raising sea levels that endanger coastal communities.

The formation of coastal dead zones is an important hazard to the environment and human wellbeing. Those dead zones form in the summer when the warmed surface waters float on the cooler deep waters. This creates stratification, with little mixing of the two layers. As such, life forms in the isolated deeper waters use up the available oxygen, creating the dead zone conditions (Diaz & Rosenberg, 2008). The reader can see why understanding a bit about H-bonds and temperature is important to fathom the workings of natural waters.

The expansion and contraction of hydrogen bonds takes a lot of energy. As such, a surprising amount of energy is exchanged when water either warms or cools and so much so that scientists use water as the defining substance for the concept of specific heat. The specific heat of a substance is defined as the amount of energy it takes to increase or decrease the temperature of 1 gram (g) of that substance 1°C (Centigrade, this is calculated at 25°C, at sea level). For example it would take 10 calories to increase the temperature of one gram of water 10°C. Water has a very high specific heat compared to most other substances (Becker & Wentworth, 1973). It is 1 cal/g for water compared to 0.19 cal/g for quartz sand (Engineering Tool Box, 2015). Thus it takes about 5 times the amount of heat to warm a gram of water 1° C as it does to warm a gram of sand. This explains why the range of temperatures for natural waters is about -2 ° C to 38 ° C (Levinton, 2014), and for deserts like the Gobi in Asia, from -55 °C to 40 °C (Weather Online, 2015). The high specific heat of water also explains in part why humans (who are 60% water by mass) are able to maintain a near constant temperature. One can thank the power of H-bonds for the coolness of the ocean breeze on a hot day, and as will be seen below, for the ability of humans to cool themselves.

Figure 4. The molecular arrangement of liquid water is shown on the left, and that of ice on the right. Note that there is more space between the molecules of ice than liquid water. This makes the ice less dense then liquid water and is why ice floats on the surface of lakes or a polar ocean sea.
https://www.google.com/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAcQjRw&url=http%3A%2F%2Fcommons.wikimedia.org%2Fwiki%2FFile%3AMicelle_scheme-en.svg&ei=ytcEVYmMH8vboASnqIDYDA&bvm=bv.88198703,d.cGU&psig=AFQjCNFs5yk_uJ2t2-zgpHmAIKp4Ti_1rw&ust=1426467128161952



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While it takes a lot of energy to warm a gram of water, it takes much more to transform it from liquid to gas. When a gram of water is at 100° C it takes 540 calories to evaporate that water to a gas. This is called the heat of vaporization. All that energy is required to completely break the hydrogen bonds between the water molecules. Once the added heat breaks those bonds, the individual water molecules float away as a gas. When humans become too warm they perspire. The sweat evaporates from the skin surface, using heat from the body. Since it requires so much energy to evaporate water, sweating is a powerful way for humans to cool themselves. Evaporation is also a key feature of the global water cycle and central to determining the climate on Earth as will be explained later.

When water is at 0° C it will turn into ice with the removal of 80 calories of heat per gram. Adding back that same amount of heat would melt the ice to liquid water. This is called the heat of fusion. Melting ice does take a lot of heat, but only about 1/7 the amount of heat needed to evaporate the same mass of water.

Recall that water molecules are polar with negatively and positively charged ends. Polar solutions like water will dissolve other polar molecules. For examples of other polar molecules just look to what is commonly dissolved in natural waters. The list includes ions (such as Ca++, Mg++, Na+, K+, HCO_3^-, Co_3^{--}, SO_4^{--}, Cl^-), and gases (O_2, N_2, CO_2) (Garrison, 2001).

Non-polar substances do not dissolve well in water. They have molecular shapes that produce even distribution of charge, rendering them non-polar. This includes most hydrocarbons, molecules assembled from, carbon and hydrogen. Lipids (oils, fats and waxes) are hydrocarbons modified with the addition of oxygen into carbohydrates, and also are non-polar (Armstrong, 1983).

Water is the universal solvent because it will dissolve all polar substances, and to some degree many non-polar molecules. While water certainly is polar the actual matrix of water molecules is dynamic and permits localized charge environments that dissolve some non-polar molecules. Take benzene, for example. It is a naturally occurring hydrocarbon found in petroleum, products of combustion, and various manufactured chemicals. At standard conditions of 25 C° in fresh water, it has a solubility of 1.8 grams/liter. Recall that there are 1,000 grams of water in a liter, so at most a liter of fresh water would be 0.18% contaminated by benzene. That is still 36 times the safe limit for drinking set by the United States Environmental Protection Agency (USEPA a, 2015). So although many toxins are of low solubility in water, not much is needed to produce dangerous effects for humans and wildlife.

Another important point about non-polar toxins in water is the way they interact with the food chain. In the chapter entitled Industrial and Agricultural Sources and Pathways of Aquatic Pollution and the chapter entitled Health Professions Can Protect Water Quality: Tools for Educators, Advocates and Practitioners, the reader will learn more about the action of certain chemicals used as fire-retardants. These chemicals have low solubility in water, but enough to interact with bacteria, protozoans, worms, fishes and other living organisms. The non-polar contaminant tends to accumulate in the lipids of living cells, as it is much more soluble there then in the surrounding water. Since many cells have no way to destroy or excrete the toxins they accumulate, the contaminants are moved up the food chain with every meal. The worm that eats contaminated bacteria will tend to accumulate almost the entire toxic load from its diet. The fish that eats that worm will do the same. The animals at the top of the food chain will have the highest levels of toxins as a consequence of this process of biological magnification. Consequently humans that eat predatory fishes such as tuna get elevated loads of mercury and other toxins in their diets.

Some of the contaminants are polar and easily dissolve in water. In the chapter entitled Cyanobacteria Toxins in Water Sources and their Impacts on Human Health discusses the role of excess nutrient ions from agriculture in promoting the overgrowth of Cyanobacteria, also known as blue-green algae in

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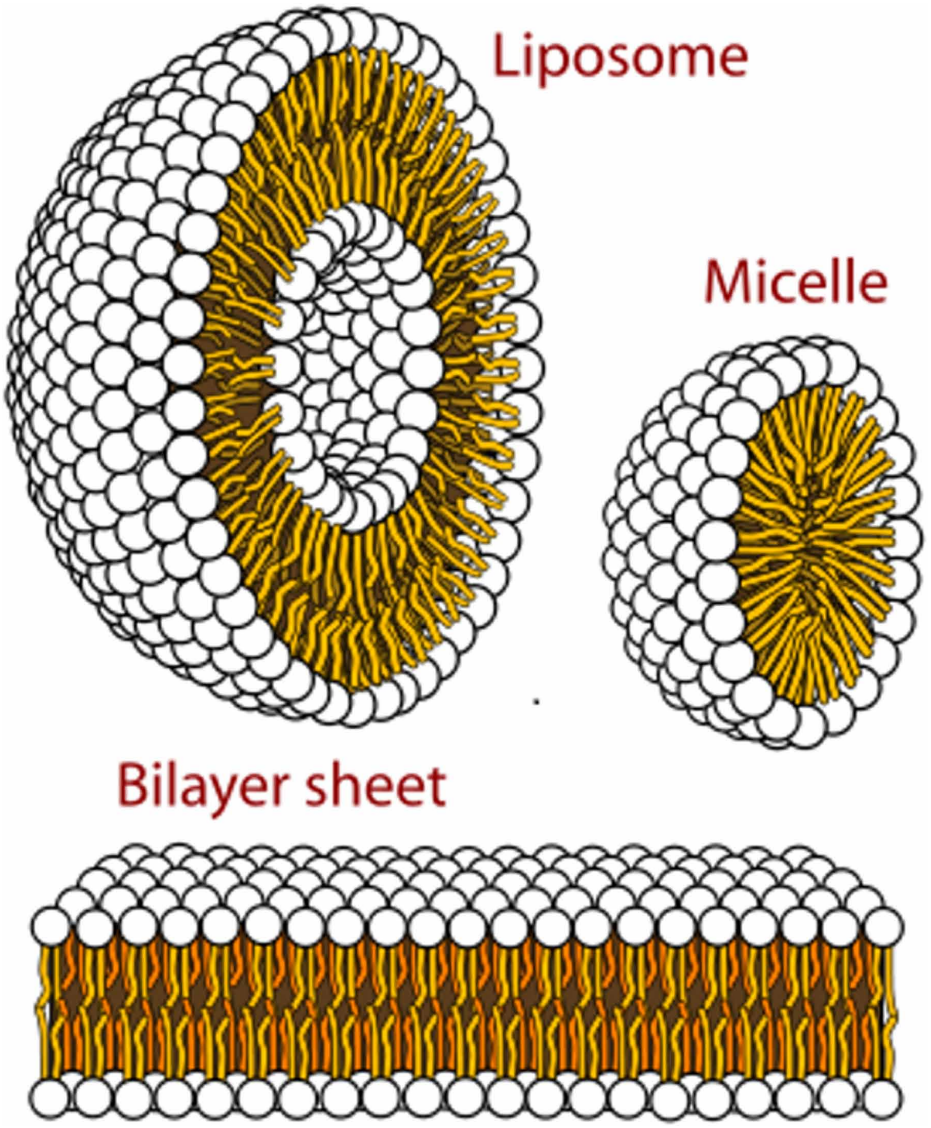
Figure 5. Example of amphipathic molecules forming a micelle. Non-polar substances like grease can dissolve in the centers of micelles, allowing the grease to remain in the water rather than floating to the surface.
http://commons.wikimedia.org/wiki/File:Micelle_scheme-en.svgby SuperManu



contaminated waters. Although many contaminants are non-polar and don't easily dissolve in lakes or the ocean, they may still have devastating effects on natural waters. Generally non-polar contaminants form associations with other molecules that are polar on one end and non-polar on the other. Such amphipathic molecules form tiny spheres (micelles) in water, with the polar heads facing out and the non-polar tails facing in. The non-polar contaminants like pesticides and petroleum dissolve in the non-polar environment inside the micelles. This is how soap is used to wash non-polar grease from cooking pans (Armstrong, 1983).

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Non-polar pollutants like the pesticide DDT never appear in high concentration in water itself, but often accumulate in the non-polar environments within living cells, or on the non-polar surfaces of bits of plastic floating in the sea. A more detailed discussion on pesticides in general and DDT specifically is provided in the chapter on industrial and agricultural pollution.

Revisit the structure of water molecules, H_2O, with H and O atoms sharing electrons. Pure water is a weak acid. That is some of the water molecules disassociate to form ions of OH^- and H^+. For a strong acid, such as sulfuric acid (H_2SO_4,) there is a much higher rate of disassociation than for water.

Water is a weak acid because its disassociation leads to an imbalance of OH^- and H^+ ions, with more H^+ than OH^- in the solution. For a base, the imbalance is the other way, with more OH^- than H^+. The measure of acidity is called pH. Neutral pH is 7. That is when the concentrations of OH^- and H^+ ions are equal. Pure water has a pH of about 6.1. The pH of natural waters ranges from about 3.5 in acid bog lakes to as high as 10 in soda (sodium carbonate) rich watersheds (Wetzel, 1981; Lampert & Sommer 1997). The entire acid-base scale goes from zero, most acidic, to fourteen, most alkaline, or base (Becker & Wentworth, 1973).

The pH scale is deceptive. A drop in pH from 7 to 5 is actually a 100-fold increase in H^+ ions. This is because pH is based upon the $^-$log of the H^+ concentration. Every pH unit represents a 10-fold change in acidity.

Adding or subtracting H^+ or OH^- ions to water will change its pH. However natural waters contain various amounts of dissolved salts that can absorb some of the excess ions. These are called buffers. The buffer salts disassociate and recombine with the extra H^+ or HO^- ions. Calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) are important buffers in natural waters. When in high concentrations these buffers maintain constant pH levels in natural waters. But many inland lakes occur in areas with low concentrations of those buffers. Consequently those lakes are very susceptible to the acids contained in rain and snow. This acid precipitation is produced from the sulfuric and nitric acids in the smoke from burning fossil fuels. The emissions from burning coal with high sulfur content are a major source of acid precipitation. The Clean Air Act of 1990 authorized a system of cap-and–trade in the U.S. to restrict acid-causing pollutants from coal burning power plants. This very successful program pioneered the system of cap-and-trade where companies have to either reduce their emissions or pay for other companies to reduce theirs (Miller & Spoolman, 2015).

Oceanographers once considered the ocean a very well buffered system and paid little attention to pH, which typically remained around 8.2 in surface waters. However, the extensive burning of fossil fuels that commenced during the industrial revolution increased the CO_2 concentration in the atmosphere by 43% as of 2015. While the added CO_2 is well known as a greenhouse gas that causes global warming, it

Figure 6. Equation showing disassociation of water.

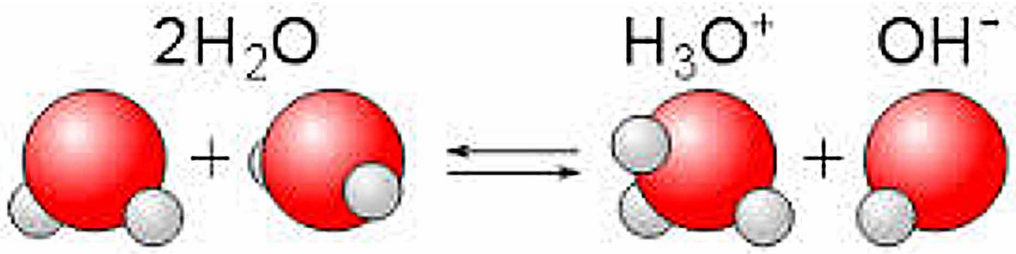

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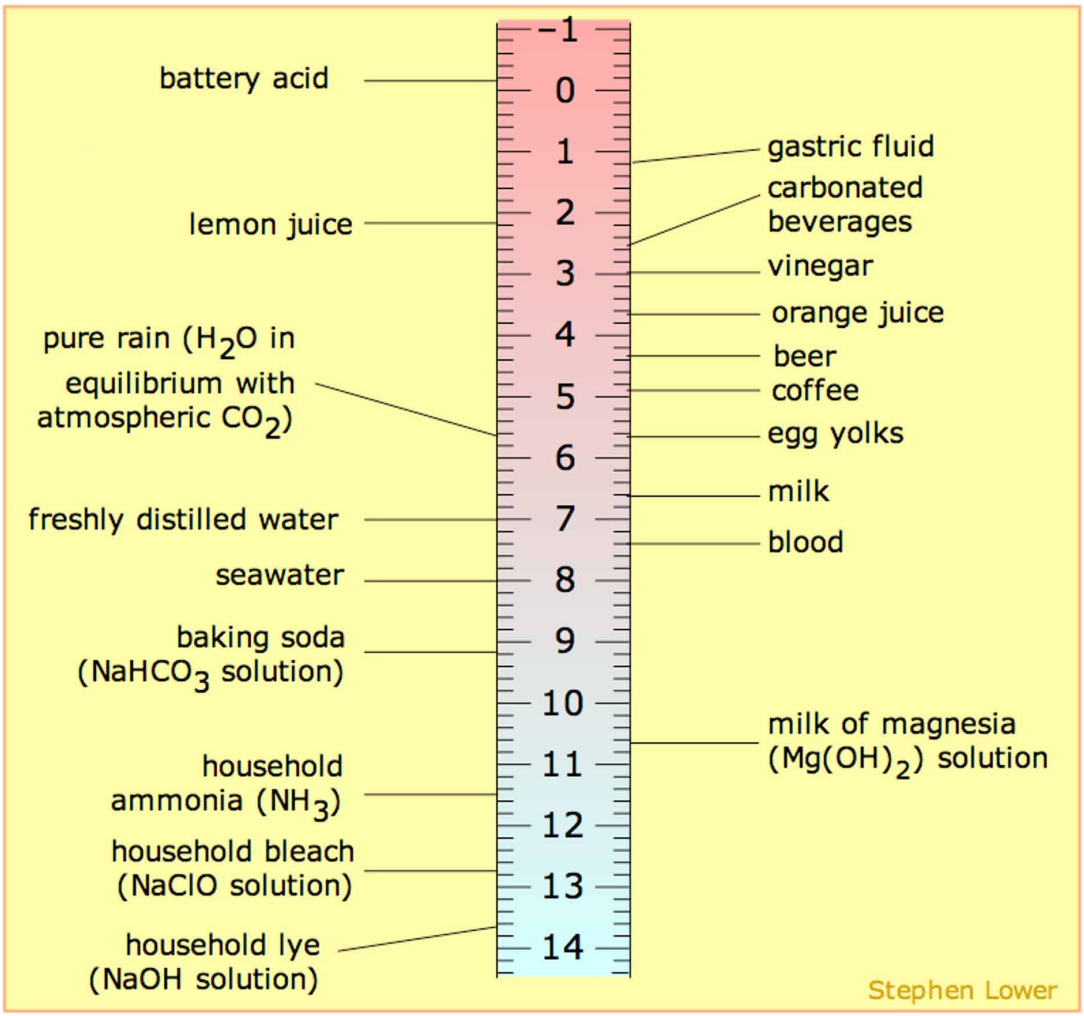
Figure 7. The pH scale with example liquids
http://chemwiki.ucdavis.edu/@api/deki/files/8232/639px-PH_scale.png?revision=1 by Stephen Lower



is also acidifying the ocean. A growing amount of the CO_2 in the atmosphere is dissolving in the ocean, creating carbonic acid. Consequently average ocean pH levels have dropped from 8.2 to 8.1. This might not seem like much but recall that the pH scale is logarithmic, meaning that acidity has increased by 30% since the beginning of the Industrial Revolution. More alarming is that acidity will increase by 150% by the end of the 21st Century if fossil fuel consumption continues as the same rate (National Oceanic and Atmospheric Administration [NOAA], 2015].

Extremes in pH are directly dangerous to life in water as the high concentrations of ions react with molecules of life on the cell membranes. Yet even seemingly minor changes in pH can be detrimental to life. For example, the acid precipitation mentioned above acidified lakes in New England during the 1970's. Consequently the charge state of aluminum ions (Al) changed, and the Al^{+++} ions proved toxic to fishes in those poorly buffered lakes (Lampert & Sommer, 1997). There is evidence that the 0.1 unit acidification of the ocean is also harming corals, oysters, and other sea life that uses $CaCO_3$ as part of body structure (NOAA, 2015).

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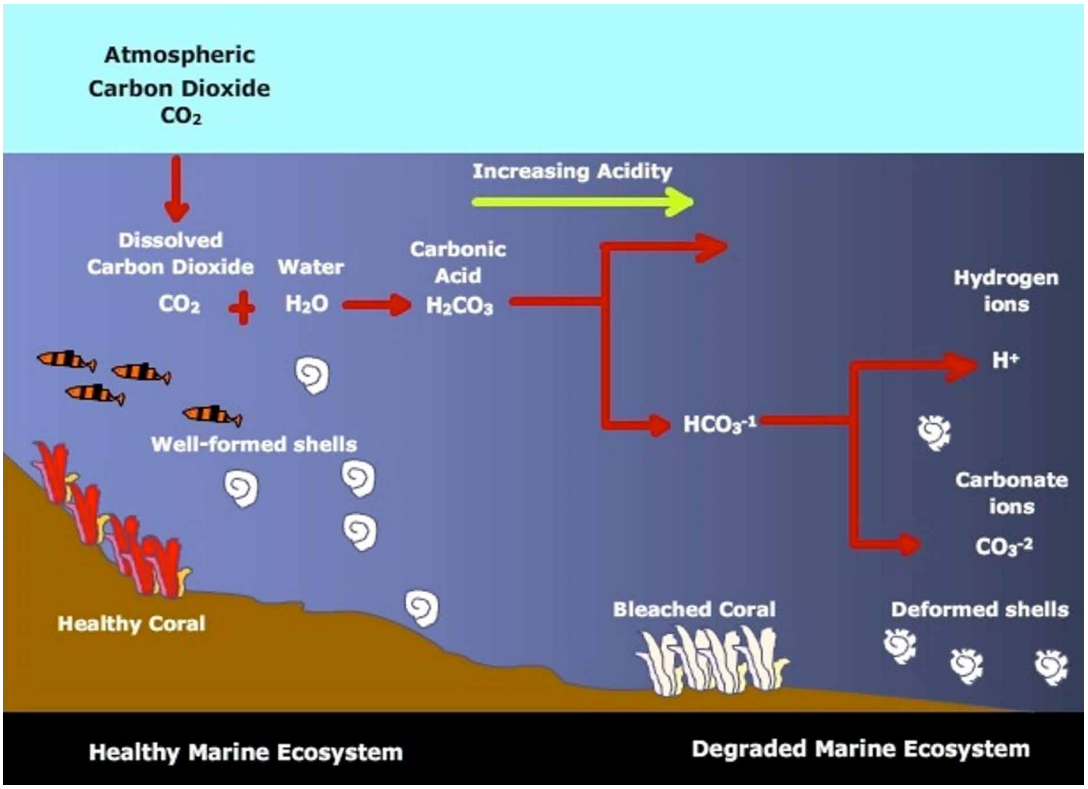
Figure 8. The impact of elevated atmospheric CO2 levels on the global ocean ecosystem
https://theotherco2problem.files.wordpress.com/2009/11/ocean-chemistry.gif



Restricting the range of pH variations is also important in the human body. Bicarbonate and carbonic acid buffer pH changes in blood. The phosphate buffer system regulates pH in cells (Armstrong, 1983).

Carbon dioxide (CO_2) in the air is in equilibrium with natural waters. Since CO_2 is increasing in the atmosphere there is net movement into bodies of water. The dissolved CO_2 reacts with water to produce carbonic acid (H_2CO_3), which is in equilibrium with bicarbonate (HCO^{3-} and H^+). Carbonate ($CO3^{2-}$) reacts with water to also form carbonic acid. Carbonate also reacts with calcium ions ($Ca^{2+)}$ to form calcium carbonate ($CaCO_3$). All of the reactions are reversible. When extra acid (H^+) or base (OH^-) is added to the water, the reactions maintain the pH by incorporating those ions. As such this system serves to buffer natural waters from changes in pH. Too much acid or base exceeds the buffering capacity of the water and the pH will change, as is now occurring in the ocean due to excess CO^2.

KINDS OF NATURAL WATERS AND HOW THEY ARE AFFECTED BY HUMANITY

Consider a system of classification for natural waters. Streams, brooks and springs drain the land that surrounds them called, the watershed. These small running-waters flow together to form larger rivers. Estuaries occur along the margins of the ocean where rivers empty into the sea.

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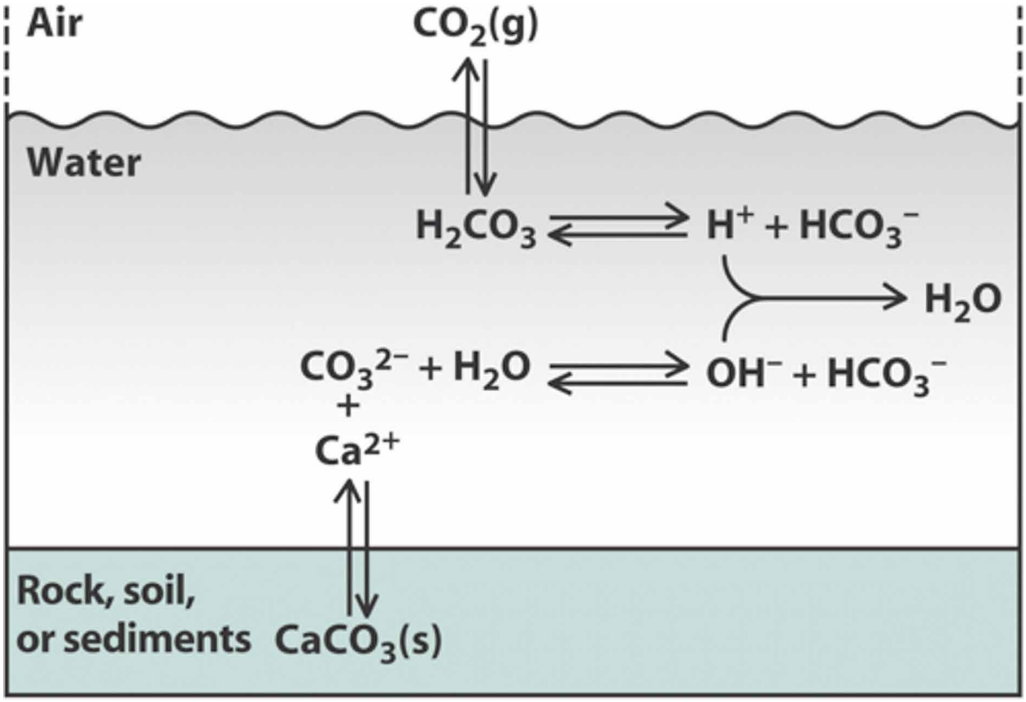
Figure 9. The carbonate buffer system in natural waters



Estuaries

Estuaries are semi-enclosed basins where the freshwater from the river mixes with the saltwater from the sea. These are very important ecosystems, LC feature very productive food chains that support extensive fishing activity.

Lakes, Ponds and Reservoirs

Unlike rivers and streams, lakes, ponds and reservoirs contain relatively still waters. As such there is much less mixing than in flowing water systems. This sets up conditions that may lead to a lack of oxygen in bottom waters or build-up of contaminants due to lack of dilution (Levinton, 2014). Note that reservoirs are artificial lakes created by damming rivers.

The Ocean

The ocean is the largest of all bodies of water. It contains 97% off all the water on Earth. The ocean is much more than a gigantic salty lake. The action of tides, wind, freezing water and evaporation all combine to keep ocean waters in motion. This motion is seen in currents that may move faster than a person can run (Levinton, 2014; National Aeronautics and Space Administration [NASA a], 2015). While ocean currents can sweep away oil spills and dumped trash from a particular shore, know that the contaminants going away from one area means their transport to another place. In Chapter Two the reader will learn about the role that plastics play in environmental problems.

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Glaciers and Sea Ice

In addition to the familiar types of waters given above, there are other important kinds. Glaciers are massive blocks of ice on land that formed from frozen precipitation. Naturally glaciers occur where it is cold, at high altitude (mountains) and at high latitude (the Arctic and Antarctic). Over geological time Earth's climate cycles through periods of warming and cooling. The last great period of cooling reached its peak about 15,000 years ago. At that time a sheet of ice over 1 km thick covered much of Canada, the northern states of the US, and northern Europe. As a consequence of so much water being stored in ice, the sea level was 100 m lower during that period (Stanley, 2009). Currently Earth is in a period of rapid warming, accelerating the melting of remnant glaciers. The rapid heating is driven by human production of greenhouse gases (GHGs) mentioned in the chapter entitled Nurses, Health Care and Environmental Pollution and Solutions. The greenhouse gases produced by health care are referred to as part of the cycle of harm that must be broken to protect water and health. Some 70% of Earth's freshwater is stored in glaciers. Mountain top glaciers are important sources of melt-water, filling streams and rivers that flow into otherwise dry areas. The flow of Ganges River in India depends on the seasonal melting of glaciers in the Himalayas. This flow is threatened as the glaciers continue to shrink with the warming climate (Shiva, 2002).

Sea ice forms in the Polar Regions during the long cold winters. The persistent low seasonal temperatures cause the surface waters of the ocean to freeze. The salts dissolved in the freezing seawater are excluded from the forming ice crystals. This creates a layer of cold and salty brine below the sea ice that sinks due to its high density. This annual cycle of freezing produces a current of cold salty water that is essential to the natural circulation of the sea. The system of ocean circulation takes about 1,000 years to make the circuit around the Earth and along the way redistributes heat around the globe. The system also circulates nutrients for the ocean food chain and oxygen.

As with glaciers, global climate change is reducing the rate of sea ice formation, and its persistence during the summer. This threatens the patterns of ocean circulation. For the first time in recorded history the sea ice covering the Arctic Ocean now undergoes extensive melting (USEPA b, 2015). This summer-time loss of reflective white ice means that the newly exposed waters of the Arctic Ocean are further warmed by the penetration and absorption of sunlight, exasperating the effects of global warming. Additionally, changes in the ocean circulation system will render some regions significantly cooler and others much warmer. New England, England and northern Europe may lose much of the heat presently transported by the Gulf Stream (Rahmstorf et al., 2015). Thus the result of overall global warming will actually decrease annual average temperatures in some places (Levinton, 2014; NASA b, 2015).

Groundwater and Aquifers

Much of the world's freshwater occurs underground. That portion found near the surface is referred to as groundwater. Rain and melt-water percolates through the soil to recharge groundwater. Groundwaters may reappear in downslope springs that feed streams. Groundwater may also drain into porous geological formations called aquifers. Humans drill wells to gain access to groundwater and aquifers. In many regions of the world the rate of withdrawal of water from wells far exceeds the rate of recharge. Wells must be drilled deeper as the water table and aquifer levels decline. Eventually many over-drawn wells

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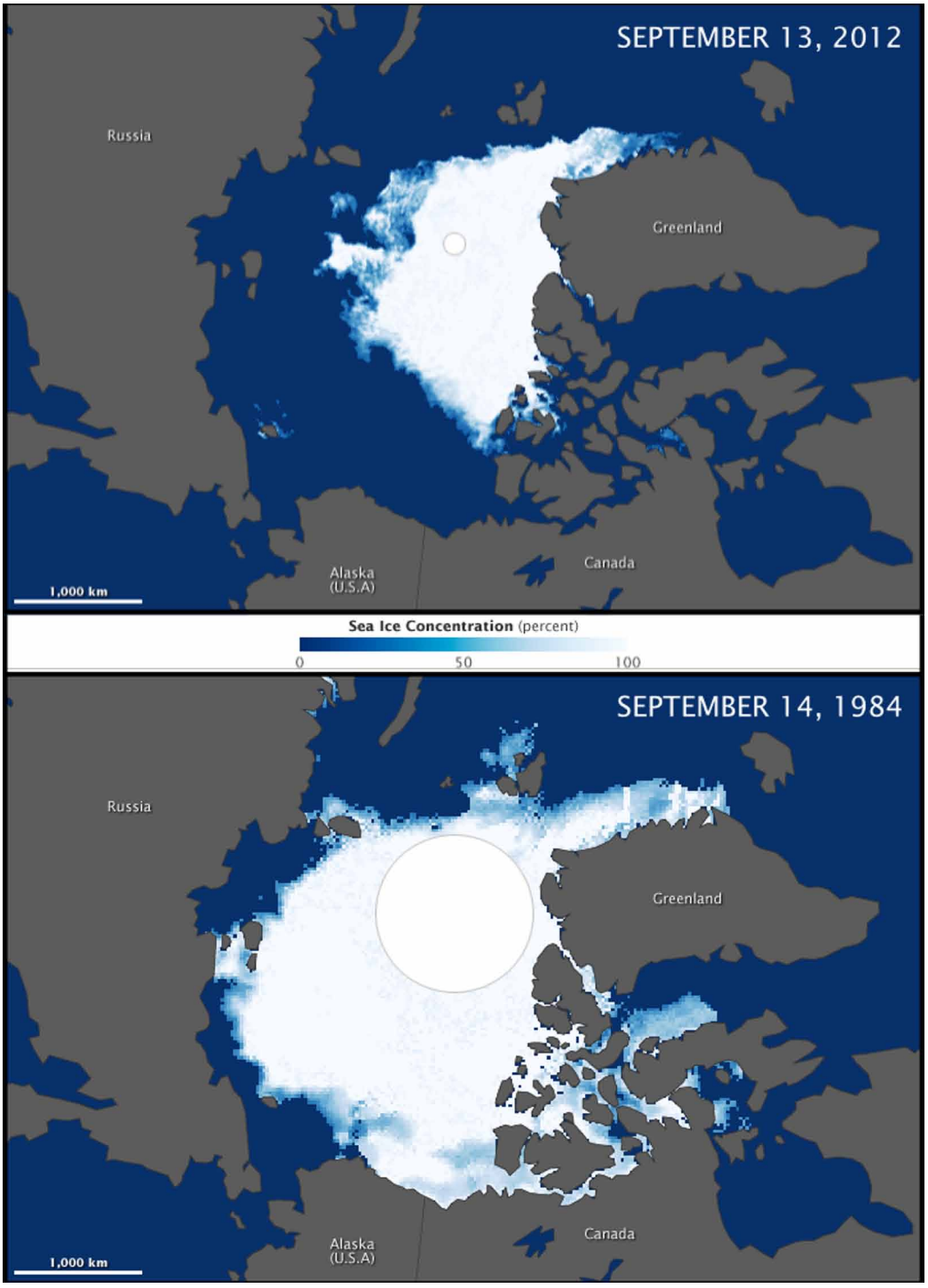
Figure 10. Image showing extent of sea ice melt in the Arctic Ocean, 1980 – 2012.
http://en.wikipedia.org/wiki/Climate_change_in_the_Arctic by Jesse Allen from NASA Earth Observatory images.



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run dry. The loss of undergroundwater has several consequences. Communities lose their source of drinking water. Sometimes the overlying land subsides or sinkholes develop. In coastal areas salt water from the adjacent ocean seeps in the aquifers rendering them useless as source of freshwater (Shiva, 2002).

The so-called Green Revolution in India clearly illustrates the unstainability of unrestricted use of groundwater. In the 1960' and 1970's Western scientists working with the government of India introduced high-yield strains of wheat and other crops to the agricultural system. While these new varieties produced more food per unit area, they demanded much more water and fertilizers. The subsequent overuse of water drained aquifers, leaving once fertile lands useless for agriculture. This displaced the farmers, driving them to overcrowded cities. The ancient system of agriculture that once sustained vibrant communities over millennia were thus lost to a seemingly good idea that ultimately proved otherwise. Presently there is a movement in India to return to the time-tested practices of the past that worked harmoniously with the natural availability of water (Shiva, 2002).

Groundwater and aquifers are susceptible to contamination from industrial and agricultural pollutants. The heavy use of chemical fertilizers and toxic pesticides characterizes contemporary industrial agriculture. These pollutants seep into groundwater and aquifers. Many rural communities can no longer use well water for drinking as the groundwater contains excessive levels of nitrates that came from over application of artificial fertilizers (Powers & Schepers, 1989). Nitrates in groundwater increase rates of infant mortality (Johnson & Kross, 1990).

The recent expansion of oil and gas production in the US and other parts of the world is driven by the process called fracking or hydraulic fracturing. This involves injecting in wells a toxic mixture of chemicals under high pressure. The pressurized fluid shatters the layer of shale rock, allowing the escape of natural gas and petroleum. The fracking fluid that returns to the surface is gotten rid of by reinjection into other wells. This process often contaminates groundwater (Myers, 2012).

It is nearly impossible to remove pollutants from contaminated groundwater and aquifers. A section of river polluted by a toxic spill will usually recover quickly as the flowing water flushes away the contaminants. Since flow is very slow or non-existent for underground waters, there is no natural mechanism to remove persistent contaminates.

The Atmosphere

There is one more pool often neglected when thinking about natural waters, yet it is the most dynamic part of the water cycle that ties together all of the rest. It is the atmosphere. Earth's atmosphere consists of 78% nitrogen gas (N_2), 21% free oxygen (O_2), and whole host of other gasses that despite their concentrations play major roles in the functioning of the environment. The list includes carbon dioxide, water vapor, methane, oxides of nitrogen and sulfur, and so forth (Miller & Spoolman, 2015).

First consider the role water and the atmosphere plays in determining Earth's climate. The moon and Earth are about the same average distance from the sun, yet the average temperature of the moon is only -5 C^o. That for the earth is about 15 C^o. The difference is due to the greenhouse effect of earth's atmosphere and the ability of the ocean to absorb and redistribute heat from sunlight. The mass of the Earth is 81 times that of the moon. So the earth has sufficient gravity to keep gases from floating away, allowing for the formation of an atmosphere. The less massive moon lacks a significant atmosphere as gasses simply float away. Lacking a significant atmosphere and an ocean, the moon can't retain as much heat as the Earth.

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Sunlight consists mostly of short wave radiation, primarily visible light and invisible ultraviolet radiation. This short wave radiation easily penetrates Earth's atmosphere. Only about half is reflected away. The rest is absorbed by the atmosphere or by surface features (land, forest, ocean, etc.). When absorbed the shortwave radiation is changed to long-wave radiation (also known as infrared radiation or simply heat). While earth's atmosphere is fairly transparent to shortwave radiation, it blocks some of the longer wave radiation from bouncing back to space.

Consider a closed automobile sitting in the sunshine on a cold day. The temperature in the car might be 30° C above that of the outside air. The glass windows allow the shortwave radiation to enter but block much of the longer wave radiation from leaving. This is what the greenhouse gasses (GHGs) do in the atmosphere. They let in sunlight and reduce the back-radiation of heat. Two of the most important GHC's are water vapor and carbon dioxide (Miller & Spoolman, 2015).

The amount of water vapor in the atmosphere is dependent on a host of parameters including temperature and pressure. As such concentrations vary from 0.01% for cold dry regions to 4.24% in warm tropical air masses. Overall, water vapor is responsible for 60% of the greenhouse effect, followed by carbon dioxide (26%), ozone (8%), methane (4.4%) nitrous oxide (1.5%) and others (0.1%) (Climate Data Information [CDI], 2015).

Despite the leading role of water vapor, most discussion on GHCs centers on CO_2. In a broad sense humans do influence the water vapor concentrations of the atmosphere. Deforestation, irrigation and other human endeavors alter concentrations of water vapor. But these pale in the face of how humans have increased concentrations of CO_2 in the atmosphere.

At the beginning of the industrial revolution CO_2 concentrations were about 280 ppm (parts per million). In 2015 concentrations reached 400 ppm or 0.04% of the atmosphere. While seemingly tiny by percentage, CO_2 is very effective in trapping long-wave radiation. The increased CO_2 and to a lesser extent the other GHGs are responsible for Earth's average temperature increasing about 1 C° over the last 250 years. Projections for the future have the earth's temperature raising another 3 – 6 C° by 2100 (Miller & Spoolman, 2015). The increased temperature will disrupt the climate with increasing frequency and intensity of droughts, floods, and storms. The chapter entitled Nurses, Health Care and Environmental Pollution and Solutions will discuss the human health consequences of these climate change related events. This all traces to the burning of fossil fuels; first coal, than natural gas and oil. Over 100's of millions of years photosynthesis had taken CO_2 from the atmosphere and fossilization of plants has stored much of that in the ground. Almost overnight in a geological sense, the mining and burning of fossil fuels has returned much of that CO_2 to the atmosphere. This has created a new geological period of rapid warming and climate change.

THE WATER CYCLE

The ocean, rivers, lakes, estuaries, groundwater, glaciers, sea ice, water vapor and clouds are all linked together by the water cycle. This cycle is powered by solar radiation. Indeed, about 25% of the sun's energy falling on Earth goes to evaporating water, which is the beginning of the cycle (NASA b, 2015).

Some 75% of the Earth surface is covered by water. The bulk of that water is stored in the ocean (96.5%) and is salty. The remaining 3.5% is in freshwater. About half of the freshwater is frozen (1.7% is found in ice caps, glaciers and snow). An equal amount (1.7%) is in lakes, rivers, streams, soil and groundwater (United States Geological Services [USGS a], 2015). So only 1.2% of the world's freshwater

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Figure 11. The greenhouse effect of gases in the atmosphere.
http://commons.wikimedia.org/wiki/File:Earth%27s_greenhouse_effect_(US_EPA,_2012).png by USEPA

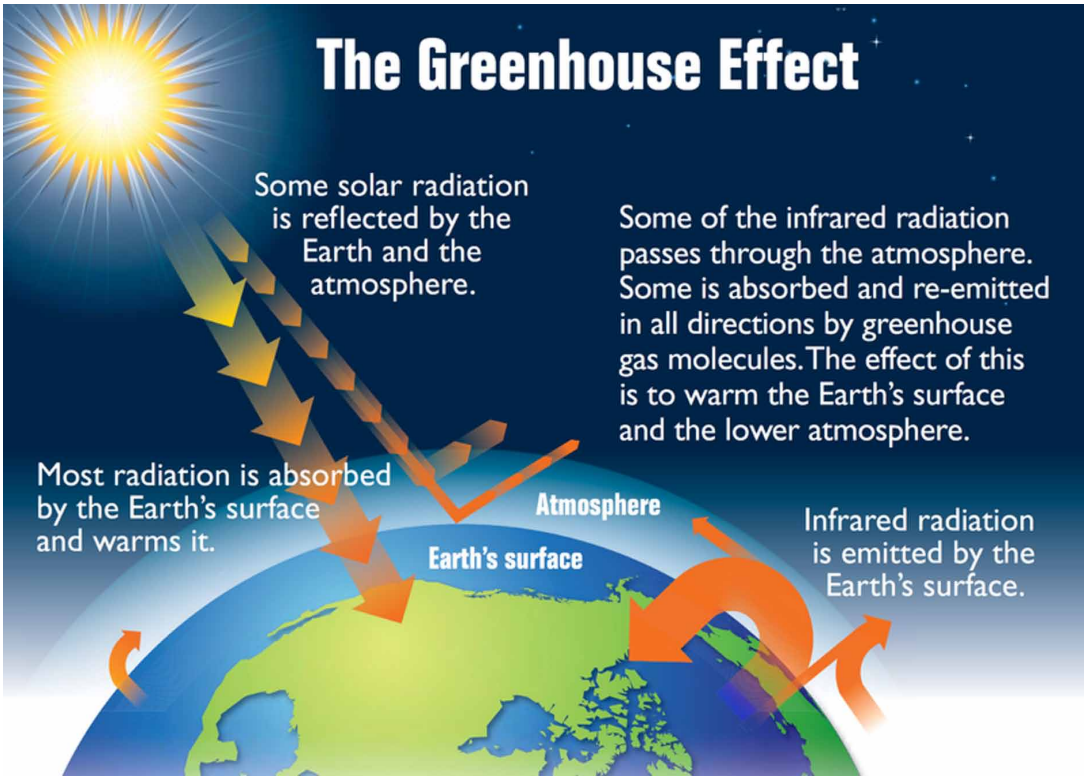
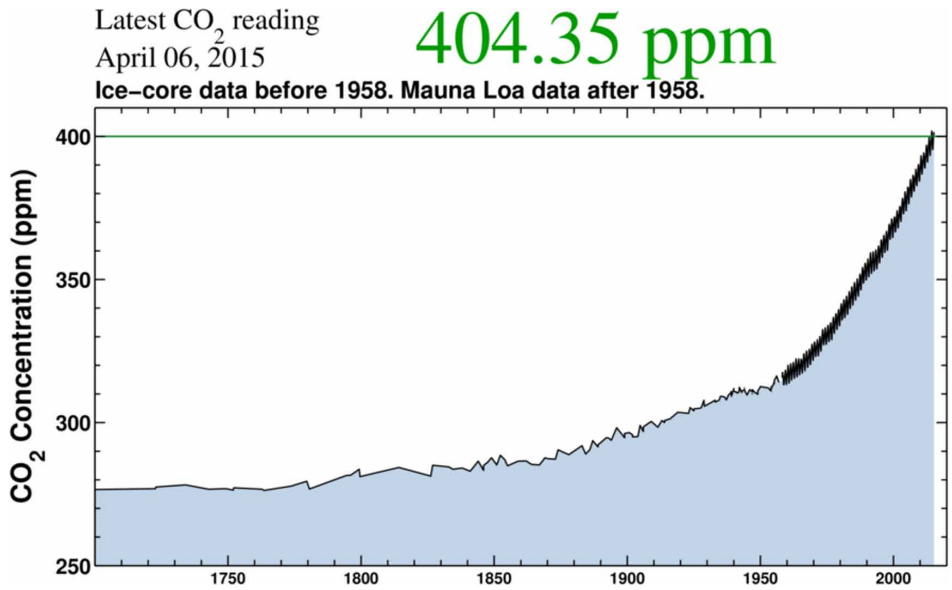


Figure 12. The increasing concentrations of carbon dioxide in the atmosphere since the advent of the industrial revolution.
https://scripps.ucsd.edu/programs/keelingcurve/wp-content/plugins/sio-bluemoon/graphs/co2_800k_zoom.png by Scripps Institute of Oceanography



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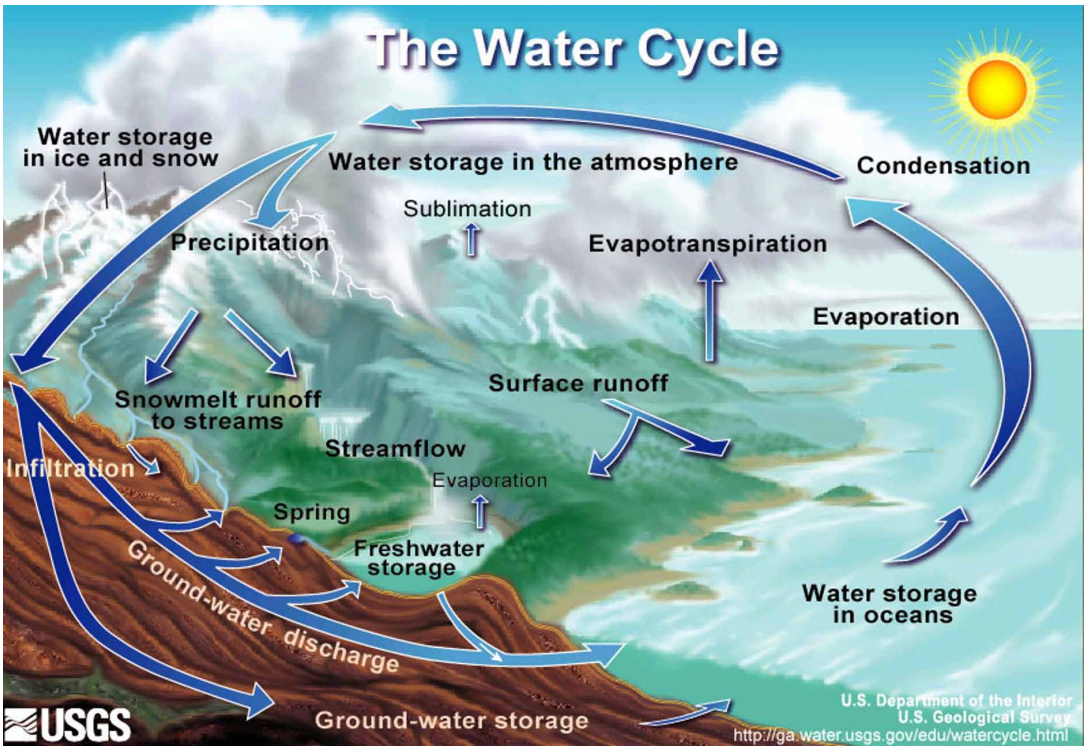
is available as surface water (lakes, ponds, rivers and streams). Water vapor and clouds constitute only a tiny fraction of Earth's water, 0.001%. Yet atmospheric water is a dynamic pool tying the rest of the hydrologic cycle together.

Solar radiation drives the evaporation of water from the sea, land and plants. The water vapor produced in this process is cleaned of any salts or contaminants. It is just molecules of water floating in the atmosphere. The atmosphere can hold only so much water at any given time or place. Warmer air and higher pressure accommodates more water vapor. Yet as air masses circulate they cool and experience lower pressures. This causes the air to exceed levels of saturation, and the vapor condenses to form clouds or fog. Further cooling causes the clouds of water droplets to coalesce to form precipitation in the form of rain, snow, sleet and hail. In some climates clouds and fog encounter the ground and plants, forming dew, which is another form of precipitation.

Note that once water condenses into droplets, it then includes dust particles and atmospheric gases. This is how rain and snow becomes contaminated with atmospheric pollutants resulting in acid precipitation and the like.

While the ocean contains the vast bulk of water on earth, most of it stays there a very long time, about 3,200 years. In contrast a liter of water in the atmosphere will stay there only about 9 days. So there is a constant supply of freshwater coming from the atmosphere. This is critical to humans and all terrestrial life, as creatures of the land require access to freshwater. While most (80%) of the freshwater precipitation falls directly to the sea, the rest nourishes the land. Some is stored in ice, aquifers, soil,

Figure 13. The global water cycle
http://upload.wikimedia.org/wikipedia/commons/9/94/Water_cycle.png by U.S. Geological Survey



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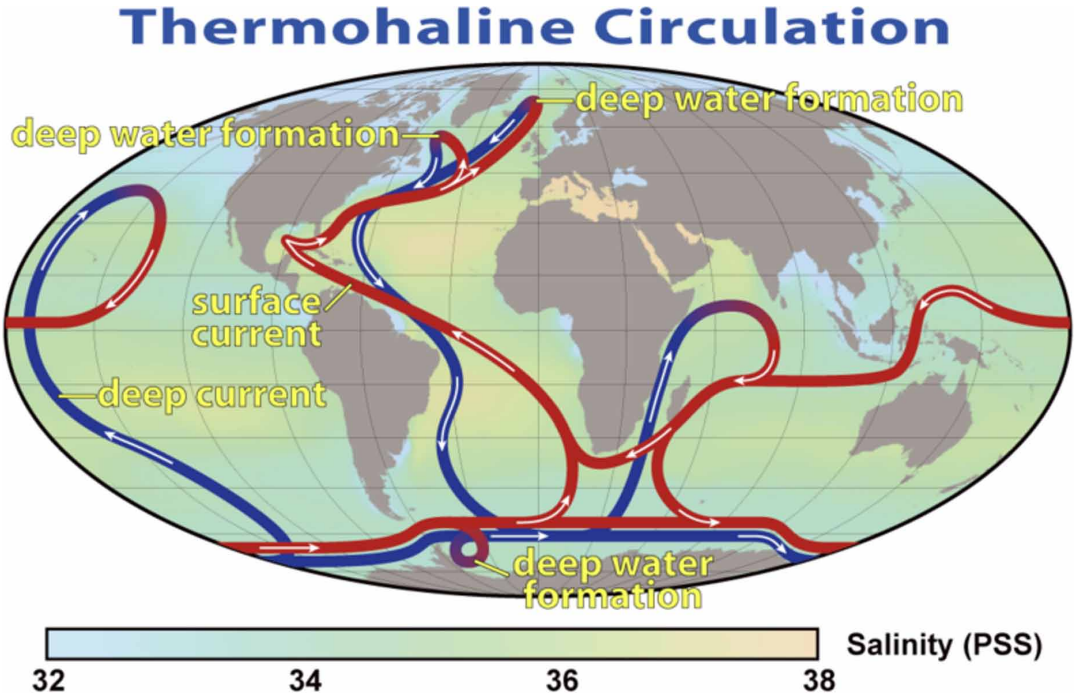
living tissue, lakes, rivers and streams. Evaporation and precipitation adds to or subtracts from these compartments. The pull of gravity draws flowing waters to the sea (University Corporation for Atmospheric Research [UCAR], 2015).

Global climate change is altering the water cycle. This is evident from the disappearing glaciers mentioned above. The once frozen water mostly flows into the sea. This along with thermal expansion of the warming ocean accounting for an average rise in sea level of about 13.9 inches (30.9 cm) between 1900 and 2015. Rising sea levels cause massive destruction and migration of populations from low-lying coastal areas and islands. Some projections of sea level rise are as high as an additional 39 inches (1 m) by 2100 (Levinton, 2014).

The general global warming also increases the rate of evaporation and the ability of the atmosphere to hold water vapor. Since water vapor is a powerful GHG, this is an example of a destabilizing positive-feedback system. The warmer Earth gets, the more water vapor will be in the atmosphere to inhibit back-radiation. Consequently Earth will continue to warm at an even faster rate. As noted above, sea-ice in the Arctic Ocean is now much reduced. This enables new offshore drilling for oil. As that new Arctic oil goes to the market its use will further increase the emission of CO_2 and consequently global warming.

Figure 14. Circulation of seawater via the Ocean Conveyer Belt system.
http://en.wikipedia.org/wiki/File:Thermohaline_Circulation_2.png by Robert Simmon, NASA with minor modifications by Robert A. Rhode.



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THE CONSTITUENTS OF NATURAL WATERS

Knowing about the basic chemistry of pure water is important but tells only a small part of the story of the composition and functioning of natural waters. Scientists and mangers differentiate natural waters by what they contain other than water. Sea water typically has about 34 grams of salts dissolved in a liter of water. Oceanographers use the measure of PPT (parts per thousand), so salinity of seawater is about 34 PPT. Most inland waters are considered freshwater, as they contain small levels of dissolved solids (<0.5 ppt). The salinity of the sea is primarily due to the following ions: Cl^-, Na^+, $SO4^{--}$, Mg^{++}, $HCO3^-$, Ca^{++}, K^+ (Garrison, 2001).

Humans require freshwater for drinking and the irrigation of agricultural plants. Drinking saltwater causes; vomiting, diarrhea, and dehydration. Irrigation of crops with salty water will cause the plants to dehydrate and wither. In very dry regions irrigation often results in salt build-up in soils. As the irrigation water evaporates it leaves behind the small amount of salt it contained. Over time the accumulation of salt renders the soil useless for continued agriculture (Shiva, 2002).

The estuaries mentioned above are places where freshwater and saltwater mix. These coastal features contain waters of intermediate salinity, called brackish water. Many marine animals rely on these brackish water environments to complete their life cycles. Juvenile fishes, and crabs thrive in estuaries. Estuaries typically attract extensive human habitation. Agriculture, industry and urban environments produce contaminants that often pollute estuaries. This threatens the health of the plant and animal residents of the estuaries as well as the human populations that consume seafood from contaminated systems (Levinton, 2014).

Natural waters contain dissolved gases. Surface waters in direct contact with the atmosphere contain the same gasses as that in air; including nitrogen (N_2), Oxygen (O_2) and (CO_2). Of these, oxygen is most critical to sustaining higher forms of marine and aquatic life.

Oxygen is necessary for the process of aerobic respiration. This is the metabolic sequence that cells use to release energy from sugars and other organic molecules. Oxygen removes the low-energy electrons at the terminus of the electron transport chain. Without oxygen this chain stops, and so does the production of ATP (Adenosine Triphosphate). ATP powers most of the processes in cells (Armstrong, 1983). Depriving a human of oxygen for just a few minutes proves fatal, illustrating the importance of this process. Oxygen is just as important for fishes and other forms of multicellular life in natural waters. Water in equilibrium with the atmosphere contains from 7-14 mg of oxygen per liter (mg/l) depending on temperature and concentrations of dissolved salts. Oxygen concentrations below 3 mg/l tend to exclude animal life. The amount of gas that can dissolve in water decreases with increasing salinity and temperature. So cold freshwater lakes will contain more oxygen than warm tropical seas (Garrison, 2001).

Oxygen gets into natural waters two ways. Winds promote mixing of surface waters with the atmosphere, speeding the diffusion of oxygen from the air to the water (Garrison, 2001). The other way oxygen enters natural waters is by the process of photosynthesis (Levinton, 2014). Green plants and algae use the energy of sunlight to split water. This supplies the plants and algae with high-energy electrons to power the metabolism of the plant with ATP. Most of that ATP powers the conversion of carbon dioxide into sugars, proteins and fats. Oxygen is released as a waste product of photosynthesis. This waste product of photosynthesis proves necessary for animal life.

Shallow waters generally have sufficient oxygen supplies from mixing with the atmosphere and photosynthesis. Since photosynthesis requires sunlight it is restricted to the top 100 m or so of lakes and the ocean (Levinton, 2014; Wetzel, 1983). This is due to the absorption and scattering of light by

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the water molecules and substances dissolved and suspended in the water. Consequently deeper water relies on the mixing down of surface waters to sustain a supply of oxygen. During the warm months of the year, temperate lakes and ocean waters are stratified by temperature. That is the warm surface waters float atop the cooler deeper waters, forming two distinct layers separated by a thermocline (region of rapid temperature drop). The difference in density prevents the warmer upper and the cooler lower layers from mixing. This becomes a problem in places where the bottom waters are subjected to overloading with decaying organic matter. The microbial digestion of the excess organic matter uses up the supply of available oxygen in those deeper waters. This creates a so-called dead zone, excluding higher forms of life (Levinton, 2014).

There are two ways excess organic matter gets into the deep water. First, the process of photosynthesis occurring in surface waters forms organic matter. This happens in all natural waters, and is the basis for the food chains in those systems. The photosynthesizing algae and rooted aquatic plants use the sun's energy to convert carbon dioxide into organic matter. The floating algae are called phytoplankton. Tiny animals comprising the zooplankton consume them. Small fishes and various other animals consume the zooplankton. Larger fishes, birds, and aquatic mammals may be the next step in the food chain.

In most cases the growth rates of the phytoplankton are controlled by the supply of certain essential nutrients; phosphorus, nitrogen, iron and silica. The addition of excess nutrients (usually phosphorous in freshwaters and nitrogen in seawater) promotes the overabundance of algae. This is called an algal bloom. Most of the phytoplankton of an algal bloom escapes consumption by zooplankton and instead sinks into the deeper water as it ages. Bacteria and other microorganisms consume the dead algae as it sinks and accumulates in the sediments on the floor of the lake or sea. The bacteria will deplete the oxygen as they consume the remains of the algae (Levinton, 2014).

Some lakes naturally occur in watersheds that supply high loads of nutrients and display regular algal blooms and the accompanying loss of oxygen in bottom waters. These lakes are called eutrophic. Lakes that have low rates of natural inputs of nutrients, and thus don't experience algal blooms or depletion of oxygen from the bottom waters are called oligotrophic (Wetzel, 1983).

Nutrient pollution from agriculture and sewage convert once oligotrophic lakes and coastal areas to eutrophic systems. This process is called cultural eutrophication. The extent of cultural eutrophication and the resulting dead-zones grew dramatically during the last half of the 20th Century. Changing agricultural practices, patterns of habitation and overall population size, drives cultural eutrophication. Agriculture based upon inputs of artificial fertilizers, pesticides and fossil fuels creates sever water pollution that feeds algal blooms. This type of industrial agriculture also reduces the need for human labor, driving rural populations to urban areas. The nutrient rich urine and feces created by residents of urban areas is not making its way back to fertilize cropland. But instead it is dumped into rivers and coastal areas, causing algal blooms and dead zones (Shiva, 2001; Diez & Rosenberg, 2008).

Sewage is the second way excess organic matter enters natural waters. Humans absorb only a fraction of the organic mater, which they consume in their diets. As such they produce organic-rich feces. Modern wastewater treatment plants remove most of that organic matter, but such infrastructure is missing in most of the developing world. As such, organic matter from feces fuels the oxygen-consuming bacteria in many coastal areas, contributing to formation of dead zones. The inadequate or missing facilities and potential solutions are discussed in the chapter entitled On-Site Sanitation System for Low-Income Countries. Related discussion on constructed wetlands will be found in the chapter entitled Constructed Wetlands: Description and Benefits of an Eco-Tech Water Treatment System. Both of these chapters are noted to contain suitable material for use in developing countries as does the chapter entitled Access to Safe Drinking Water.

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LIFE IN WATER

Natural waters team with life. On average even the cleanest ml of water from an ocean or lake will have one million bacterial cells (Levinton, 2014) and ten million viruses (Breitbart, 2012). Life is built upon a complex framework of organic molecules, carbon based structures of sugars, lipids, amino acids and nucleic acids. Surprisingly, for any square meter of ocean or lake, there is more mass in dissolved organic molecules then there is in the rest of the food chain. This supply of dissolved organic molecules comes from decomposition of dead cells or excretion from living cells. The bacteria feast on this pool of organic matter, feeding protozoans that in turn feed higher forms of life. This food chain is called the microbial-loop.

While very important to the ecology of natural waters, the microbial-loop food chain is much less familiar than the traditional food chain based upon photosynthesis. In the sea and lakes tiny green cells called algae do the process of photosynthesis. They are harvested by microscopic animals, which intern feed somewhat larger animals, then small fishes, larger fishes, mammals and birds.

Figure 15. The aquatic food web.
http://en.wikipedia.org/wiki/Food_chain by Matthew C. Perry, U.S. Geological Service

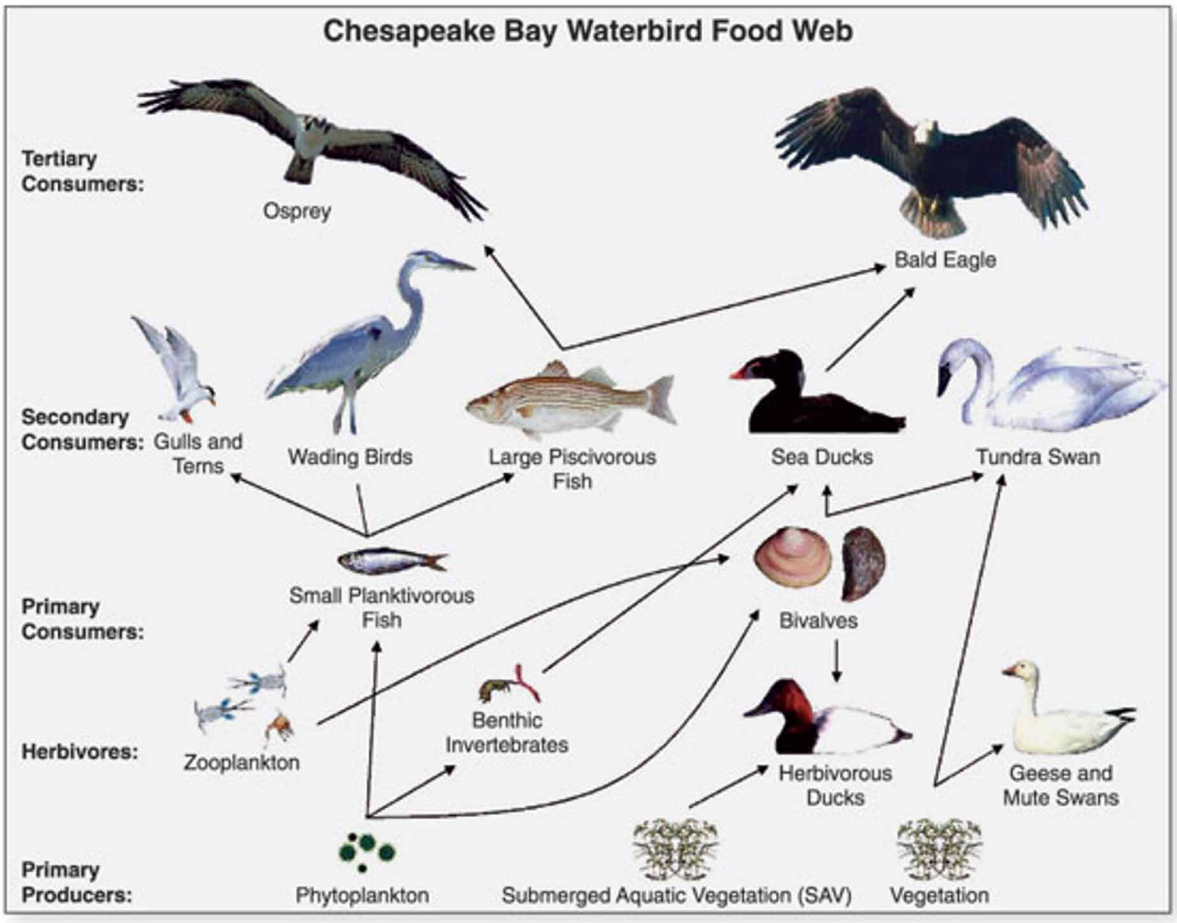

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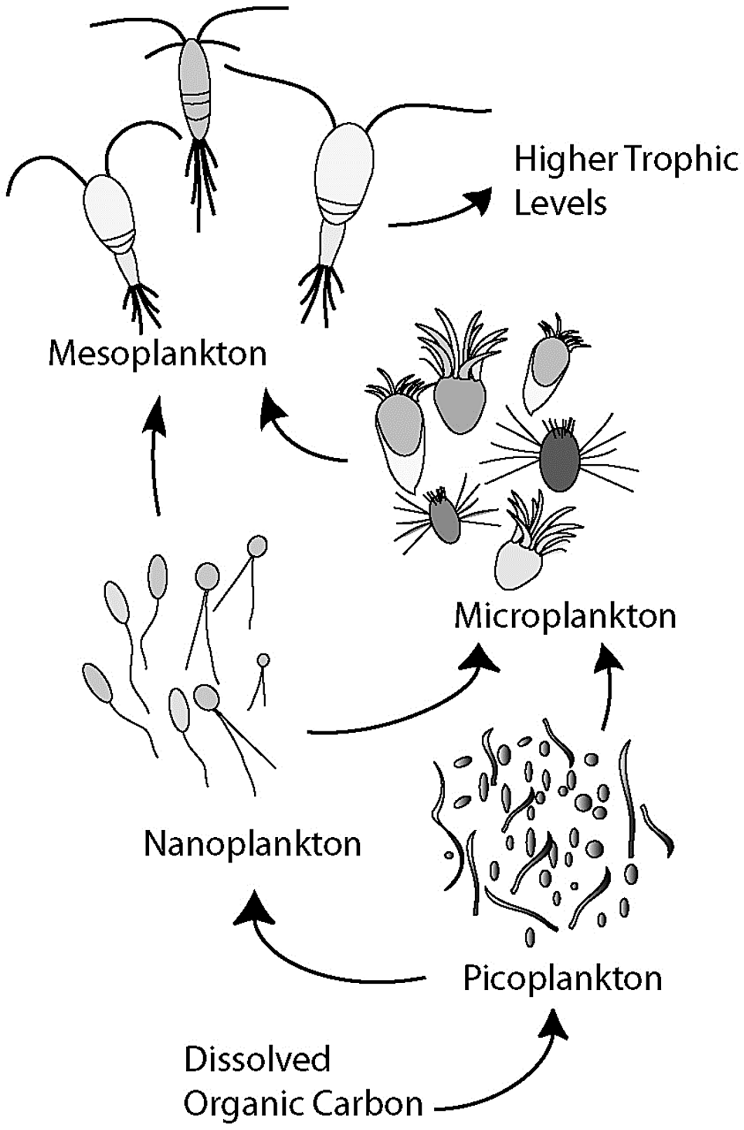
Figure 16. The microbial loop. Bacteria harvest dissolved and particulate organic carbon making that source of energy available to higher levels of the food chain.
http://www.google.com/url?sa=i&source=imgres&cd=&cad=rja&uact=8&ved=0CAwQjRwwAA&url=http%3A%2F%2Fcommons.wikimedia.org%2Fwiki%2FFile%3AMicrobial_Loop.jpg&ei=7vhlVcW9Oo6KyASOiYHABg&psig=AFQjCNEF9Sos3XqbSynf_P1SxrxxueU8Vg&ust=1432832623066480 by Umarina



It is convenient to classify aquatic life into different categories. Tiny plants and animals that float or swim are called plankton. Phytoplankton are plant- like and photosynthetic, zooplankton are tiny animals that eat the phytoplankton and bacteria plankton. Some plankton are quite large, like jelly fish but still classified as plankton as they are weak swimmers. Nekton refers to the stronger swimmers, such as fishes, squid, turtles and whales. Benthic animals and plants live on the seafloor or attached to structures. Think of flatfishes oysters, clams and worms.

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The life cycles of many aquatic creatures includes membership in different categories. Almost all sea creatures have gametes or larvae that are distributed in the plankton. Some settle to the bottom to join the benthos and others grow into strong swimmers of the nekton. There are important exceptions. Marine mammals and some sharks give live birth to competent swimmers. In freshwater, planktonic phases of benthic animas are rare. The Asian zebra mussel and quahog mussel are two freshwater benthic forms with planktonic larvae, which has led to their status as damaging invasive species in the Great Lakes and elsewhere in the US (USGS b, 2015).

Life in natural waters is mostly fueled by photosynthesis. Yet in special habitats ranging from marsh sediments to deep-ocean vents, inorganic compounds form the basis of the food chain. Energy rich compounds such as H_2S (hydrogen sulfide) and CH_4 (methane) fuel chemosynthetic bacteria. Before the evolution of photosynthesis such chemicals fed the primordial food chains of Earth. Today chemosynthesis is locally important but contributes little to the energy economy of the living Earth (Levinton, 2014).

Since photosynthesis is so important to the aquatic food chain, it is not surprising that the availability of light is essential to understanding life in salt and fresh waters. Typically photosynthesis is restricted to the top 100 m or less of the water column. Deeper than that, heterotrophy (eating and decomposition) prevails. Note that the average depth of the world's ocean is 3,800 m. So significant illumination and photosynthesis is restricted to the top 2.6% of the water column. Most of the ocean is deep, dark, cold (3^o C), and dependent on the sinking or swimming of life from above (Garrison, 2001).

POLLUTION

Much of this book is about water pollution. One way to look at pollution is to consider it a misplaced resource. The extra nutrients (N and P) that cause eutrophication in lakes and coastal waters are important fertilizers for crops that are misplaced by runoff from land into waters. Carbon dioxide is essential for photosynthesis, but its overproduction from burning fossil fuels is acidifying the sea and warming the planet. Plastics used to make water bottles, bags, cigarette lighters, and thousands of other manufactured goods are finding their way to the sea where they kill marine creatures and poison food chains. Almost every water pollutant from antibiotics to petroleum is made from useful resources that are allowed or encouraged to be disposed of in our natural waters. The reader will learn more about pharmaceuticals in waterways in the chapter entitled A Review of Emerging Contaminates in Water and the chapter entitled Pharmaceuticals and Personal Care Products as Emerging Water Contaminants.

Scientists classify water pollutants by their source. Point sources of pollutants were the first to be tackled by the landmark laws of the 1970's and 1980's. These are mostly pollutants traced to pipes draining from industrial processes. Coming from single points those pollutants were relatively easy to measure and regulate. For example, it was easy to determine how much phosphate was being produced from a wastewater treatment plant simply by sampling what was coming out of the effluent pipe. A sinking oil tanker or leaking underwater oil well are other examples of point sources of pollution. Both point source and non-point source pollution is discussed further in the chapter entitled Floodplain Infrastructure and the Toxic Tide. Also the chapter Industrial and Agricultural Sources and Pathways of Aquatic Pollution, deals with the same issues of pollution sources.

Non-point source pollutants emanate from large portions of the landscape and are more difficult to trace to their sources. Much of the mercury pollution in the sea comes from the burning of coal in power plants. At the time of emission this is clearly a point source of pollution. Yet the mercury gets into the

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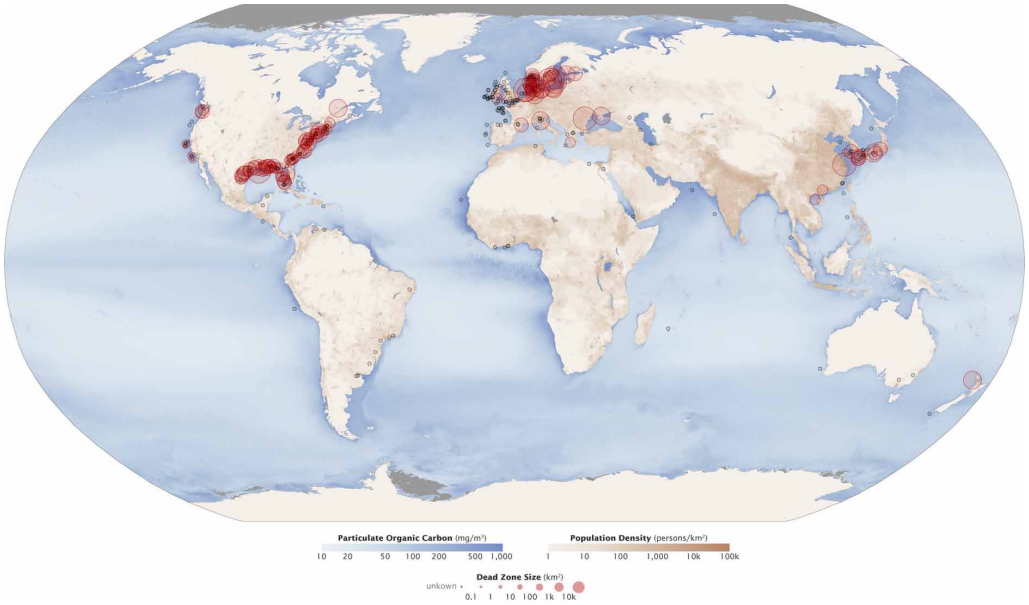
Figure 17. Distribution of coastal dead zones around the world.
http://upload.wikimedia.org/wikipedia/commons/c/c7/Aquatic_Dead_Zones.jpg by Robert Simmon & Jesse Allen, NASA Earth Observatory



sea by being released from the atmosphere, and functions more like a non-point source pollutant. Much of the carbon dioxide pollution released from land comes from automobiles that are widely distributed over the landscape; hence they are non-point source polluters.

Pollutants work in various ways to diminish the health of waterways and people. The ensuing chapters will discuss these pollutants as well as other ways humans interact with the watery environment. Chapter Five: Impacts of Artisanal and Small Scale Gold Mining on Water Quality in Mozambique and Zimbabwe will have a lengthy discussion of the health hazards of gold mining related mercury in water.

SOLUTIONS/RECOMMENDATIONS AND FUTURE RESEARCH DIRECTIONS

The entire upcoming book with deal not just with the problems related to water quality, but also suggest some solutions. Future research directions will also be discussed in other chapters. The purpose of this chapter was to present the fundamental properties of water and to point forward to other chapter's contents.

CONCLUSION

In the end it is hoped that the reader will understand the links between human health and the health of our natural waters. Further it is hoped that the reader will feel informed, empowered and motivated to educate others on the subjects of vital importance to future generations. The three chapters that lead off the second section of the book specifically deal with educational theory and practice to facilitate envi-

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Figure 18. Plastic pollution floating in the Pacific garbage patch.
https://i.embed.ly/1/display/resize?key=1e6a1a1efdb011df84894040444cdc60&url=http://voidlive.com/wp-content/uploads/2014/09/North_Pacific_Gyre.jpg&width=810

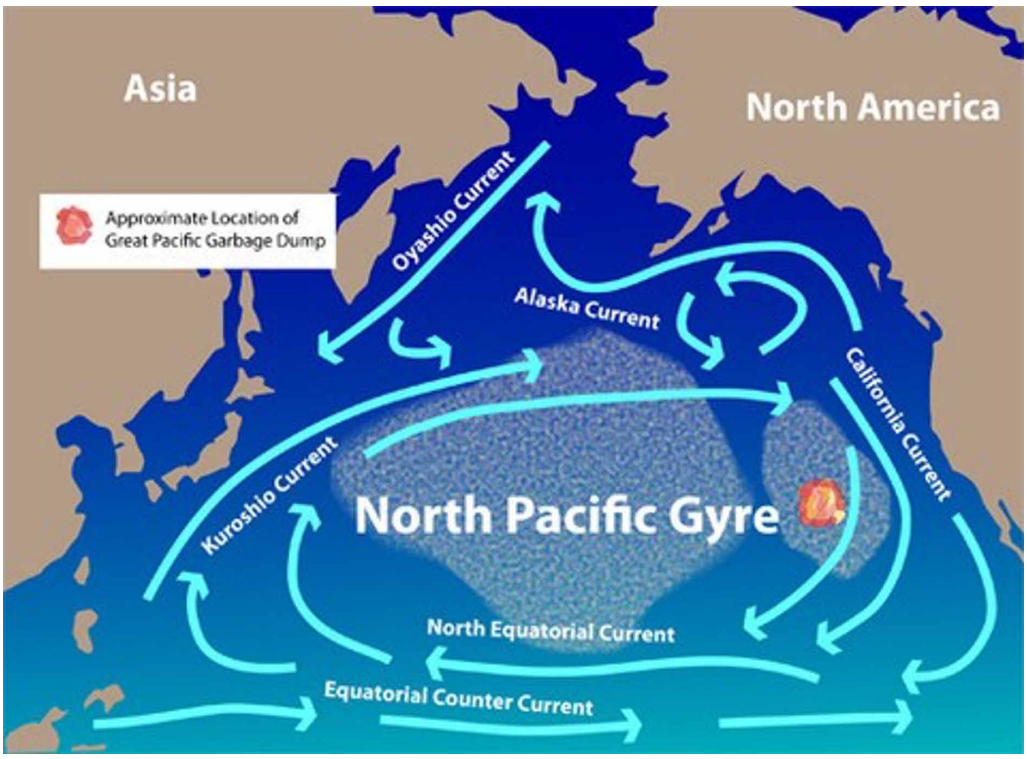
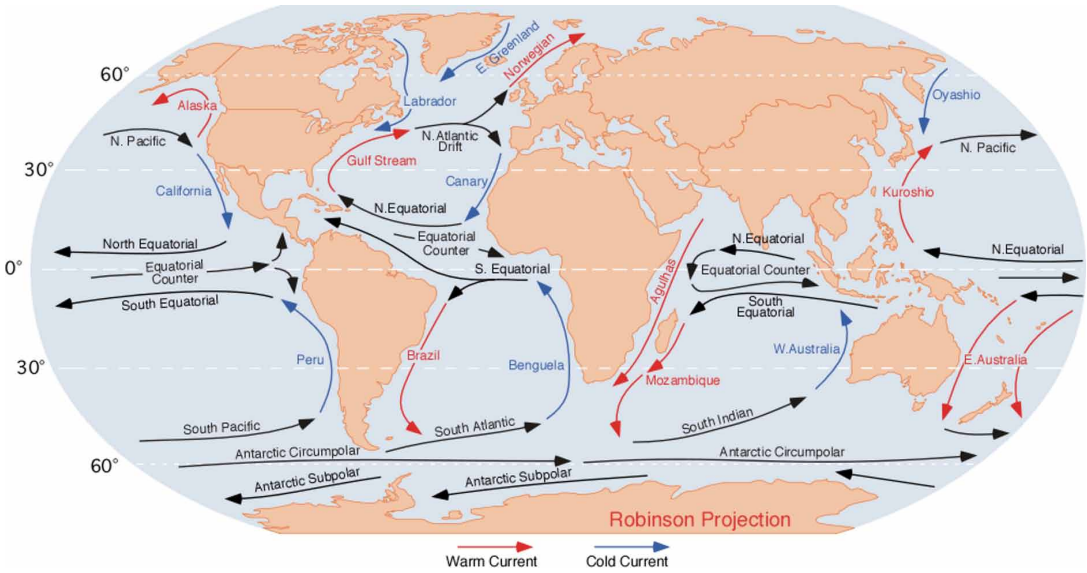


Figure 19. The pattern of circulation in the world ocean.
http://skyblue.utb.edu/paullgj/geog3333/lectures/oceancurrents-1.gif by Michael Pidwirny



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ronmentally responsible citizens. The final chapter: Water Hyacinth, Turing a Problem into a Project, is to show by example that with focus and effort, the current water conservation challenges can be turned into tomorrow's sustainable solutions.

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KEY TERMS AND DEFINITIONS

Acid: A molecule that adds hydrogen ions to a solution, causing a drop in pH.

Amphipathic Molecule: These structures have a polar head and a non-polar tail. Such molecules form the bi-layer structure of cell membranes.

Aquifer: A geological formation containing water in the free spaces between the rocks, gravel, sand or other mineral deposits. Wells are drilled into aquifers to obtain that water.

Estuary: A semi-enclosed basin formed where rivers join the sea. The water in estuaries is a mix of salt and freshwater.

Eutrophic: A term applied to waters that contain high levels of nutrients. Such waters appear green from the abundance of phytoplankton. In deeper eutrophic waters there is often very little oxygen as it is used-up by the decaying phytoplankton that sinks from above.

Fossil Fuels: This refers primarily to coal, oil, natural gas, and peat that were formed from the once living tissues of organisms now long dead. Burning fossil fuels results in excess carbon dioxide in the atmosphere and ocean, and often other types of pollution such as those containing sulfur or nitrogen.

Green House Gases: (GHC's). These are gases such as carbon dioxide, water vapor and methane that are transparent to sunlight, but block much of the heat created by the sunlight being intercepted by the atmosphere, land and water. These gases result in the increased retention of heat by the earth.

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Green Revolution: A term applied to the adoption of western-style agriculture in India and other parts of the developing world in the 1960's and 1970's. It was built around using higher yielding varieties of crops to produce more food per area of cultivation. It requires extensive use of water and fertilizer well beyond the traditional agricultural system it replaced.

Groundwater: This refers to the water held in soil and deeper layers below the Earth's surface. The term is often used interchangeably with the word aquifer. However, some will use groundwater to refer to shallower deposits and aquifer to refer to deeper and longer-term storage. To wit, the process of transpiration by plants transports water from groundwater to the atmosphere, but does not directly effect deeper aquifers.

Heat of Fusion: The amount of thermal energy released from one gram of a substances when it changes state from a liquid to a solid. The same amount of heat is added back to the solid to cause it to melt or return to a liquid.

Heat of Vaporization.: The amount of thermal energy needed to cause a liquid to change state to form a gas. The same amount of heat is released from the gas when condenses to form the liquid state.

Hydrocarbon.: A molecule containing only carbon and hydrogen, such as what forms fossil fuels.

Industrial Revolution: The period between about 1760 and 1840 when the economies and social structures of the western world changed in response to a rapid rise in manufacturing and the adoption of new technologies. Coal fueled much of the industrial revolution, leaving a legacy of reliance on fossil fuels.

Micelles.: Spherical formations of amphipathic molecules in which the heads all out and the tails all face in, or vice versa. For micelles in water, the polar heads face out and the tails face in. This allows non-polar substances found in the water to migrate into the centers of these spheres.

Microbial-Loop: This refers to the aquatic food chain linking dissolved organic matter to bacteria, protozoans, and larger zooplankton.

Oligotrophic: A term applied to natural waters that contain relatively few plant nutrients, such as phosphorus and nitrogen. Such waters appear clear as they can support only low phytoplankton populations.

pH Buffers: These are weak acids that disassociate in response to the addition of a strong acid or strong base. In doing so the buffer maintains a nearly constant pH for the solution. However, excessive additions of acids or bases will consume the buffering capacity, and the solution will change in pH. Buffers maintain pH balance human cells, the blood stream and in natural waters.

Phytoplankton: Tiny plant-like organisms that float in the water and that obtain most of their energy from sunlight using photosynthesis. Some of these cells can also use dissolved organic carbon for fuel.

Polar Molecule.: A molecule that has one end with an effective positive charge and the other end with an effective negative charge. It is not an ion, but the distribution of protons and electrons are such to create the effective charge distribution.

Salinity: A measure of how much salt is dissolved in water. Different authors use different systems for units. Earlier texts use PPT (Parts Per Thousand). Others moved to PSU (Practical Salinity Units), and more recently some authors abandon the unit all together and simply report a number. So 35 PPT is equivalent to 35 PSU or simply a salinity of 35.

Thermocline: This refers to the rapid change in temperature with increasing depth that occurs in bodies of water consisting of a warmer surface layer floating over a cooler deeper layer. For example the surface water of a lake might be 25^{o} C in the summer and the bottom water only 4o C. The rapid drop in temperature between the two layers constitutes the thermocline.

Thermohaline Circulation: This refers to the pattern of water movement in the ocean driven by differences in density. Water density is controlled by both temperature and salinity. Thermo refers to

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temperature and haline refers to saltiness. Colder and saltier water is denser than warmer and fresher water. So cold salty water sinks, driving this type of ocean current.

Specific Heat.: The amount of thermal energy used to raise the temperature of one gram of a substance one degree Centigrade at standard conditions of 25^{o} C and one atmosphere of pressure. The same amount of heat is released from that substance when it drops one degree.

Water Pollution: The contamination of aquatic systems by substances that change the character and functionality of those systems. The pollution may be the addition of excessive amounts of substances that are normally found in the water, such as excessive plant nutrients like nitrogen and phosphorus. Or the pollution maybe an exotic substance such as a pesticide or industrial compound.

Zooplankton.: Tiny animals that float or swim in the water and rely upon phytoplankton for food.

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Chapter 5
Chemical and Biological Processes for Nutrients Removal and Recovery

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ABSTRACT

This chapter gives an overview on the main technologies for nutrient removal from industrial wastewater by focusing on principles and operational parameters of real applications. A plethora of technologies can achieve the nutrients removal from wastewater depending mainly on their concentration and forms; however, biological nitrification and denitrification and chemical precipitation are the most common processes used today to remove nitrogen and phosphorus, respectively. Stripping, adsorption and membrane based processes for nutrients recovery can be economically viable only when nitrogen concentration is higher than 1.5-2 gN/L. On the other hand, phosphorus recovery should always be pursued and struvite crystalization is the most common option that should be evaluated together with biological phosphorus accumulation in sludge or plants for the following post-processing and valorization.

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INTRODUCTION

Nitrogen and phosphorus are essential elements of life, however, the continuous release of excess nitrogen and phosphorus into the environment during naturally occurring processes (e.g. weathering, leaching, erosion) and anthropogenic activities (e.g. surface run-off from agricultural and livestock activities, wastewater treatment plants, etc.), which may lead to eutrophication (i.e. algae bloom and oxygen depletion in aqueous systems) in natural water systems. The eutrophication problem is expected to increase due to the increasing population, agricultural intensification and industrialization. Nevertheless, eutrophication can be reversed by reducing the nutrients load to water bodies. One such solution is to decrease the load of nutrients discharged from wastewater treatment plants. Thus, efficient and reliable nutrients removal and/or recovery technologies are required. Nitrogen and phosphorus removal/recovery from wastewater can be achieved by biological or physical-chemical processes. The selection of nutrients removal/recovery technologies is determined by the nitrogen and phosphorus concentrations, and consequently the cost-effectiveness of the process. The nutrients removal/recovery technologies can be classified into three concentrations ranges (Mulder, 2003):

- Diluted wastewater with phosphorus concentration <40 mg P/L and ammonium concentration <0.1 g N/L. In this nutrients concentration range, biological nutrients removal is the preferable process based on cost-effectiveness. In addition, chemical phosphorus precipitation can be an option for phosphorus removal from diluted wastewater.
- Concentrated wastewater with phosphorus concentration >60 mg P/L and ammonium concentration in the range 0.1-5 g N/L. Chemical phosphorus precipitation processes are identified as interesting alternatives for the simultaneous recovery of phosphorus and nitrogen as an agricultural fertilizer (struvite) or phosphorus recovery as a raw material for the phosphorus industry (calcium phosphates). For nitrogen, biological treatment processes are also to be preferred.
- Concentrated wastewater with ammonium concentration >5 g N/L. In this range, the physical-chemical process for ammonium removal can be technically and economically feasible (e.g. ammonia stripping, selective ion exchange and breakpoint chlorination).

Thus, this chapter summarizes the methods and technologies commonly used for nitrogen and phosphorus removal/recovery from wastewater. While the processes for nutrients removal, such as biological nutrients removal or chemical phosphorus precipitation from diluted wastewater, have been widely adopted in nutrient removal plants, strategies for its recovery are still being studied. One such technology is the phosphorus recovery by struvite crystallization from wastewater streams with high phosphorus concentration. Moreover, ammonium removal from concentrated wastewater by ammonia stripping can be used because of its simple operation and high efficiency.

NITROGEN AND PHOSPHORUS IN INDUSTRIAL WASTEWATER

The characteristics of industrial wastewater vary essentially with the type of industry and the type of industrial process used (Table 1). Agro-industrial effluents, like piggery effluents or fishery discharges, slaughterhouses and meat processing, food processing, frequently combine high concentration both in

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Table 1. Industrial wastewater composition in terms of nitrogen and phosphorous content (mg/L)

Type of Wastewater	Total Nitrogen	Total Phosphorus
Slaughterhouse poultry	10-190 (NH_4^+-N)	-
Distillery	1200 (NH_4^+-N)	-
Brewery	25-35 (TKN)	20-30
Vegetable processing	-	1-30
Seafood processing	25-405	5-95
Dairy product	60-310	1-40
Personal care and pharmaceutical products	15-130	3-30
Meat processing	90-700 (TKN)	12-120

TKN: Total Kjeldahl Nitrogen
(Wun-Jern, 2006)

ammonium, phosphorus and organic matter. For many industrial wastewaters, especially in chemical and petrochemical industry, reduction of effluent total nitrogen is difficult because of batch production operations and the refractory nature of many complex organic nitrogen compounds in process chemicals.

REMOVAL VS RECOVERY: FEASIBILITY AND SUSTAINABILITY

There are different technologies for nutrients recovery from nitrogenous industrial wastewater. Besides the solid/liquid separation technologies are often involved to separate the organic and mineral forms of nitrogen, there are two main groups of technologies aiming the removal and recovery of nitrogen, respectively:

- Physical-chemical processes which separate ammonia and concentrate it in other flows, either solid, liquid or gaseous, that can be further processed to recover ammonium salts;
- Biological processes which convert ammonia into nitrogen gas that returns to the atmosphere.

Although the nutrients recovery always appears the desirable option, its sustainability for removal or recovery at large-scale applications should be evaluated as well, both from the technical, environmental, administrative/regulatory, and finally, economic aspects. However, the latter is closely linked to the market for recovered materials and the ability to compete with traditional chemical fertilizers. Maurer et al. (2003) compared the energy consumption of different technologies for N recovery from source separated urine and calculated that:

1. N recovery by air stripping followed by acid condensation and $(NH_4)_2SO_4$ production needs 90 MJ/kg N;
2. Biological removal with nitrification/denitrification with methanol as substrate needs 109 MJ/kg N;
3. Biological removal with the completely autotrophic process (partial nitritation + anaerobic ammonia oxidation) needs only 19 MJ/kg N;

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4. The Haber-Bosch process to produce ammonia from N_2 needs 45 MJ/kg N.
5. It follows that the combination of the conventional biological removal process with the Haber-Bosch process (154 MJ/kg N) results less convenient than the N recovery with air stripping (90 MJ/kgN), but completely autotrophic processes plus the Haber-Bosch process could be more energetically convenient (64 MJ/kg N).

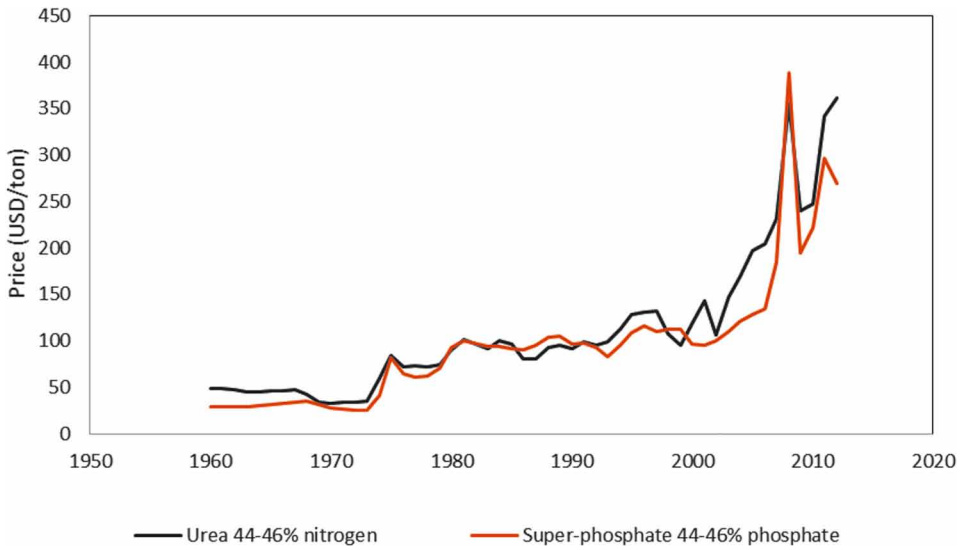
The conventional technologies for the removal of phosphorus from wastewater are chemical phosphate precipitation by adding metal salts or biological phosphorus removal processes. However, in these technologies, the phosphorus is not recovered as a sustainable product, but rather like a waste sludge that needs to be treated or disposed of in landfills. An important requisite for phosphorus recovery technologies is generating a final product with high quality, high purity and free from pollutants. Thus, the aim of phosphorus recovery technologies must be to obtain a product that has a potential to be used as fertilizer or as raw material for phosphorus industry. Thus, the technologies of nutrients recovery should not only be technically feasible, but they should also be cost-effective. The economic viability is, therefore, crucial to decide on the implementation of a nutrients recovery technology.

Market and Opportunities of Recovered Nutrients

During the last decades, the steadily growing global demand for grain crops has generated higher crop prices and higher needs of fertilizers (N and P based) with the consequent rise in the prices (Figure 1). The consumption of fertilizer in 2011 was estimated at 176.8 million tonnes. With a successive growth of 1.9 percent per year, it is expected to reach 194.1 million tonnes by the end of 2016 (FAO, 2012).

Nitrogen is recovered from concentrated industrial wastewater often as ammonium sulfate which has potential applications as fertilizer. Ammonium sulfate account for about 4.7% of the world nitrogen fertilizer market (www.ihs.com, Chemical Economics Handbook Ammonium Sulfate). There are no

Figure 1. Price for urea and super-phosphate procurement during the years from 1960-2013
Source: USDA, 2013



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serious environmental concerns involved with the use of ammonium sulfate as a fertilizer material. The global ammonium sulfate market size was estimated at USD 2.86 billion in 2014, and the forecast is for a further increase in the next seven years (Grand View Research, 2016). Although the total nitrogen fertilizer market grew substantially between 1987 and 2013 and it is expected further growth for 2018, the bulk of the world demand for nitrogen fertilizer is being filled by urea, another solid fertilizer material with a higher nitrogen content.

Struvite is considered as a potentially marketable phosphorus product from wastewater streams. Some potential applications of struvite are: secondary phosphate ore (as raw material), source of phosphate in other industrial processes or slow-release fertilizer (Schuiling & Andrade, 1999). The possible use of struvite as a raw material is associated with the production of elementary phosphorus or P-based fertilizer. Another use could be as a raw material in magnesium phosphate cement of building materials (p.e. fire resistant board material).

The most promising use of struvite is as a slow release fertilizer. Struvite can have low rates of leach and, thus, to slowly release nutrients (El Diwani, Rafie, Ibiari, & El-Aila, 2007; Le Corre, Valsami-Jones, Hobbs, & Parsons, 2005; de-Bashan & Bashan, 2004). The fertilizer properties of struvite have been studied by numerous researches. These studies are in agreement that the struvite is an excellent fertilizer for crops, ornamentals, vegetables, flower boards, turf grass, tree seedlings and garden grass (Rahman, Liu, Kwag, & Ra, 2011; Uysal, Yilmazel, & Demirer, 2010; González-Ponce & García López, 2007).

FUNDAMENTALS

Biological Nutrient Removal: Principles

Biological Nitrogen Removal

Biological nitrogen removal in activated sludge (AS) systems is based on two main separated but complementary processes called nitrification and denitrification (Figure 2).

Nitrification

Nitrification in AS systems is defined as the biological oxidation of the ammonium present in wastewater to its most oxidized form (nitrate). In AS systems, this process is performed by two different nitrifying bacteria communities, and thus, nitrification is considered as a two-step process. Ammonia Oxidizing Bacteria (AOB) firstly oxidize ammonium to nitrite (nitritation, Equation 1) and Nitrite Oxidizing Bacteria (NOB) perform the nitrate formation (nitratation, Equation 2). The nitrification process has the following stoichiometric equations (Wiesmann, 1994):

$$NH_4^+ + \frac{3}{2} O_2 \rightarrow NO_2^- + H_2O + 2H^+ \textit{ AOB (Nitrosonomas spp., Nitrosospira spp.,...)} \quad (1)$$

$$NO_2 + \frac{1}{2} O_2 \rightarrow NO_3 \textit{ NOB (Nitrobacter spp., Nitrospira spp.,...)} \quad (2)$$

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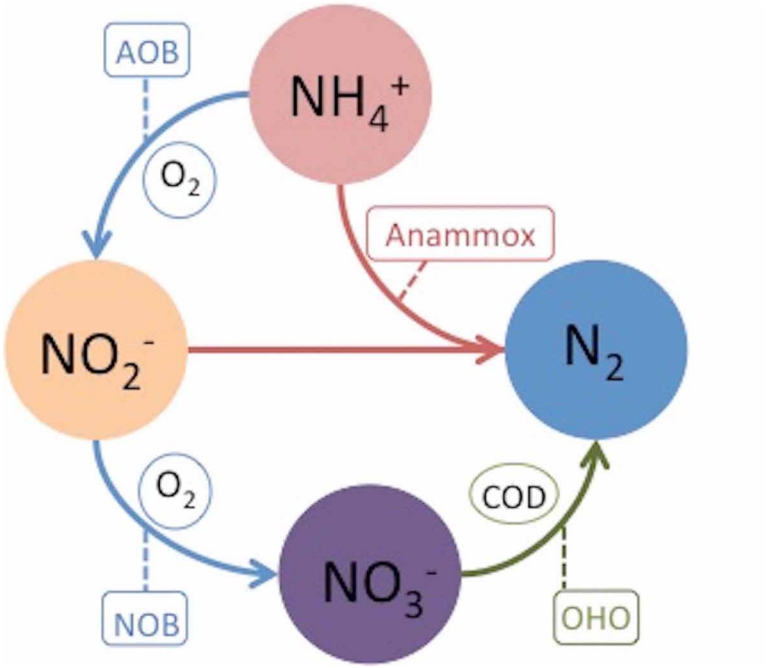
Figure 2. Biological transformations in the N cycle. Blue and green arrows represent the conventional nitrification and heterotrophic denitrification process, respectively. The anammox process is presented in red
(Adapted from Tayà, 2013)
Source: Tayà, 2013



If the synthesis of new bacteria is considered (assuming that the empirical formulation of bacterial cells is $C_5H_7NO_2$), the above equations are modified as follows (Haug & McCarty, 1972):

$$55\ NH_4^+ + 76\ O_2 + 5\ CO_2 \rightarrow 54\ NO_2^- + 52\ H_2O + 109\ H^+ + C_5H_7NO_2 \quad \textit{Nitritation} \tag{3}$$

$$400NO_2^- + 195O_2 + 2H_2O + NH_4^+ + 5CO_2 \rightarrow 400NO_3^- + H^+ + C_5H_7NO_2 \quad \textit{Nitratation} \tag{4}$$

It is important to take into account the affectations or inhibitions in the nitrification process. Temperature, pH (Metcalf & Eddy, 2003), free ammonia (FA) and free nitrous acid (FNA) concentration (Anthonisen, Loehr, Prakasam & Srinath, 1976; Kim, Lee, & Kellet, 2006; Torà, Lafuente, Baeza & Carrera, 2010) or the lack of inorganic carbon presence (Wett & Rauch, 2003; Guisasola, Petzet, Baeza, Carrera, & Lafuente, 2007; Torà *et al*., 2010; Ganigué, Volcke, Puig, Balaguer & Colprim 2012) are one of the most deeply studied parameter that could affect this process.

Current knowledge on nitrification process has attributed to the nitritation step the majority of nitrous oxide (N_2O) and nitric oxide (NO) emissions detected in WWTP (Kim, Mishurov & Kiely 2010; Wunderlin, Mohn, Joss, Emmenegger & Siegrist 2012). Among them, N_2O has received increasing attention due to the detrimental effects that it can cause as greenhouse gases (GHG) and as a toxic to living organisms (Guerrero, 2014).

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Denitrification

The following step inside de nitrogen removal is the denitrification. Denitrification is the reduction of nitrate to nitrogen gas (N_2), which is removed from the system achieving the wastewater nitrogen removal. This process is composed of different steps (Equation 5) starting with nitrate reduction to nitrite, followed by nitrite reduction to nitric oxide and nitrous oxide and finally to nitrogen gas (Gujer, Henze, Takahashi & van Loosdrecht 1999).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{5}$$

The stoichiometry of total denitrification to N_2 when using ethanol as carbon source is showed in Equation 6 (Wiesmann, 1994):

$$12NO_3^- + 5C_2H_5OH^- \rightarrow 6N_2 + 10CO_2 + 9H_2O + 12OH^- \tag{6}$$

The synthesis of new bacteria follows the stoichiometry presented in equation 7 (Liu, Qin & Yang, 2007):

$$97NO_3^- + 50C_2H_5OH \rightarrow 46N_2 + 75CO_2 + 84H_2O + 97OH^- + 5C_5H_7NO_2 \tag{7}$$

Conventional denitrification in AS (i.e. heterotrophic denitrification) is mainly conducted by one microbial population called ordinary heterotrophic organisms (OHO). Under anoxic conditions, where the electron acceptor is nitrite or nitrate, OHO can use them for organic matter (organic electron donor) oxidation to CO_2 and H_2O. Although the amount of organic carbon present in urban wastewaters is commonly enough for total nitrogen denitrification, some industrial influents have low COD/N ratios limiting this process. Among other possible solutions, a biodegradable external carbon source can be used for these cases. As an example, in the north of Europe the addition of methanol is a widespread practice to enhance the denitrification capacity of urban WWTP (Purtschert, Siegrist & Gujer, 1996), however treating industrial wastewater an external carbon source has to be added to complete the denitrification and therefore the BNR.

For some years, it is being studied the denitrification process as a contributor of N_2O and NO emissions because they are intermediate compounds of nitrate or nitrite reduction to nitrogen gas (Equation 5). Although low emissions are related to denitrification in comparison with nitrification for normal WWTP operation, some specific conditions have been focused as possible factors to favour N_2O and NO accumulation under anoxic conditions. Carbon source limitations, low pH or high nitrite concentrations are some examples (Thörn & Sörenson, 1996; Itokawa, Hanaki, & Matsuo, 2007). At present, there is still a lack of studies about understanding the influence of environmental factors and operational configurations on N_2O and NO emissions, being then current hot research topics (Guerrero, 2014).

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Advanced Nitrogen Removal Processes

Novel advanced N removal processes have been developed in the recent years mainly focused on reducing organic carbon necessities for denitrification step. Most of them are based on nitrification and denitrification via nitrite pathway (i.e. shortcut biological N removal). This process has the following stoichiometry (Henze, van Loosdrecht, Ekama, & Brdjanovic, 2008):

$$NH_4^+ + {}^{3}\!/\!_{2}\, O_2 \rightarrow NO_2 + H_2O + 2H^+ \textit{ Nitritation (AOB)} \quad (8)$$

$$8\ NO_2^- + 3\ CH_3COOH \rightarrow\ 4\ N_2\ + 6\ CO_2 + 2\ H_2O\ + 8OH^-\ \textit{Denitritation (OHO)} \quad (9)$$

The first step consists in a partial nitrification where ammonium is oxidized to nitrite (nitritation) but not to nitrate. Consequently, total NOB washout is mandatory to ensure nitratation suppression. Several methods have been proposed so far for selecting AOB against NOB, which are based on decreasing growth rate of the NOB over AOB under some specific operational conditions.

For complete biological N removal through nitrite, a second step for nitrite reduction, autotrophically or heterotrophically, has to be included. Comparing with conventional nitrification/denitrification process, the combination of partial nitritation (Equation 8) and heterotrophic denitritation (Equations 9) has some advantages since it results in a decrease of 25% in oxygen requirements, around 30-40% less of carbon source requirements for denitrification step and a reduction of 40% in biomass production (Turk & Mavinic, 1987; Van Hulle et al., 2010). In addition, the anoxic volume can be reduced because denitrification rates from nitrite are around 1.5-2 times faster than denitrification from nitrate (Peng & Zhu, 2006; Aslan & Dahab, 2008).

Regarding autotrophic denitrification, the anaerobic ammonium oxidation (anammox) is the most innovative nitrogen removal process. Under anoxic conditions, anammox microorganisms oxidize ammonium to nitrogen gas by using nitrite as an electron acceptor. Hence, differently to heterotrophic denitritation, for anammox process only 50% of the ammonium entering the system has to be previously oxidized to nitrite. As can be observed in anammox stoichiometry (Equation 10) no carbon source is needed during this process, and around a 10% of the nitrogen treated is converted to nitrate (Strous, Heijnen, Kuenen & Jetten, 1998).

$$NH_4^+ + 1.32NO_2^- + 0.0066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2.03H_2O + 0.0066CH_2O_{0.5}N_{0.15} \quad (10)$$

This process presents different advantages (Liu et al., 2008):

1. Overall energy savings around 40-50% related to low oxygen requirements,
2. There is no need for carbon source supply and
3. The amount of sludge produced is lower due to low biomass substrate yield of anammox bacteria.

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On the contrary, the slow growth rate of such microorganisms, the inhibitory effect of oxygen presence and the complexity to find a proper inoculum enriched in anammox results in long-term start-up periods. In spite of this, several treatment processes that combine nitritation and anammox have been already developed: SHARON/Anammox (two reactors system; Hwang, Min, Choi & Yun, 2005), CANON (complete autotrophic N removal over nitrite; Vázquez-Padin et al., 2009), OLAND (oxygen-limited autotrophic nitrification and denitrification; Vlaeminck et al., 2010) or NAS (floc-based partial nitritation and anammox process; Desloover et al., 2011).

Some other autotrophic denitrification processes have also been studied during last decade not based on anammox bacteria. In these cases, autotrophic denitrification is carried out by using hydrogen (H_2) as electron donor (Lee & Rittman, 2002; Rezania, Oleszkiewicz & Cicek, 2007) or sulfur compounds such as H_2S, S, $S_2O_3^{-2}$ or SO_3^{-2} (Batchelor & Lawrence, 1978; Sierra-Alvarez et al., 2007; Fajardo, Mosquera-Corral, Campos & Méndez 2012; Mora, Lopez, Gamisans & Gabriel 2014). As also occurred with anammox microorganism, the organic carbon source is neither needed during denitrification. This process presents the same advantages as anammox systems over heterotrophic denitrification. However, the high alkalinity required during the process and the sulfate production due to the oxidation of sulfur compounds constitute the main drawbacks.

Biological Phosphorus Removal: Enhanced Biological Phosphorus Removal (EBPR) Process

EBPR aims at removing and recovering phosphorus using biological processes and thus, without the addition of chemicals, which increases the costs and produces a chemical undesired sludge. This process is based on the enrichment of activated sludge with polyphosphate accumulating organisms (PAO) under alternating anaerobic/aerobic or anaerobic/anoxic conditions. Under anaerobic conditions, PAO can uptake organic substrates (preferably volatile fatty acids, VFA) and store them as a polyhydroxyalkanoates (PHA). This storage requires energy provided by hydrolysis of poly-phosphates (poly-P) resulting in P-release into solution. The reduction power is provided mainly by the catabolism of stored glycogen. The release of phosphate produced under anaerobic conditions is compensated by its aerobic P-uptake. In the aerobic stage, PHA is used as a carbon and energy sources for growth, and the replenishment of internal glycogen and poly-P pools (Mino, van Loosdrecht & Heijnen, 1998). A schematic representation of the PAO metabolism most widely accepted is presented in Figure 3.

The two most common VFA present in municipal wastewater are acetate and propionate. The metabolism of acetate and propionate by PAO has been amply studied (Oehmen, Zeng, Yuan & Keller., 2005; Pijuan, 2004; Hood & Randall, 2001; Lemos, Serafim, Santos, Reis & Santos, 2003; Lu, Oehmen, Virdis & Yuan, 2006; Chen, Randall & McCue 2004; Thomas, Wright, Blackall, Urbain & Keller, 2003). Depending on the carbon source used, PHA polymers are produced with a different composition. Pijuan et al. (2009) studied the effect of carbon sources on the type and quantity of PHA synthesis obtained with different EBPR microbial communities enriched with acetate or propionate. It was shown that the same carbon source produced different PHA composition in each community. The PHA composition was also strongly influenced by the carbon source. Acetate produced PHB-PHV copolymer with a much higher amount of PHB (70%), propionate produced PHV (53%) or PH2MV (49%) copolymer, while other non-identified PHA monomers were also detected with butyrate (Tayà, 2013).

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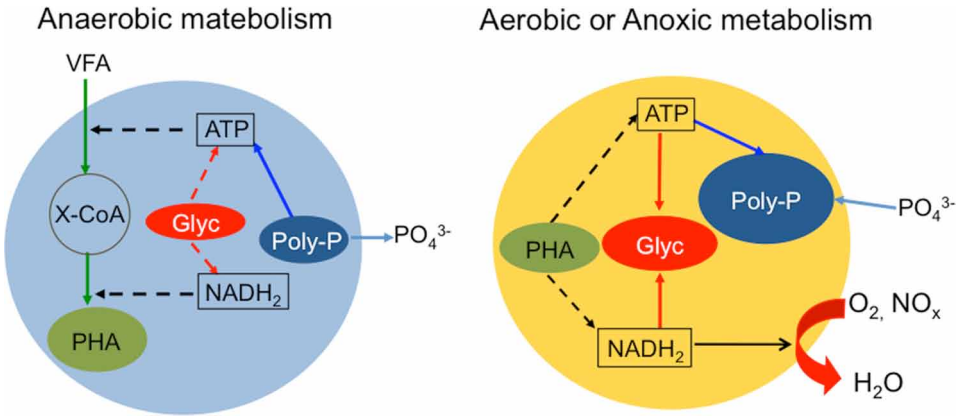
Figure 3. Schematic representation of PAO metabolism
(Tayà, 2013)
Source: Tayà, 2013



Through microbial techniques, *Acinetobacter* was first proposed to be the primary organism responsible for P removal in EBPR (Fuhs & Chen, 1975), and was long believed to be the sole PAO present in EBPR plants. However, the use of fluorescence *in situ* hybridization (FISH), 16S rRNA-based clone libraries or denaturing gradient gel electrophoresis (DGGE), showed that a high diversity of phylogenetic groups are present in lab- and full-scale EBPR sludge (Seviour, Mino & Onuki, 2003; Hesselmann, Werlen, Hahn, van der Meer & Zehnder 1999; Crocetti et al., 2000; Liu et al., 2001; Ngunyen, Le, Hansen, Nielsen, & Nielsen 2011).

However, one of the large known failures on EBPR systems is the presence of other microorganisms able to survive under anaerobic/aerobic conditions and compete with PAO for donor electron (carbon source). These microorganisms are able to uptake the carbon source under anaerobic conditions without any P activity (Cech & Hartman, 1990, 1993; Crocetti, Banfield, Keller, Bond & Blackall, 2002; Liu, Mino, Nakamura, & Matsuo, 1994; Nielsen, et al., 1999; Satoh, Mino & Matsuo, 1994; Wong, Tan, Ng, & Liu, 2004). The term GAO (glycogen accumulating organisms) was proposed by Mino, Liu, Kurisu, & Matsuo, (1995), and is defined as the phenotype of organisms that store glycogen aerobically and consume it anaerobically as their primary source of energy for taking up carbon sources and storing them as PHA. These microbial competitions in the EBPR systems is influenced by several factors, such as the carbon source, pH, temperature and aeration (Filipe, Daigger, & Grady, 2001; Brdjanovic et al.,1998a,b; Oehmen, Zeng, Yuan & Keller, 2005; Oehmen, Saunders, Vives, Yuan, & Keller, 2006a: Oehmen et al., 2006b; Lopez-Vazquez et al., 2008; 2009; Lu, Oehmen, Virdis, & Yuan, 2006).

Main Schemes Applied for Conventional and Advanced BNR for Industrial WWTP

Treatment of wastewater by means of biological processes has been widely implemented for classical urban and industrial wastewater. Moreover, there are many biological nutrient removal systems to deal with nutrient removal such as: Phoredox (A/O) (Figure 4), A^2/O (Figure 5), Five-stage Bardenpho (Figure 6), UCT (University of Cape Town) (Figure 7), modified UCT (Figure 8) and VIP (Virginia Initiative Plant) (Figure 9) (Metcalf & Eddy, 2003).

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Figure 4 describes the A/O process, which is a patented version of Phoredox by *Air Products and Chemicals, Inc*. The main difference is the use of multiple-staged anaerobic and aerobic reactors. This process is used for combined carbon oxidation and phosphorus removal. In this process there is no nitrification, and the anaerobic retention time is 30 min to 1 h to provide the selective conditions for the biological phosphorus removal (Tayá, 2013).

A^2/O process (Figure 5) is patented by *Air Products and Chemicals, Inc*. It is a modified A/O process to provide an anoxic zone for denitrification. The operation is relatively simple compared to other processes. With this process it is achieved simultaneous nitrogen and phosphorus removal. In the anoxic zone there is a low oxygen concentration, but nitrite and nitrate can be used as an electron acceptor from the recycle of the aerobic zone. However, it requires high COD/P ratios.

On the other hand, Barnard (1975) first achieved phosphorus removal in a mainstream process later called Bardenpho process. Figure 6 shows a 5-stage Bardenpho process, which provides anaerobic, anoxic, aerobic stages for phosphorus, nitrogen and carbon removal. A second anoxic stage is provided

Figure 4. Phoredox or A/O process

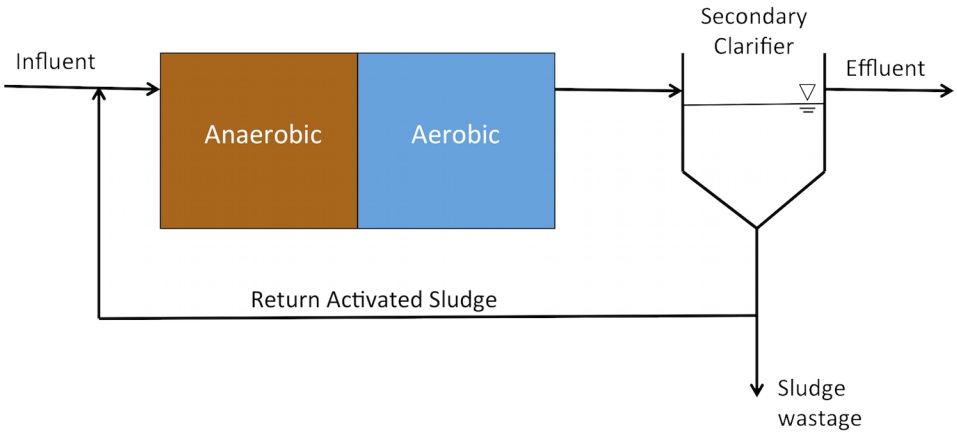
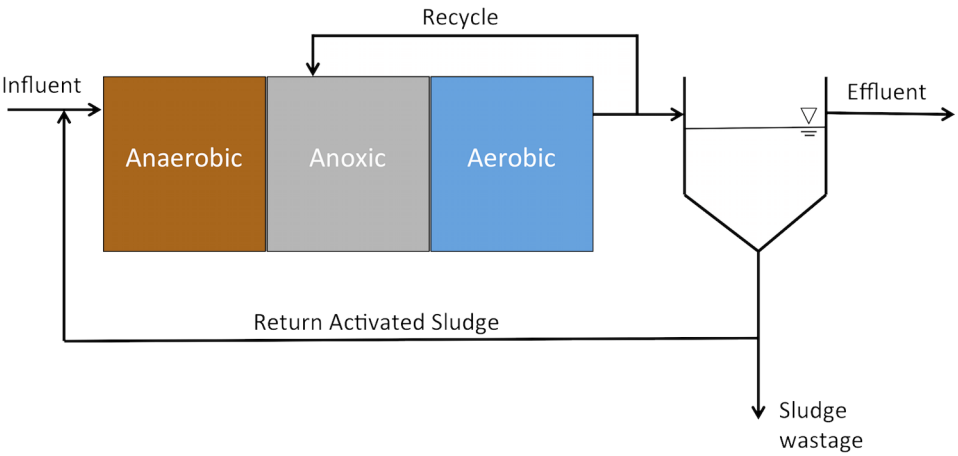


Figure 5. A2/O process



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for additional denitrification using nitrate produced in the aerobic stage as the electron acceptor and the endogenous organic carbon as the electron donor. The final aerobic stage is used to strip residual nitrogen gas from solution to prevent rising problems and to minimize the P-release in the final clarifier (Metcalf & Eddy, 2003).

The UCT process (Figure 7) was developed at the University of Cape Town and is similar to the A^2/O process. There are two differences:

1. The return activated sludge is recycled to the anoxic reactor instead of the anaerobic stage, and
2. There is an additional recycle from the anoxic phase to the anaerobic phase. This configuration decreases the amount of nitrate recycled to the anaerobic reactor, increasing the organic matter availability for EBPR.

The modified UCT process (Figure 8) splits the anoxic zone into two stages. The nitrate rich recycle from the aerobic zone is recycled to the head of the second anoxic stage. The nitrate contained in the return activated sludge is recycled to the first anoxic stage where it is denitrified. Next, the denitrified

Figure 6. Modified Bardenpho (5-stage) process

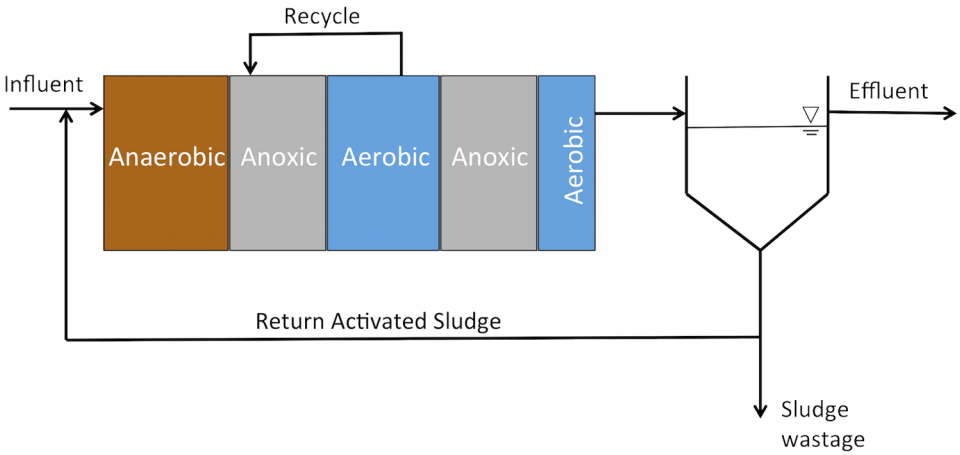
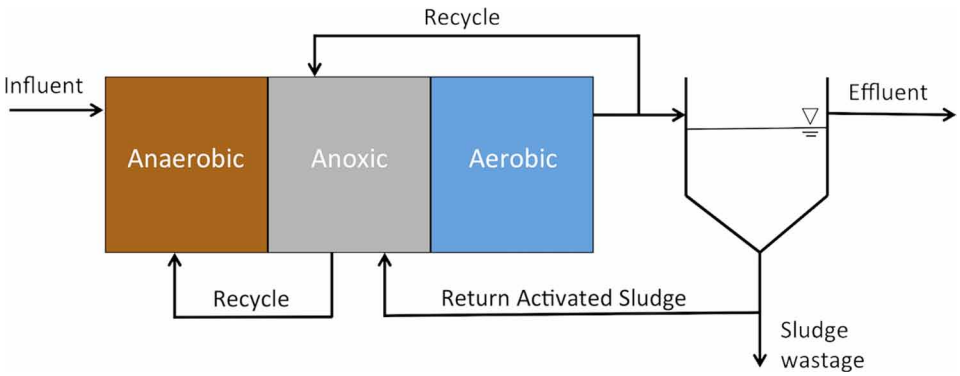


Figure 7. University of Cape Town (UCT) process



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returned activated sludge is recycled from the end of the first anoxic stage to the head of the anaerobic stage and mixed with the incoming wastewater

The VIP process (Figure 9) (from Virginia Initiative Plant in Norfolk, US) is similar to A^2/O and UCT processes except for the methods used for recycling. The return of activated sludge is discharged to the inlet of the anoxic zone along with nitrified recycle from the aerobic zone. The mixed liquor from the anoxic zone is returned to the head end of the anaerobic zone. The organic matter in the process influent is stabilized through anaerobic mechanisms in the anaerobic zone, which reduces the oxygen requirements of the process (Metcalf & Eddy, 2003).

The Sequencing Batch Reactor (SBR) (Figure 10) is a single tank where the biological processes and settler occur under distinguished temporal sequence. The SBR is often applied for the treatment of both domestic and industrial wastewater because allowed high removal of the pollutant and flexibility of the operations. The principle of the SBR is the operation in cycles which involves the same pattern of phases, which typically are: 1) Filling; 2) Batch reaction wise (aerobic and/or anoxic and/or anaerobic); 3) Settling; 4) Discharging; 5) Idle. For continuous-flow applications, at least two SBR tanks must be provided so that one tank receives flow while other completes the treatment cycle (Metcalf & Eddy, 2003).

Figure 8. Modified UCT process

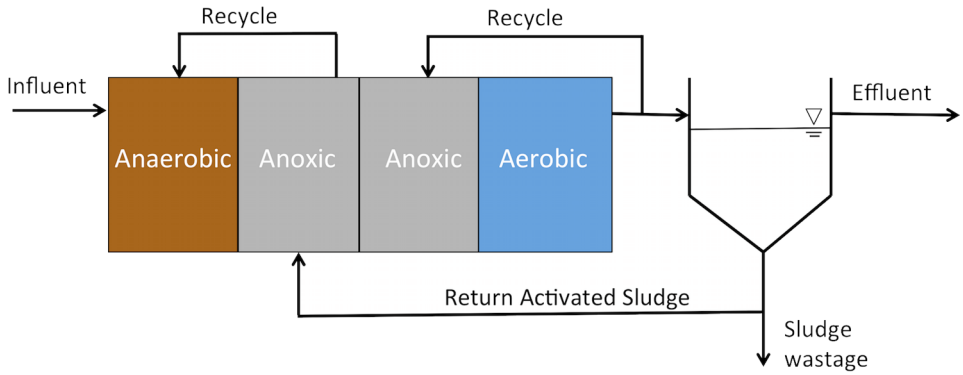

Figure 9. Virginia Initiative Plant (VIP) process

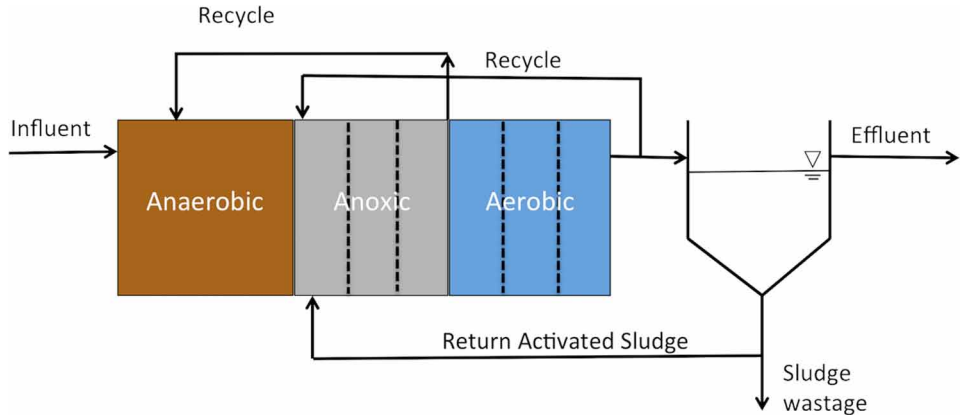

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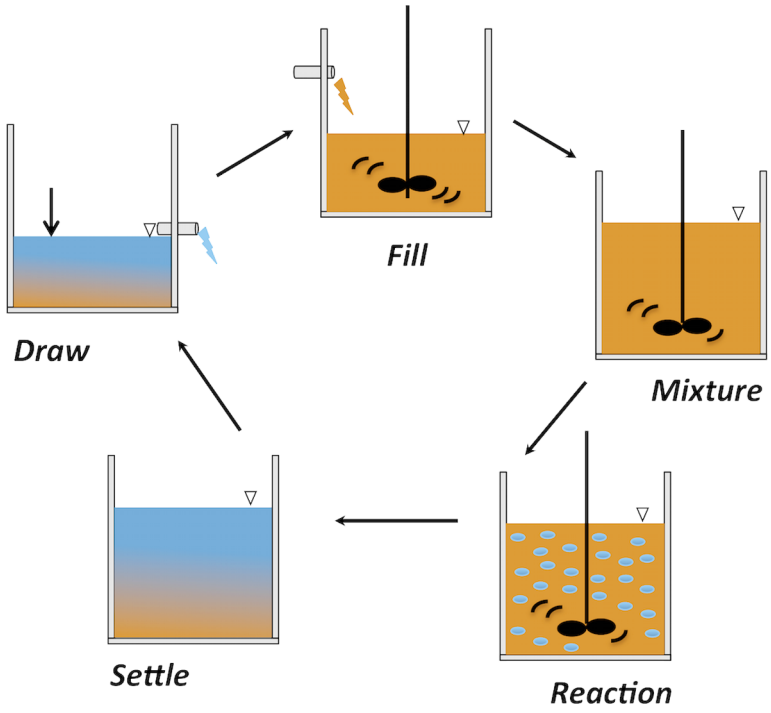
Figure 10. Sequencing Batch Reactor process



Nitrogen Stripping, Adsorption, and Vacuum Distillation, Processes: Principles

Stripping of Ammonia

Ammonia removal from high nitrogenous wastewaters can be accomplished by air or steam stripping. Ammonia stripping is a well-known application to concentrate nitrogen in concentrated wastewater treatment (e.g. landfill leachate, supernatants of anaerobic digestion processes, specific flows of the petrochemical industry), while very few applications in sewage treatment are reported in the literature (Capodaglio, Hlavínek, & Raboni, 2015).

The stripping of ammonia requires a high pH (around 10 to 12), which is usually achieved by addition of base in significant amounts:

$$NH_4^+ + NaOH \rightarrow NH_3 + H_2O + Na^+ \quad (11)$$

$$NH_4^+ + Ca(OH)_2 + HCO_3^- \rightarrow NH_3 + CaCO_3 + 2H_2O \quad (12)$$

The equilibrium is governed by pH and temperature, according to the Equation 13 describing the reaction's ionization constant (K_{eq}).

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$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \cdot 10^{-5} \text{ at } 25\ ^\circ\text{C} \tag{13}$$

The stripping factor (S) describes the balance between gas and water at the upper end of the stripping column (Morales et al., 2013). The minimum required amount of air (Q_{Air}) in relation to the supernatant (Q_{Liquid}) is in accordance with Equation (14) (Siegrist, Laureni, & Udert, 2013) to be at least $1/H_{NH3}$ where H_{NH3} is the NH_3 Henry's constant.

$$S = \frac{Q_{AIR}}{Q_{LIQ}} \geq \frac{1}{H_{NH_3}} \tag{14}$$

There are two ways to strip the ammonia out the water (Figure 11):

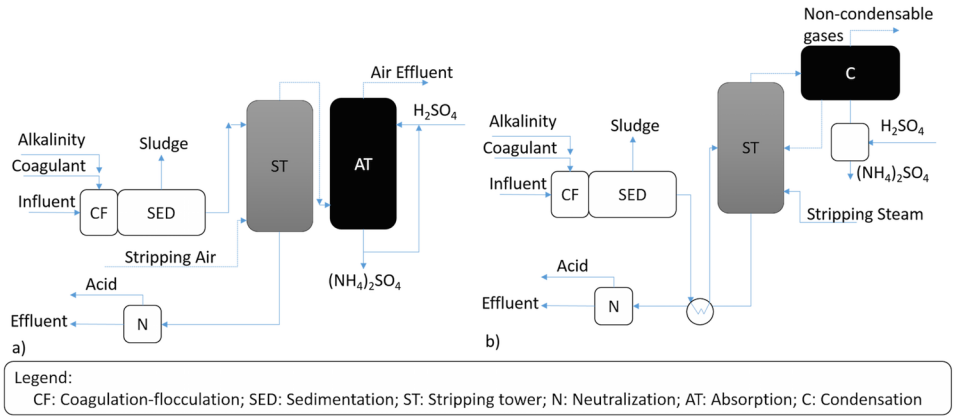
a. Air stripping: air is bubbled through the wastewater and takes up the gaseous ammonia. This gas has to be washed out in a second reactor under acidic conditions.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{15}$$

b. Steam stripping: steam is blown through the water and after condensation a concentrated ammonia solution is produced.

This process requires 2.4 kg/kg N calcium oxide for increasing the pH above 9 and 7.0 kg sulphuric acid each kg of ammonia nitrogen absorbed (Purtschert, Siegrist, & Gujer, 1996). The electricity requirement for the aeration is an estimated 26.3 MJ/kg N and the following energy data are used for the calculations (Patyk & Reinhard, 1997).

Figure 11. Typical flow diagrams of the stripping processes with air (a) and steam (b)
(Adapted from: Raboni, Torretta, Viotti, & Urbini, 2013)
Source: Adapted from Raboni et al., 2013



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The stripping process is not applicable for wastewater of low strength. Certain wastewater, like from manure, from the production of PU-foams or digester supernatant in municipal WWTP, can be treated economically.

Air stripping is often used in the treatment of municipal solid waste (MSW), landfill leachate (or groundwater polluted by the same leachate). An example of the process is represented in Figure 12. The system consists of: 1) coagulation-flocculation at pH > 11; 2) water heating at 38°C and ammonia air stripping; 3) ammonia recovery by absorption with a sulfuric acid solution.

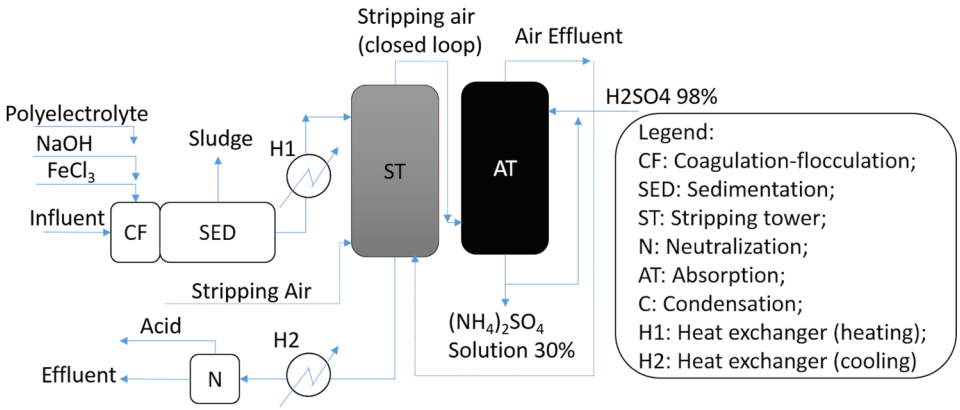
Raboni et al. (2013) obtained a reduction of ammonia from 199 mg/L (as N) down to 22.5 mg/L (as N). The plant showed severe scaling issues, with an increase in weight of the single filling components (Pall rings) up to seven times their original weight. The progressive scaling produced an 18% loss of ammonia removal efficiency, caused by the reduction of both the packing interfacial surface and the air/water ratio due to head loss increase. Periodical (every six months) chemical washing of the stripping towers with a 30% HCl solution was carried out to avoid scaling build-up. Closed-loop air recirculation allowed the water temperature inside the column to be maintained in the range of 25-38°C, even during winter, but caused a gradual decrease in the solution's pH within the tower. This was due to the acidic characteristics of the stripping air coming from the ammonia absorption tower. Subsequent experiences proved the actual possibility of achieving high ammonia removal efficiencies (greater than 95%) by operating the stripping towers at 38°C with liquid rates below 4.5 $m^3/(m^2 \cdot h)$ and air/water ratios above 1500 Nm^3/m^3 (Viotti & Gavasci, 2015).

Vacuum Distillation

In the case of highly concentrated streams vacuum distillation is a viable solution for ammonia recovery (EPA, 2013).

Vacuum flash distillation processes (Figure 13) have been applied to ammonia recovery from centrate of manure digested sludge, using as a heat source the biogas generated by the anaerobic digestion (Orentlicher, Brown, & Hall, 2009). The ammonia can be removed from approximately 1000 mg

Figure 12. Diagram of a physical-chemical process for leachate treatment, with wastewater pre-heating and a closed-loop air stripping process
(Adapted from: Raboni et al. 2013)
Source: Adapted from Raboni et al., 2013



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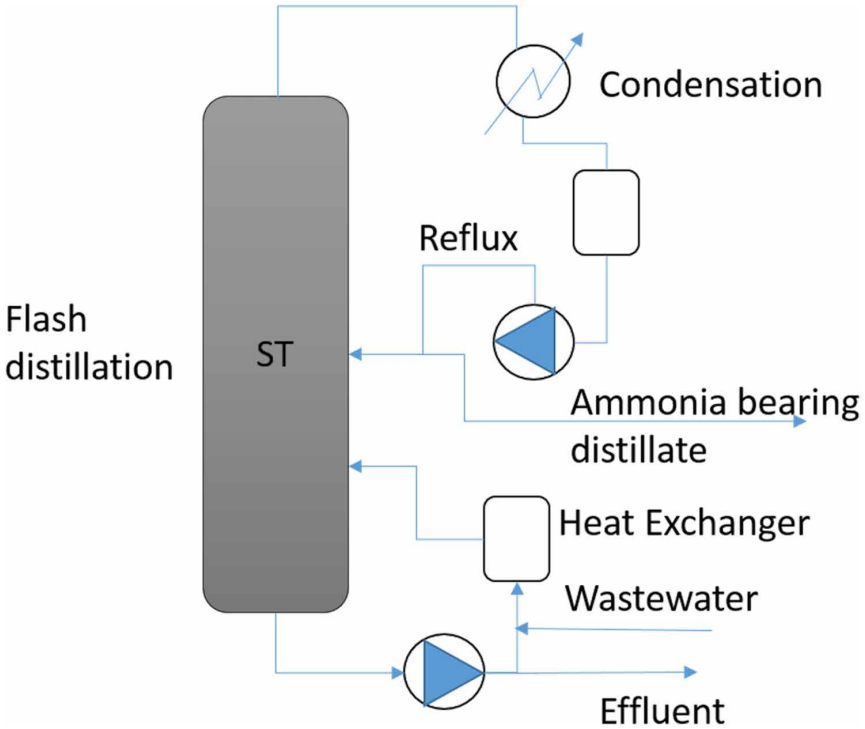
NH_3–N/L to less than 100 mg NH_3–N/L operating at a pH value of 9.5 and a temperature of 60°C under vacuum (Orentlichter et al., 2009). Other combinations of temperature and pH achieve similar high free ammonia fractions, allowing an effective stripping process. The resulting ammonia-rich distillate is a marketable product or it can be converted into an ammonium sulfate solution. If desired, such a solution can be further concentrated, using multiple vacuum distillation stages.

Adsorption

Zeolites and other mineral like clay or tuff have ion exchange properties and are used to adsorb ammonium when is present at low concentration. A common approach is to pump wastewater through columns packed with zeolite. Ammonia concentrations of 25 to 50 mg NH_4-N/L can be lowered to levels around 1 mg NH_4-N/L (zeolites: Booker, Priestley, & Fraser, 1996; Nishimura, Somiya, Tsuno, & Iwabu, 1996; Nguyen & Tanner, 1998; Komarowski & You, 1997; Cooney, Booker, Shallcross, & Stevens, 1999; Lahav & Green, 2000; tuff: Ibrahim, 2001; clay: Gisvold, Odegaard, & Follesdal, 2000).

Buday (1994) used cation exchange resins to reuse ammonia from wastewater of an ammonium nitrate fertiliser plant. The exhausted resins were regenerated with nitric acid, gaining an ammonium nitrate solution that is recycled into the fertiliser production. Chen et al. (1999) successfully tested the use of different cellulose acetate fibres for the adsorption and recovery of proteins. Kioussis et al. (2000) developed polymer hydrogels that remove nitrate, nitrite and phosphate from aquaculture wastewater. They claim to achieve following qualities: 10 mg N/L for nitrate and 0.08 mg N/L for nitrite. Gel regeneration is accomplished by flushing 1 M sodium hydroxide solution.

Figure 13. Diagram of a typical flash distillation process for ammonia recovery



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Chemical Phosphorus Precipitation and Crystallization: Principles

Chemical Phosphorus Precipitation Processes

The chemical phosphorus precipitation by addition of metal salts is widely used due to its simple operation and implementation. However, the disadvantages of chemical precipitation are high sludge production and costs of chemicals. The sludge produced during chemical phosphorus precipitation cannot be applied to agriculture lands because it has a low bioavailability (Morse, Brett, Guy, & Lester, 1998). Chemical phosphorus precipitation process is widely used to remove phosphorus from diluted wastewater streams. Generally, chemical phosphorus precipitation process is based on the addition of metal salts to wastewater, producing an insoluble metal phosphate precipitate. This precipitate is separated from the liquid phase using conventional separation technologies such as sludge filters or centrifuges. The phosphate precipitation efficiency by metal salts addition is highly dependent on the solids separation process. Even though phosphorus removal by adding metal salts is usually used, it is not appealing for recovering phosphorus because the obtained precipitates are difficult to manage, and so they are often disposed to landfills. This is because the aluminium in aluminium phosphates may be toxic to many plants and some soil organisms. Meanwhile, phosphorus in iron phosphates is usually considered to be unavailable for plants, therefore reducing its suitability for replacing phosphate fertilisers (Rittman, Mayer, Westerhoff, & Edwards, 2011). Iron phosphates are no significant industrial outlets for recovered ion phosphates because its recycle is very expensive at present. Regardless, phosphorus in aluminium phosphates can be used as raw material for phosphorus production by using the electrothermal process of Thermphos (Schipper et al., 2001).

The most important parameter for the chemical phosphate precipitation process is the dose of metal salts added. The amount of metal salts used influences the performance and the economy of the precipitation process. The metal ions should be added in excess relative to phosphate concentration to achieve a low concentration of phosphate in the effluent (Rybicki, 1997). The amount of metal salt added cannot be determined only by the concentration of phosphate, and it should be determined for each case. It also depends on the wastewater characteristics, operational pH, method of chemical addition, flocculation method, chemical addition feeding point(s) and time after chemical addition, and it is usually determined by on-site testing (EPA, 2010). It is possible to calculate only an approximate dose of metal salts for removing phosphorus. Several side reactions can take place alongside the precipitation of phosphate during the phosphate removal process. The EPA Design Manual (1987) recommends a 20% excess of aluminium ions to reduce phosphate by around 80%, while the 100% excess is suggested to obtain a phosphate removal of 95%.

Phosphorus Crystallization Processes

Phosphorus crystallization processes can be considered separately than phosphorus precipitation by adding metal salts because the chemistry involved in both technologies is quite different. Like in phosphorus precipitation processes, phosphorus crystallization allows transferring soluble phosphorus from wastewater to solid phase. However, phosphorus crystallization process is only used for removing phosphorus from wastewater but also generates a final product that has a potential to be used as fertilizer or as raw material for phosphorus industry.

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Calcium Phosphate Precipitation

Phosphorus can be recovered from wastewater by crystallization processes either using lime to produce calcium phosphates, or adding magnesium salts to produce magnesium ammonium phosphate (struvite). Calcium phosphates are less valuable than struvite as a multiple source of nutrient and fertilizer. However, calcium phosphate can be recovered and recycled into phosphate and fertilizer industries. Calcium phosphate is a suitable form of recovered phosphorus because they are similar to phosphate rocks. Different calcium phosphate species may precipitate from wastewater. The nature of calcium phosphate is influenced by the wastewater characteristics and the operating pH. Hydroxyapatite ($Ca_5(PO_4)_3OH$) is thermodynamically the most stable calcium phosphate species, but hydroxyapatite does not precipitate readily. Amorphous calcium phosphate ($Ca_3(PO_4)_2 \cdot n\ H_2O$), dicalcium phosphate dihydrate or brushite ($CaHPO_4 \cdot 2\ H_2O$), dicalcium phosphate anhydrous or monenite ($CaHPO_4$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5\ H_2O$) can be precursors of hydroxyapatite, depending on the operational conditions.

As mentioned above, lime is usually used to recover phosphorus from wastewater. This calcium compound can be added either as quicklime (CaO) or hydrated lime ($Ca(OH)_2$). Lime is an effective phosphate removal agent, but it produces large volumes of sludge. This chemical has been widely used to remove phosphorus from wastewater, but its use has been declining due large amounts of lime are required to obtain low levels of phosphorus (Metcalf & Eddy, 2007; EPA, 1987). Thus, phosphorus recovery by adding lime can produce large volumes and high chemicals costs.

Usually, the dose of lime added to the precipitation system is higher than the amount required to remove phosphate from wastewater. Lime reacts with phosphate to form insoluble precipitates of calcium phosphates, and it can also react with the alkalinity of wastewater to produce calcium carbonates (EPA, 2010). The operating pH must be fixed at high values to obtain a high phosphate removal efficiency (i.e. pH values higher than 10), and the amount of lime added must be approximately 1.5 times the total alkalinity (expressed as mg $CaCO_3$/L) (Rybicki, 1997). Thus, the amount of produced precipitates will be influenced by the level of bicarbonate alkalinity in wastewater.

Struvite Crystallization

The crystallization of struvite is one of the most recommended technologies to phosphorus recovery from concentrated phosphorus wastewater, such as effluents from anaerobic digesters or sludge dewatering process (Desmidt et al., 2015). The reason is that the crystallization of struvite is not only used for recovering phosphorus from wastewater but also generates a product with a commercial value as a fertilizer.

Struvite is a magnesium ammonium phosphate salt ($MgNH_4PO_4 \cdot 6H_2O$) that usually crystallizes in a reversible reaction and produces crystals with a Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio of 1:1:1. Struvite can be used as a slow release fertilizer, either directly or after processing by fertilizer industry (El Diwani et al., 2007; de-Bashan & Bashan, 2004). The formation of struvite is conditioned by a combination of factors, including the presence of seed crystals, thermodynamics and mass transfer between solid and liquid phases, and reaction kinetics. At the same time, these factors are influenced by several physical-chemical parameters such as pH, the chemical composition of the wastewater, mixing energy and temperature (Doyle & Parsons, 2002). The most important parameters that must be controlled are: pH, temperature and presence of other ions.

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The pH is one of the key factors in struvite crystallization process. Theoretically, there should be a direct relation between the efficiency of phosphorus recovery as struvite and pH. This is because the ionic equilibriums involved in the struvite crystallization are very pH dependent, which in turn could affect the struvite formation (Andrade & Schuiling, 2001). A slight variation in the pH can significantly affect the crystallization of struvite because it varies the distribution of the struvite constituents, affecting their availability for struvite formation. The pH range in which struvite may crystallize is between 7.0 and 11.5, but the suitable pH range is from 7.5 to 9.0 (Rahman et al., 2014). The solubility of struvite is also conditioned by the pH of the solution. It is highly soluble at acidic pH and highly insoluble at alkaline pH (Doyle & Parsons, 2002).

Temperature also influences the struvite crystallization process, struvite characteristics and its thermal stability. Temperature affects the struvite solubility in a way that its solubility increases with the temperature increase, and thus the formation of struvite is more difficult to occur at high temperatures (Le Corre, Valsami-Jones, Hobbs, & Parsons, 2009). So, struvite solubility product is inversely proportional to the variation of temperature (Ben Moussa, Tlili, Batis, & Ben Amor, 2011; Aage, Andersen, Blom, & Jense, 1997).

The presence of other ions in solution, also known as foreign ions, affects the performance of struvite crystallization process because these foreign ions can interfere with struvite crystallization by competing for magnesium and phosphate to form other precipitates species. So, the efficiency of struvite crystallization is affected by the presence of foreign ions, such as calcium and/or carbonate, and also the formation of calcium and/or carbonates precipitates affects the purity of the produced struvite. In this regard, the struvite crystallization is more affected by the presence of calcium at low phosphate concentrations (<40 mg $PO_4^{3-} \cdot L^{-1}$) (Desmidt et al., 2013). Crutchik & Garrido (2011) indicated that a high ammonium concentration could be highly beneficial to the reaction of struvite crystallization, so to obtain a relatively pure solid phase in terms of struvite purity. Thus, it could be possible to obtain a high purity regarding struvite, instead of precipitates of calcium phosphates in high ammonium wastewater.

Moreover, the economic viability of struvite crystallization is highly influenced by the availability of magnesium in the raw wastewater, the cost of alkali used or the cost magnesium source used. This is because wastewater usually contains a low amount of magnesium compared with phosphate and nitrogen and it is necessary to supply a magnesium source to promote the crystallization of struvite. In the literature, the use of high grade magnesium sources, such as $MgCl_2$, $MgSO_4$, MgO or $Mg(OH)_2$, has been reported (Rahaman et al., 2014; Hutnik et al., 2013; Jaffer, Clark, Pearce, & Parsons, 2002; Nelson, Mikkelsen, & Hesterberg, 2003). Nevertheless, the utilization of these high grade and expensive magnesium sources can lead to high operating costs compromising the viability of the process. In this sense, the use of low cost magnesium sources, such as industrial grade MgO or $Mg(OH)_2$, seawater or bittern, can significantly reduce the cost of struvite crystallization. MgO and $Mg(OH)_2$ can be used in a dual function, as magnesium and alkali sources. Unlike for NaOH, the use of MgO and $Mg(OH)_2$ does not produce drastic pH changes. Meanwhile, seawater, brine and bittern can be added to promote struvite crystallization for those urban or industrial WWTP located near the seashore (Liu, Giannis, Zhang, Chang, & Wang, 2013; Señoráns, Barros, García, & Garrido, 2011; Lee, Weon, Lee, & Koopman, 2003; Matsumiya, Yamasita, & Nawamura, 2000).

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FULL SCALE APPLICATIONS

Biological Nutrients Removal by SBR from Industry

The SBR system has demonstrated high removal efficiency, and thus, it is an optimal process for the treatment of nitrogenous industrial wastewater, such as landfill, textile effluent, tannery, meat product processing, toxic and slaughterhouse wastewaters, because of its simplicity in operation and economic aspects. Table 2 shows the typical application of SBR with various kinds of wastewaters. Among them, the leachate showed a very low BOD_5/COD ratio, a high concentration of COD, NH_3-N, heavy metals, and other toxic compounds which decrease the activity of the biomass and the treatment capacity of the SBR as a consequence (Uygur & Kargi, 2004). Typically, the treatment of leachate for nutrients removal using the SBR is reported in the literature (Guo, Abbas, Chen, Liu, & Chen, 2010; Spagni, & Marsili-Libelli, 2009; Klimiuk & Kulikowska,2006). Although leachate may have a very low BOD_5/COD ratio (0.09 to 0.3), with the addition of an external carbon source high nutrients removal efficiency can be achieved.

The variability in the operating conditions of the SBR is mainly related to the type of the wastewater fed and the quality of the final effluent. Table 3 reports the operating conditions for the treatment applied to leachate.

Table 2. Type of industrial wastewater treated using Sequencing Batch Reactor

Type of Wastewater	Pollutants/Removal	Removal	Reference
Landfill leachate	COD	<83	Timur & Ozturk (1999)
Dairy wastewater	COD Total Nitrogen	80.2 38.3	Li & Zhang (2002)
Landfill leachate	COD NH_4-N Phosphate	75 44 44	Uygur & Kargi (2004)
Tannery wastewater	COD NH_4-N	80-82 83-99	Ganesh, Balaji, & Ramanujam (2006)
Slaughterhouse wastewater	COD Total nitrification	96 96	Li et al. (2008)
Landfill leachate	Nitrification Nitrogen COD	98 95 20-30	Spagni & Marsili-Labelli (2009)
Meat products processing wastewater	COD BOD_5 NH_4-N	99 98 71	Rodriguez, Pino, & Penuela (2011)
Piggery wastewater	COD TN TP	98 98 98	Tilche et al. (2001)

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Table 3. Industrial wastewater (leachate) treated using Sequencing Batch Reactor

N°	Reference	HRT (d)	SRT (d)	MLSS (mg/L)	OLR (kg COD/m^{3}d)
1	Timur & Oztuk (1999)	1.5-10	9-22	-	-
2	Kennedy & Lentz (2000)	0.5-1.0	-	-	0.4-9.4
3	Neczaj, Okoniewska, & Kacprzak (2005)	-	10	4000	-
4	Klimiunk & Kulikowsk (2006)	2-12	17-51	-	-
5	Leatinen, Luonsi, & Vilen (2006)	-	10-40	-	-
6	Bu et al. (2010)	-	-	4400	1.7

HRT: hydraulic retention time; SRT: solids retention time; MLSS: mixed liquor suspended solids; OLR: organic loading rate.

Nitrogen Recovery from Industry and Agrowaste

Nitrogen and Phosphorus Recovery from Anaerobic Effluent in Glattbrugg, Switzerland

A full-scale stripping reactor including a CO_2 pre-stripper was located in the Kloten/Opfikon Wastewater Treatment Plant (60,000 population equivalent, Glattbrugg, Switzerland). It was the first of these reactors installed in Switzerland (Böhler & Liebi, 2012a). The ammonia stripping process was set in operation for the first time in fall 2010. Some of the characteristics of the stripping reactor were summarized in Table 4, while the scheme of the overall process is shown in Figure 14. The stripping columns (ST) use special UV-stabilized Fluorpolymere packing with a honeycomb shape (CF 12F, Hewitech GmbH & Co, Ochtrup, Germany). This material has 12 mm of channel opening, a specific surface of 300 m^2/m^3 and a cross-flow channel structure. The ammonium rich stream is fed to the top of the CO_2-pre stripper where the air is fluxed in counter flow. The CO_2 stripping increases the pH of the liquid due to the displacement of carbonic acid system equilibrium (Cohen & Kirchmann, 2004).

Table 4. Dimensions and operational condition of the stripping system

Parameter	Value	Units
Column height (CO_2 and Ammonia)	10	M
Packing bed height	6	M
Diameter	0.98	M
Liquid inflow	5-12	m^3/h
Air flow to ammonia stripper	1000-6250	Nm^3/h
Gas flow to the CO_2 stripper	50-200	Nm^3/h
Average NH_4-N concentration inlet	1000	mg/L
Average NH_4-N concentration effluent	30	mg/L
Maximum removal rate	99	%

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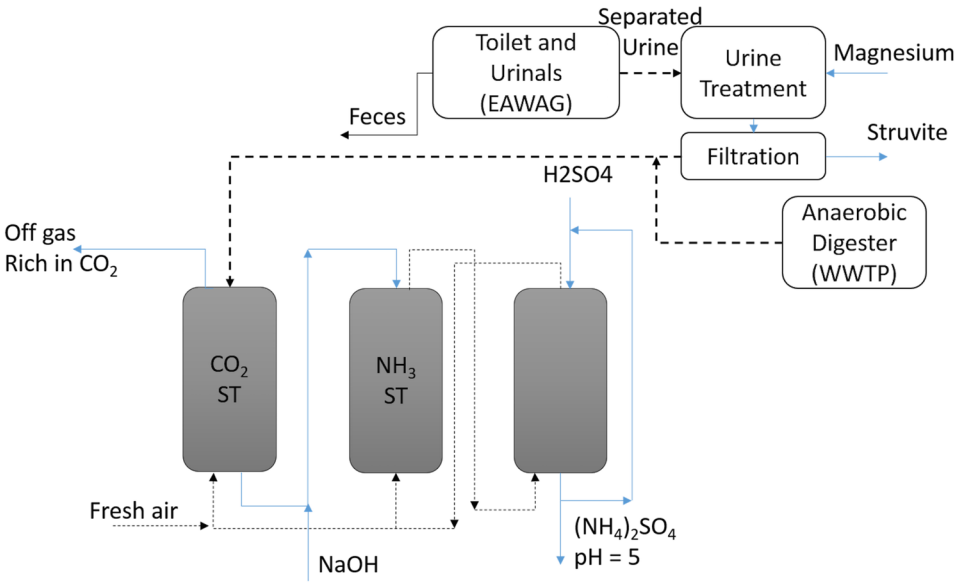
Figure 14. Flow-chart of the co-treatment of sludge liquid and treated urine
(Adapted from: Morales, Boehler, Buettner, Liebi, & Siegrist, 2013)
Source: Adapted from Morales et al., 2013



To avoid a CO_2 accumulation in the column the CO_2 rich gas was discharged after this unit, and fresh air was provided. The pH of the liquid in the ammonia stripper was increased using sodium hydroxide up to a fixed value to favor the equilibrium displacement towards the NH_3, as showed in Equation (16):

$$NH_4^+ + OH^- \leftrightarrow NH_{3(aq)} + H_2O \quad (16)$$

This liquid was fed by the top of the stripper reactor, where the ammonia solved in the liquid phase is stripped to the gas phase. The flow rate of the urine maintained up to around 5.1 m^3/h, while the operation Q_{Air}/Q_{liq} ratio used in the air stripping unit was in the range of 700–750 Nm^3/m^3 at 60 °C, because higher air to liquid ratios resulted in higher electricity consumption (Böhler, Büttner, Morales, Liebi, Schachtler, & Siegrist, 2012b). Then, the ammonia rich gas was washed in the sorber unit using a sulfuric acid solution (H_2SO_4 at 32% solution, 1.16 kg/L, Thommen-Furler AG, Büren, Switzerland) and ammonia sulfate was recovered (Equation 15) obtaining a final density solution of 1.2 kg/L.

Acid cleaning of the stripping reactor is executed daily using hydrochloric acid at pH 0–2 (HCl at 35%, Thommen-Furler AG, Büren, Switzerland) with an automated pH control. Each kg of N removed need at least 3.5 kg of H_2SO_4 and will produce 4.7 kg of $(NH_4)_2SO_4$. In a cost study for a full-scale stripping plant with a CO_2 pre-stripper, the estimated costs for treatment were around 3–4.5 €/kg N recovered (Zuleeg et al., 2012).

Cold Stripping and Water Recovery from Liquid Manure in Remedello (Brescia, Italy)

The N-Free® plants is a patented process installed in the North of Italy, which is considered a Nitrate Vulnerable Zone by the Nitrate Directive (91/676/EEC).

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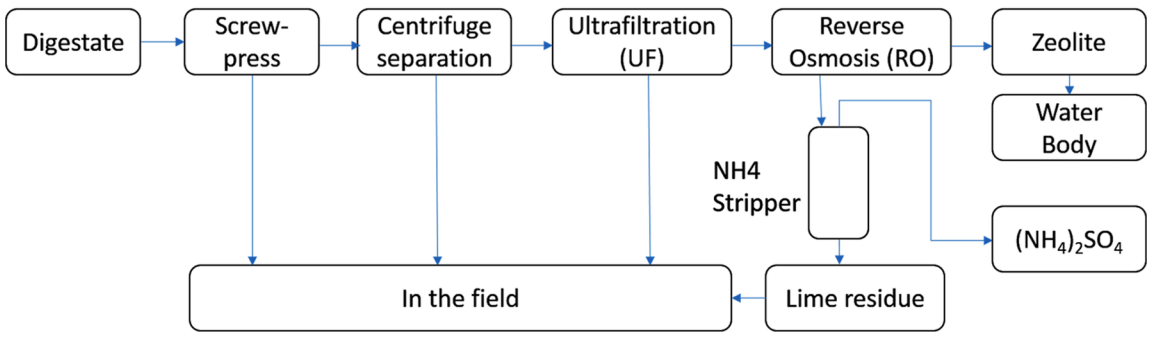
The N-Free® process (Fiolini e Savani s.r.l., Brescia, Italy) is characterized by a series of physical/chemical treatments which allow separation and concentration of the liquid fraction of the digestate and a final stripping for the production of ammonium sulfate (Figure 15). The N-Free® unit operated in batch mode and treated up to 100 m^3/day of raw anaerobic digestate (about 14 m^3 each batch cycle). The overall process scheme is composed by the following steps:

1. Rough solid/liquid separation achieved by a screw press (SC) separator (Doda, Mantova-Italy).
2. Conditioning (with polyamide flocculant) of the liquid fraction from the screw press and effective solid/liquid separation by decanter centrifuge (DC) (MAMMOTH 570/3, Pieralisi, Jesi-Italy).
3. Ultrafiltration (UF) of the liquid effluent from the decatenter by a 40 kDa grafted polyacrylonitrile membranes (PAN) (Orelis, France), operating at 3.5 to 4.5 bar of exercise pressure.
4. Treating of the UF permeate in a two-stage reverse osmosis unit (Dow, USA).
5. Refining in zeolites bed of the final reverse osmosis permeate before the final discharge in the water body.
6. Cold stripping of the reverse osmosis (RO) concentrate by air blowing recirculation and through addition of 15-18 kg/m^3 sludge of lime which allows pH raising up to 12-12.5. At these conditions, the equilibrium NH_4/NH_3 is completely shifted to NH_3 which is easily stripped as gaseous ammonia by the controlled air flow. Air plus ammonia is then scrubbed with sulfuric acid producing liquid ammonium sulfate (8% on a wet weight basis as N).

Finally, the cold stripping resulted in RO ammonia reduction of 78% from the anaerobic digestate, a significant reduction of the exportable volumes, leading a more sustainable livestock farming.

Electrical consumptions and use of reagents during the operation led to a total cost of 2 €/m^3 of digestate, while up to 4.2 €/m^3 considering personnel cost for assistant and depreciation charge. However, the income could be related to the savings regarding less transportation volume required (about 1 €/m^3 of digestate) and incomes related with ammonium sulfate trade (about 0.5 €m^3 of ammonia sulfate at 6-8% as N).

Figure 15. Simplified scheme of N-Free® plant; (1) Screw press separation, (2) Centrifuge separation, (3) Ultrafiltration-UF, (4) Reverse Osmosis – RO, (5) Zeolites refining, (6) Cold ammonia stripping
(Adapted from: Ledda, Schievano, Salati, & Adani, 2013)
Source: Adapted from Ledda et al., 2013



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Chemical Phosphorus Precipitation from Industry

The DHV Crystalactor© was developed by DHV Consulting Engineers (The Netherlands) to remove calcium from drinking water. Later, this technology was used to remove other compounds, such as phosphate, from wastewater streams. This technology utilizes a cylindrical fluidized bed reactor to recover phosphorus by phosphate precipitation in which sand is used as seed material. Phosphorus can be recovered either by calcium phosphate precipitation or by struvite crystallization, which takes place over these sand grains (Giesen, 1999; Eggers, Dirkzwager, & Van der Honing, 1991). For calcium phosphates precipitation, $Ca(OH)_2$ solution is added to the precipitation system and the dosage is controlled by the measurement of operational pH. Efficient calcium phosphate crystallization requires an operational pH around 9. Most of phosphate recovery technologies are based on the same crystallization chemistry of the DHV Crystalactor© technology, but with some variation (e.g. in seeding materials).

Struvite Recovery from Industry

The full-scale facilities of struvite crystallization have the potential to produce a commercial product, which could be used in combination with fertilizers from mined phosphate. Struvite can be produced using different crystallization technologies. The technology chosen will likely be a determining factor in the quality of the produced struvite. The particle size of struvite may vary with the operating conditions and reactor configuration used. According to particle size, struvite can be divided into two categories: fine crystals and pellets. In order to obtain a product suitable for application to agricultural lands, struvite pellets must be produced. Struvite pellets are much easier to handle and to transport than fine crystals. Thus, the quality product determines the user-friendliness of struvite, and consequently it can influence the cost-effectiveness of struvite crystallization process. Up to date, the main technologies to recover phosphate by struvite crystallization at full-scale are DHV Crystalactor©, Unitika Phosnix© process, Ostara PEARL© process, Phospaq™ process, NuReSys© process and Multiform Harvest™ (Table 5). Currently, several full-scale facilities based on the aforementioned technologies have been developed in Europe. These facilities tend to be concentrated in certain countries: Belgium, The Netherlands, Germany and United Kingdom, and the struvite crystallization technologies implemented in these countries are: Ostara PEARL©, NuReSys© and Phospaq™.

The first applications of struvite crystallization at full-scale were implemented in Japan. The Unitika Phosnix© process is based on the struvite crystallization in a fluidized bed reactor (FBR), in which the crystallization of struvite is promoted by adding sodium hydroxide and magnesium hydroxide as alkali and magnesium sources, respectively. Additionally, struvite seed crystals are added to facilitate the phosphorus recovery by struvite crystallization (Ueno & Fuji, 2001). Another technology developed is the Ostara PEARL© process, which is based on the phosphorus crystallization using a two-phase fluidized bed reactor. This system is composed by a column comprising some sections. The diameter of the column increases stepwise between the sections. This technology uses magnesium chloride when required, and sodium hydroxide as magnesium and alkali sources to facilitate the struvite crystallization (Koch, Mavinic, Yonemitsu, & Britton, 2009). Like in the Unitika Phosnix© process, Ostara PEARL© process uses recycled struvite as seed material. The Phospaq™ process recovers phosphorus by struvite crystallization in a continuous stirred tank reactor (CSTR) aerated. In this technology struvite crystallization is facilitated by the increase of pH via stripping of carbon dioxide (CO_2) and the addition of magnesium oxide as magnesium source (Abma, Driessen, Haarhuis, & van Loosdrecht, 2010). This

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Table 5. Phosphorus recovery technologies at full-scale (in operation)

Technology Name	Crystalactor©	Ostara Pearl®	Multiform Harvest™	NuReSys©	Phosphaq™
Type of reactor	FBR	FBR	FBR	CSTR	CSTR with diffused air
Name of product recovered	Struvite, CaP, MgP	Crystal Green®	Struvite	BioStru®	Struvite
Efficiency of recovery (%)	10-40% NH_3-N 85-95% P (struvite) >90% P (CaP)	10-40% NH_3-N 80-90% P	10-40% NH_3-N 80-90% P	5-20% N >85% P	10-40% NH_3-N 80% P
Nº of full scale installations	4	8	2	7	3

technology removes biological degradable chemical oxygen demand (COD), phosphate and ammonium in the same reactor. Aeration provides optimal conditions for struvite crystallization and the oxygen for the biological conversion of COD. The NuReSys© process is based on two CSTRs: a stripping reactor and a stirred crystallization reactor, in which magnesium chloride and sodium hydroxide are added to promote struvite crystallization (Moerman, Carballa, Vandekerckhove, Derycked, & Verstraete, 2009). Finally, Multiform Harvest™ uses a cone-shaped fluidize-bed crystallizer for struvite crystallization. Sodium hydroxide and magnesium chloride are added to produce struvite crystals from a stream with high concentrations of nitrogen and phosphorous (Bowers & Westerman, 2005).

CONCLUSION

This chapter presents and discusses the main options for nutrient management in industrial wastewater treatment, including the parameters to optimize the processes and the different technology readiness levels. Phosphorus recovery should always be pursued in order to recycle a critical raw material. Struvite recovery is a robust technology which optimization is mainly related to the reactor configuration and magnesium source. However, other possible technologies for P recovery, including enhanced biological P removal or novel ion exchange resins should be promoted especially for low concentrated streams. On the other hand, nitrogen recovery should be evaluated case by case on the basis of its economic and environmental sustainability. Ammonia stripping and recovery as ammonium sulfate is the most traditional and reliable system, but it could be limited by the legislation restriction. If the biological process can be applied, nitrogen deammonification and its recovery via Haber-Bosh process are energetically favorable. In the case of biological processes, the via-nitrite pathway represents an advance over conventional activated sludge systems, and the best carbon source may enable the optimization of denitritation with the concurrent anoxic phosphorus uptake.

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KEY TERMS AND DEFINITIONS

Aerobic Process: Biological process in which, microorganisms depend on oxygen for their metabolic activities.

Anaerobic Process: Biological process that occur in the absence of any form of oxygen available for metabolic activities of microorganisms.

Anoxic Process: Biological process, that occur in the absence of molecular gaseous oxygen, but other forms of oxygen can be present and they are used for metabolic activities of microorganisms.

Biodegradable: A substance that can be broken down by biological processes (e.g. by bacteria, fungi, and other microorganisms) under aerobic, anoxic and/or anaerobic conditions.

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Biological Nutrient Removal (BNR) Processes: An adapted process of the conventional activated sludge process where anaerobic and anoxic zones are included to biological reactor to create the conditions in which microorganisms are able to remove carbon, nitrogen and phosphorus.

Chemical Precipitation: A chemical reaction, in which two or more compounds react to form a precipitate, resulting in the formation of a separable solid substance from a solution.

Nutrient: Any element that is essential for the growth of animals, plants and humans. Usually nitrogen and phosphorus in wastewater streams.

Nutrient Recovery: Recovery of nutrients from wastewater streams through physico-chemical processes (e.g. precipitation) or other biological technologies.

Struvite: A magnesium ammonium phosphate salt ($MgNH_4PO_4 \bullet 6H_2O$) that usually precipitates from wastewater with high concentrations of phosphorus. This precipitate is a crystalline substance that may be used in agriculture as slow release fertilizer.

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Chapter 6
Introduction of Environmental Materials

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ABSTRACT

Advances in environmental materials are described especially concerning about utilization of natural source and their waste, for example biomass and their re-uses. They strongly support development to sustainable society. So, these classify and demonstrate environmental technologies, which strongly contribute to overcome pollution environment for the purpose of sustainable society. In view point of green chemistry and the related technologies to representative biomasses and inorganic wastes are applying for advanced functional materials. Since biomass and inorganic wastes are very interesting candidates for regenerated materials, it is very meaningful to understand and attention to environmentally and friendly materials and technologies. This is because that an increasing environmental concerns to sustainability.

INTRODUCTION

Chemistry brings comfort in modern life. For example, clothing is made with a synthetic fiber, and dye of various clothing is a product of the chemical industry. Computers have each outside of home electric appliances made with plastic and metal. These are mostly made from oil and a mineral through many chemical steps. So, chemistry greatly contributes to securing of richness of the human and supports to construct the high civilization. On the other hand, pollution of air, water and soil increases as industry becomes active. The pollution has influenced human health and been injured. However, many developed countries including Japan have overcome the pollution now, and the global environment has been improved by green technologies. However, the problem of the global environment was gradually actualized. Resources and the acceleration of the energy consumption lead to anxiety of earth resources. Furthermore, the consumption of a large quantity of fossil fuel causes the sharp increases of carbon dioxide and soot particles such as particle pollution (PM2.5) in atmosphere (Liu, Hsu, Lee, Ye, Zheng, Liu, Li, & Cui, 2015). When the growth of the human reaches the limit by the resources drying up and environmental aggravation, the report “The limit grow” of 1972, in particular, Club of Rome, sounds an alarm bell

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(Meadows, Meadows, Randers, & Behrens,1972). Therefore, this has reviewed the development of the economy that the earth is infinite. This also comments that to keep world balance is important. In addition, the toxic substance has an influence on the people and gives uneasiness in the society. For sustainable development, the planethood has various actions and global environment improvement has been directed to deeply consider it, for example, by United Nations Environment Programme (UNEP) (UNEP, 2014) In late 2014 world climate change was already affecting many contents in global warming. This gives strong impact to food security and therefore, emphasizes the chemistry and the related technology with the global community. It is desirable to develop the consideration for environment conservation, since green chemistry can solve problems in energy, a material, an environmental pollution to pull sustained society. In other words, because the green chemistry strongly relates to eco-friendly manufacturing, the harmony with environment and the process adapted to technical development leads to development of clean technology (Williams, 2001; Andrews, Brecombe, Jikel, & Brianreid, 2004). Recently, therefore, attention has been increasingly devoted to bio-based environmentally and friendly materials because of increasing environmental concerns related to sustainability.

BACKGROUND

As already mentioned, people should recognize a limit of the growth of the global environment. The coexistence of global environmental conservation and the industrial activation becomes extremely important. This is because that, as one of example, the danger signals such as the frequent abnormal weather strongly suggest an importance in sustainable society. From such a background, the practice of the concept called “green” becomes required in a chemical technique and materials development for the sustainable society. In the minimum waste and the recycling, people should bring highly efficient environmental symbiosis in energy technology, reuse of the biomass waste and the switch to a re-used material and to the remediation technology, which is applied to the earth pollution for the conservation of our environment. Therefore, the substantial use is urgent in this century. In this chapter, an action to the sustainable society and green chemistry is introduced in the points of view of the green technology using about biomass and waste re-utilization for environment materials.

Green Chemistry for Sustainably Renewable Sources

Sustainable means operating with a long-term mindset that includes responsibly maximizing our use of renewable resources. So one of the goal of sustainability is for renewable resource management (Rosenberg, Fogarty, Sissenwine, Beddington, & Shepherd, 1993). To provide both positive examples of sustainable resource use and lessons for future improvements in materials, a renewable resource is mainly an organic natural resource and can replenish to overcome usage and consumption. In such a background, United States Environmental Protection Agency (EPA) proposed green chemistry in 1994. In green chemistry, people design chemical products and processes for reduction or elimination of the use or generation of hazardous substances. Now, green chemistry strongly relates with the product life cycle by approaching its design, manufacture, use, and ultimate disposal. So it is also known as sustainable chemistry. The rapid development of new chemical technologies and the vast number of new chemical products in the last decades turned the attention of environmentalists to remedial actions for the negative impacts. Two decades after the implementation of EPA, the Pollution Prevention Act (1990) was created

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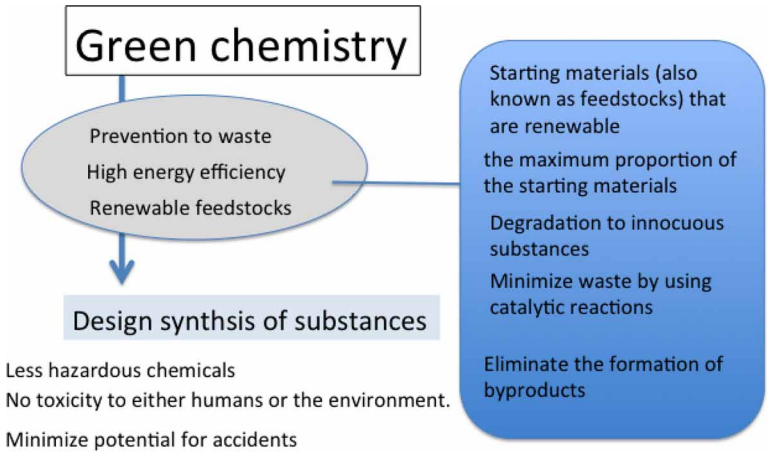
Figure 1. Green chemistry



to enforce eco-friendly strategies. The EPA defines green chemistry as following principles (Figure 1) (EPA,1990); Prevention of pollution at the molecular level, application to all areas of chemistry, not a single discipline of chemistry, innovation of scientific solutions to real-world environmental problems, results in source reduction because it prevents the generation of pollution, reduction of the negative impacts of chemical products for better reflection on human health and the environment, sometimes elimination of hazard from existing products and processes, designs of chemical products and processes to reduce their intrinsic hazards.

What is different point in green chemistry and general remediation process unlike cleaning up pollution? The remediation processes involve treating waste streams or cleanup of environmental spills and other releases. So remediation mainly relates to removal process for hazardous materials from the environment. Green chemistry, on the other hand, keeps the hazardous materials out of the environment for purpose of clean up environmental contaminants. Here, this needs technology to remove pollutant. The green chemistry technology also includes remediation technology, but also relates to non-disposable technology. This contains that processes prevent waste, high energy efficiency and effective uses of renewable feedstocks and then can produce less hazardous chemicals with no toxicity to either humans or the environment. Also this minimizes potential for accidents with explosions, fires, and releases chemicals to the environment or less byproducts in the reaction. In addition these processes should have that the final product contains the maximum proportion of the renewable starting materials. To degrade after use to innocuous substances and to minimize waste in reaction, catalytic reactions without stoichiometric reagents are preferred for the prevention of chemical accumulation in the environment. Green chemistry may change all these negative impacts and through design, innovation and green processes to restore the planet's sustainable development.

To implement sustainable practices, green chemistry technologies can modify their practices in ways that provide better and cleaner tomorrow. The technology aims to be innovative to restore, protect and ensure the sustainability of water resources and also identifies the renewable energy potential of current and formerly contaminated lands. The next bre1akout to a solution of environmental problems is beneficial to improve environmental protection and human health.

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ENVIRONMENTAL MATERIALS IN SUSTAINABILITY

In such situation, now, materials science and technology intersects with the fields of environmental science and sustainability in green chemistry ways. Environmental materials are related with challenging a serious environmental problem such as an energy problem and the water pollution in a various materials technology. Both developing new materials and conducting basic science research to pollution and hazardous chemicals are included as environmental prevention technologies (Table 1). To date, most sustainability or green technologies have attempted to quantify sustainable materials and focused primarily on energy, material, and water conservation. The sustainable materials also cover lower regeneration cost and energy and long term uses for environmentally friendly materials.

Table 1. Prevention technologies for earth environment

Classification	Development Theme	Specific Examples	Materials & Technologies
Energy	Liquid fuel	Biofuel Biodiesel	Alcohol fermentation Vegetable oil Fats Peterorium
		Bioalchol	Methanol Ethanol Buthanol
	Gaseous fuel	Hydrogen	Photocatalysis Electro-decomposition of water
		Methane	Fermentation
	Solid fuel	Biomass	Tree Bagasse Coal
		Batteries Fuel cell	Electricity Hydrogen Methane Alchole
Regeneration of biomass and mine resources	Biomass	Biopolymer	Polysaccharide Protein Nucleic acid Natural rubber
		Bioplastics	Polyglycolic acid Polylactic acid
	Mine	Heavy metals	Cadmium Lead, Zinc
		Ash	Geopolymer
Environmental remediation technology	Air	Filter Adsorbents	Gas adsorbents
	Water	Chemical precipitation,	Precipitation induced by the addition of an alkali, sulfide, coagulant, or other reagent.
		Chemical stabilization	Using phosphate for treatment of solid mining wastes and reducing divalent heavy metals.
		Electrocoagulation	Technologies using an electrical current that coagulates organic constituents and suspended solids in water.
		Biochemical reactors	Microorganisms to transform contaminants in the treated water to another chemical and to increase pH; Sulfate reduction to sulfide and bicarbonate and heavy metal precipitation in high pH.
		Pressure-driven membrane separation	Thin barrier that permits selective mass transport of solutes and solvents across the barrier; Reverse osmosis, ultrafiltration and microfiltration.
		Ion exchange	Interchange or exchange of ions between a solid media and water containing ion; Various resins and peat or zeolites.
	Soil	Biosolids	Using organic phosphate to eliminate heavy metals
		Bioremediation	Controlling biological processes to reduce the contaminants of concern to target levels of heavy metals or fuel oils.
		Soil chemical oxidation	Treatment of chemical oxidation to reduction of contaminants.
		Thermal desorption	Heating certain contaminants to reduce their concentrations

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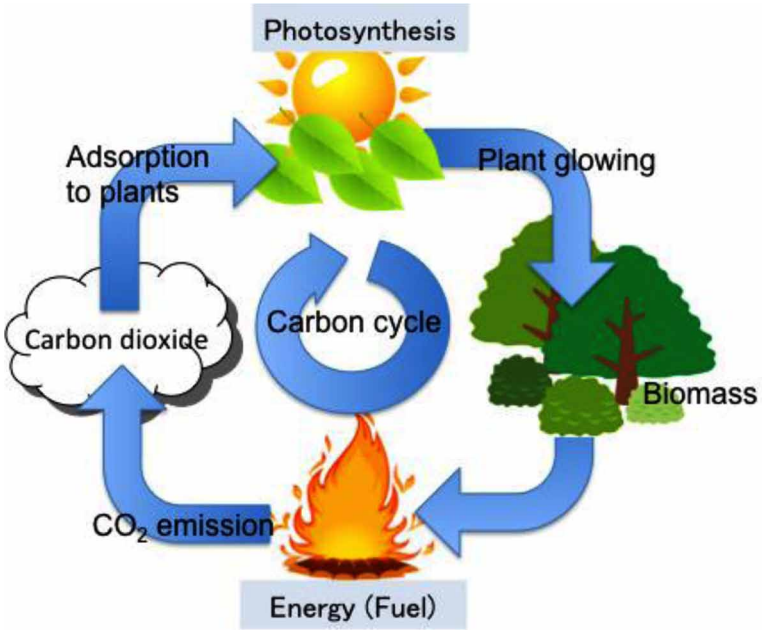
There is a way of thinking called the carbon neutral. This is based on the biomass being generated by photosynthesis with CO_2 as raw materials. So, there is an idea that the atmospheric CO_2 is not to increase even if biomass is used to burn fuel derived from biomass. This is expressed for the Carbon neutral; the CO_2 income = the expenditure zero in the atmosphere, as seen in Figure 2 for carbon cycle of biomass. However, the problem is not easy. The biomass fuel uses fossil fuel from seeding into crops cultivation, crop work, fermentation, manufacturing process with the chemical processing. Therefore, when additional injection of fossil fuel is performed and then the amount of energy is more than that of the last fuel, the process cannot be said as carbon neutral. However, although the burned carbon is returned to the atmosphere as CO_2, these processes have happened for plants on earth as the carbon cycle.

The representative trial is biofuel. The production of the biofuel is provided by converting biomass to fuel and the biofuel is available as a substitute of gasoline and the diesel. Generally, the bioethanol is made more by the fermentation of the saccharide (Bajiai, 2013; Goldemberg, 2007; Yaman, 2004; Chavez-Guerrero,& Hinojosa, 2010). The alcohol fermentation is processed, for example, by yeast to the sugarcane bagasse containing saccharide. Through this, mono-saccharides is able to be converted into ethanol and carbon dioxide; $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2$

On the other hand, oils and fats are the matters synthesized with the long chain fatty acid of 2-3 molecules to form ester combination of three values glycerin. The oils and fats are used generally by edible oil or butter. The oil and fat itself has high viscosity and is not suitable for an internal combustion engine, but, it becomes the fuel of the diesel engine with ester glyceride of mono-substitute of long chain molecules or the methanol ester. Therefore, the organic matter provided with exchange reaction of methanol with rapeseed oil or used edible oil is used for biodiesel fuel, which has low enough viscosity to allow proper atomization of the fuel. These biofuels have a characteristic not to include sulfur. However, the fossil fuel includes sulfur derived from creatures like an amino acid such as methionine and cysteine

Figure 2. Carbon cycle scheme of biomass



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constituting protein. When the fuel is burned, sulfur of the fuel becomes the sulphur dioxide, SO_2. The SO_2 released in the atmosphere finally becomes the sulfuric acid and causes acid rain in earth environment. Therefore, the biofuel without the problem attracted attention from the side of the environmental conservation. After oil crisis of the 1970s, Brazil was considered to have the world's first sustainable biofuels economy. As the biofuel industry leader, ethanol fuel program is based on the most efficient agricultural technology in this country (Hofsetz & Silva, 2012), especially for sugarcane cultivation. Its sugarcane ethanol is the most successful alternative fuel. Since 1976 the government made it mandatory to blend anhydrous ethanol with gasoline, fluctuating is between 10% to 22%. Also, alternative fuels are known to including biodiesel, bioalcohol (methanol, ethanol, and butanol), chemically stored electricity (batteries and fuel cells), hydrogen, non-fossil methane, non-fossil natural gas, vegetable oil, and other biomass sources.

In addition to the biofuel, another representative group is biopolymer and bio-plastic (Pilla, 2011). Actually, there are various kinds of nature macromolecules in the natural world. A representative macromolecule is polysaccharide, protein and nucleic acid (Kalia, 2011). For instance, glucose forms α-1,4 bond of the starch which is kind of polysaccharides. Starch is divided into amylose and amylopectin by the structure. These are soluble in warm water and are decomposed by an enzyme in the body. Also, glucose performs α-1,4 bond of cellulose and the chief ingredient constitutes the cell wall of the plant (Brett & Waldron,1990). The polymeric chains interact with hydrogen bond and form fibrous fibers. Cellulose is relatively rigid and insoluble in water. The human cannot digest cellulose due to the absence of hydrolysis enzyme in our body. Furthermore, natural rubber (NR) is the candidate in gum tree growing in the tropics and 1,4-isoprene, $CH_2=C(CH_3)CH=CH_2$, polymerizes, as NR hardens the sap of the tree. Latex is existed as water dispersed organic component in the sap. This is a material composed primarily of cis-polyisoprene $[(C_5H_8)n]$. After the latex is refined and dried, the aggregated product is NR which has elasticity property and has been used for a tire, elastic string and ball. Protein is polymer condensed between the carboxylic acid and amino groups in amino acid molecule. The amide linkage to form here is called peptide bond in particular and belongs to polypeptide;-C(=O)- N(H)-. The peptide structure of protein molecules forms hydrogen bonding in the same molecules nearby relatively peptide and takes spiral structure (α helix) (Figure 3). Also, hydrogen bonding between the molecules next to each other can take plane structure (β sheet). The former spiral structure body is fully elastic and the latter plane structure can give superior mechanical strength.

On the other hand, there is biomass plastic based on idea of the carbon neutral. The representative plastic is polyester-based material of polyglycolic acid or polylactic acid. These have already came to be industrialized and are plastics made from creature resources (biomass) made from corn or sugarcane with much content of starch and the sugar mainly. A definition of these materials is to include a polymer derived from the organic resources which can reproduce as raw material and provided by synthesizing it chemically or biologically. In other words, the renewable resources of corn and sugarcane are used for raw materials of the plastic. Therefore, there is not influence for a rise in density of the atmospheric greenhouse gas and is less cause of the global warming, even if it returns to carbon dioxide by combustion after use. For these carbon neutral materials, following future is found; Even if burn and discard it, the income and expenditure of carbon dioxide is zero, When it burns up, heat of combustion is low, but no dioxin occurs. As seen in Figure 4, polylactic acid shows hydrolysis to lactic acid and then biodegradates to H_2O and CO_2 (Steavens, 2002; Ebnesajjsd, 2013). Litter is a problem with a very negative social and environmental impact. As an environmentally-friendly solution, one way to tackle this problem is to use biodegradable plastics.

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Figure 3. Chemical structure of representative polysaccharides and biodegradable polymers

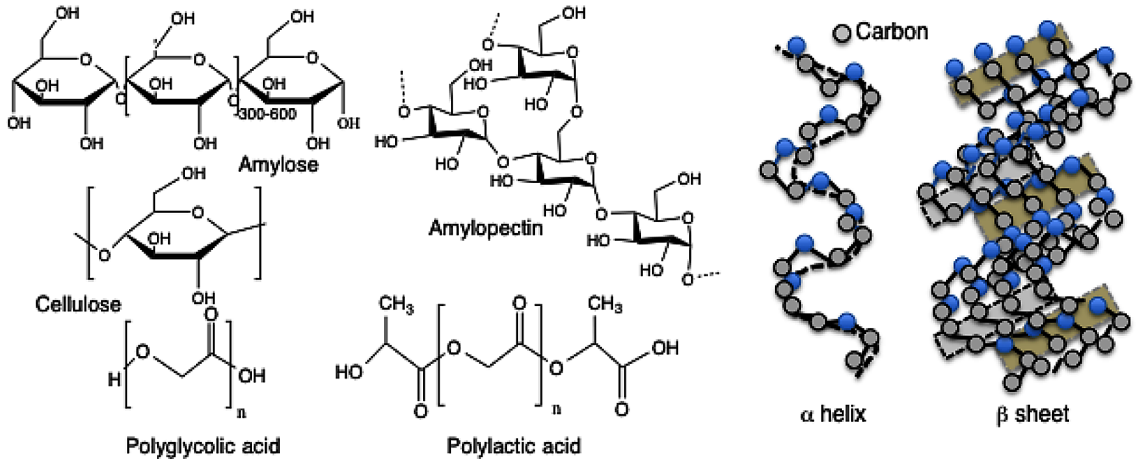
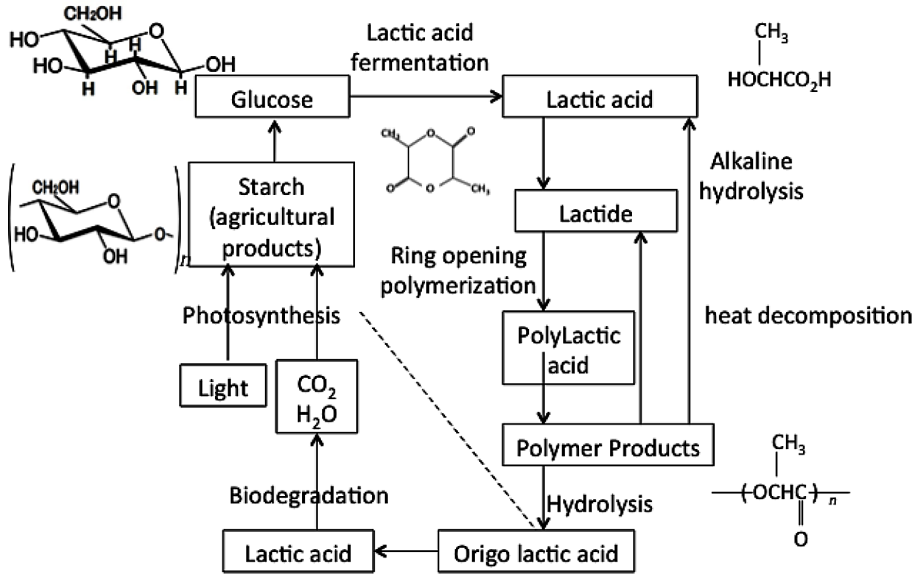


Figure 4. Polymerization and degradation scheme of polylactic acid



Environmental Green Technology

Environmental technologies, which have been developed in pollutant decontamination for the earth, incorporates environmental materials. The contribution of environmental materials to quality of the water purification and the detection of the pollutant is in particular large. The water is a resource circulating universally because of supporting our ecosystem. Therefore, it has deep relation to environment, industry and life. As shown in Figure 5, the water circulates in various forms through earth environment, as the evaporation, condensation, raining or snowing, running off, infiltration and flowing occur in the natural world. Chemicals (SO_x, NO_x, organic exhaust gas, heavy metal compound, and toxic organic compound) are carried through the medium of water and fixed to the soil and hydrosphere. In the water cycle, the

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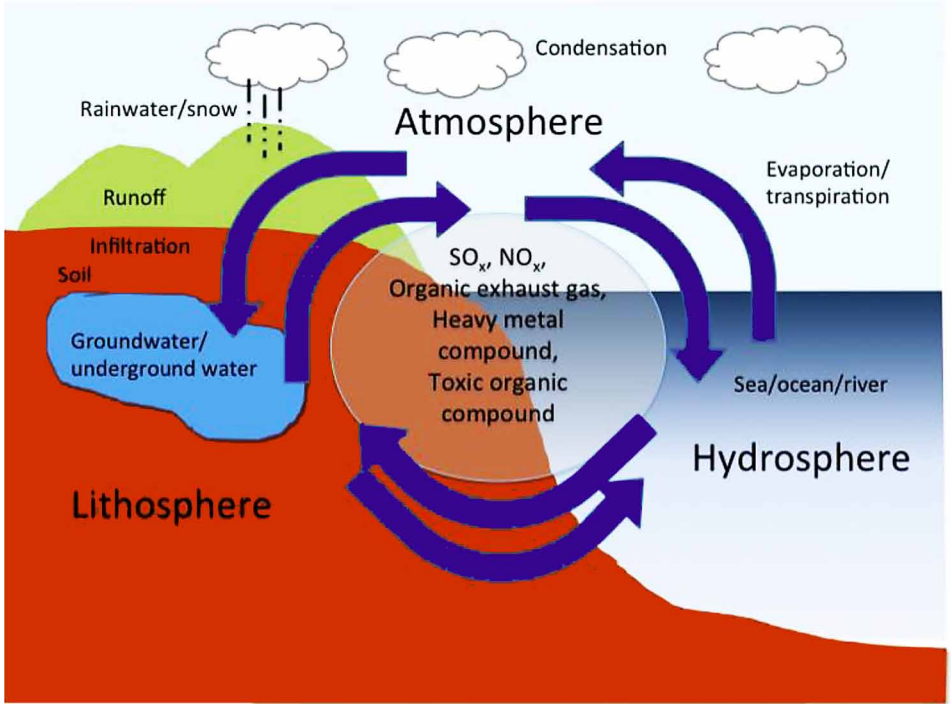
Figure 5. Water cycle with contaminants through hydrosphere-lithosphere-atmosphere



animals, fishes and plants adsorb and immobilize the chemicals in their body. Furthermore, heavy metal may dissolve by acid rain. In addition, the acid rain acidifies a river and wetlands, affects the habitation of the creature and causes deterioration of the cultural heritage. In the present when industry developed, it becomes the problem source of water pollution such as organic matter or the heavy metal.

Therefore, recovery process for decontamination to their pollutant is needed by introduction of functional adsorbents. For example, after the Great East Japan Earthquake and Tsunami damaged the Fukushima Daiichi Nuclear Power Plant during and after March 11, 2011, long-term radiation contamination ensued, presenting severe difficulties to human life and the local environment (Morino, Ohara, Watanabe, Hayashi, & Nishizawa, 2013). The neighboring inhabitants within a radius of 30km are evacuated forcibly in now when 5 years pass for the accident. It is felt uneasy about that diffusion of the radiocesium through the medium of the water from the soil and the forest polluted by emission. Figure 6 shows adsorption materials that adsorb radiocesium efficiently are developed to prevent this in Tomioka town between 2013 and 2014 (Kobayashi, Ohshiro, Nakamoto & Uchida, 2016). The porous composite fibers showed decontamination to low-level Cs in the flowing river, preventing its flow further downstream by the diffusion of radioactive Cs through water contaminant in natural environments.

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Figure 6. Pictures of zeolite composite fibers for decontamination of radioactive cesium in Tomioka town, Fukushima, Japan
Source: Kobayashi, Ohshiro, & Uchida, 2014

ENVIRONMENTAL MATERIALS IN SUSTAINABILITY

Agro-Industrial Biomass Wastes and Biopolymers

As many global issues start to influent our daily life, people begin to focus attention to renewable resources mainly included in agricultural production. In recent years, there have been many studies on the effective utilization of agro-industrial residues including sugarcane bagasse, cassava bagasse, rice husk, wheat straw and coconut fiber, etc (Pandey, Soccol, Nigam, & Soccol, 2000; Ashori & Nourbakhsh, 2010). It is currently used mainly as an biofuel for power and heat generation (Goldemberg, 2007;Yaman, 2004; Jorapur, & Rajvanshi, 1997) and in the manufacture of pulp for paper. However, eco-profile studies measure the re-generation of the waste bagasse and other inputs require to make a product obtained from the extraction process or harvesting of raw plant materials for eco-friendly, recyclable, advanced materials, especially for cellulose. The natural plant polymer, cellulose, originated from bagasse wastes is utilized for the regeneration process to cellulose (Kobayashi, 2015; Tovar-Carrillo, Tagaya, & Kobayashi, 2013). The cellulose fibrous fibers are sustainable materials in plants and have numerous functional possibilities, as expected to be developed into a broad range of applications, especially with the demand for environmentally friendly and biocompatible products.

Among them, sugarcane bagasse is generated as a biomass fibrous residue in extraction process of sugar juice from the sugarcane (Chandel, daSilva, Carvalho, & Singh, 2012). The sugarcane was produced about 1.69×10^3 million tons in the world in 2010 and generally 280 kg of humid bagasse is generated from 1 ton of sugarcane. Therefore, this is one of the largest cellulosic agro-industrial by-products. At the present time, the most of sugarcane bagasse is used as manure, feedstock and fuel of the boiler in the sugar industry (Hofsetz, & Silva, 2012). Several attempts for potentially renewable and sustainable have been made to utilize sugarcane bagasse as a low material. These contain ethanol production by hydrolysis and fermentation, synthesis of cellulose derivatives (Jorapur, & Rajvanshi, 1997) and also are converted to functional materials (Nakasone, & Kobayashi, 2016; Saucedo-luna, Castro-Montoya, Campos-Garcia, & Rico, 2010; Nakasone, Ikematsu, & Kobayashi, 2016). Also, agave tequilana weber azul, which is an economically important plant cultivated in central Mexico for the production of tequila (Goldemberg, 2007;Yaman 2004) and the bagasse is a byproduct material consisting of the cellulose tissue of the blue agave after extraction of the sap. More than 800,000 tons of agave bagasse has been

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Figure 7. Pictures in Mexico, Guanajuato, for the production of tequila and agave bagasse. The agave pinier (left)is steamed (middle) and bagasse (right) is obtained after extraction process of sugar juice

disposed as a waste product per year (Figure 7). The disposal becomes similar problem and gives attention with regard to its regeneration. It is well known that cellulose is the most abundant natural polymer consisting of β-glucose in the nature and forms about half to one-third of plant tissues (Reid,1997). The cellulose and its derivatives have attracted many researchers due to their unique properties such as low toxicity, biocompatibility and biodegradability (Kobayashi, 2015; Kobayashi, Tovar-Carrillo & Tagaya, 2015). Several research studies have been performed to offer an alternative use for their bagasse waste, but, until now, none has offered us a final solution, due to the necessity for development of new technologies to solve this problem.

Mine Wastes for Environmental Materials

Mine reuse often brings economic, environmental, and social benefits to our communities. It also may serve as a catalyst for expediting environmental risk reduction, as EPA recognizes (EPA,1990). The economical matter strongly relates with industry and the environmental one with pollution decontaminant. For example, Interstate technology & regulatory council in USA repots that heavy metal impacts in the world, primary including cadmium, lead, and zinc (ITRC, 2010; Broadbent, 1998). The specific criteria for the reuse are for lead (15 μg/L) and cadmium (5 μg/L) in potential drinking water sources by the National Primary Drinking water standards and freshwater chronic National Recommended Water Quality Criterion for zinc of 120 μg/L. The re-uses and reprocessing technologies are effective for remediation of solid mining wastes. Also, there is attractive technology to turning mining waste into beneficial products. This can decrease human and ecological exposure to contaminated materials. The toxic heavy metal contamination, for example, can be remediated by one or more of the technologies. Their remediation technologies generally refer to chemical precipitation, chemical stabilization, electrocoagulation, biochemical reactors, pressure-driven membrane separation, permeable reactive barrier. Among them, efficient removal and recovery of toxic heavy metals from industrial wastewater is a major challenge (Gaballah & Kilbertus,1998; Saeed, Akhter, & Iqbal, 2005). Furthermore, reutilization of solid wastes of coal combustion ashes is reported (White & Stegemann, 2001; Chindaprasirt, 2009) and reused to adsorbents of gaseous waste (Suchiai, Shizaka, Nakamura, Ueno, & Hattori,1996) and heavy metals (Sekhar & Chakravarthy, 2001) and also to glass ceramic (Strad, 1986) and concreat materials (Onutai, Sirithan, Thavorniti, & Kobayashi, 2015). Geopolymers are also sustainable materials, which can be prepared from mine and ash (Davidovits, 2011), as mentioned below.

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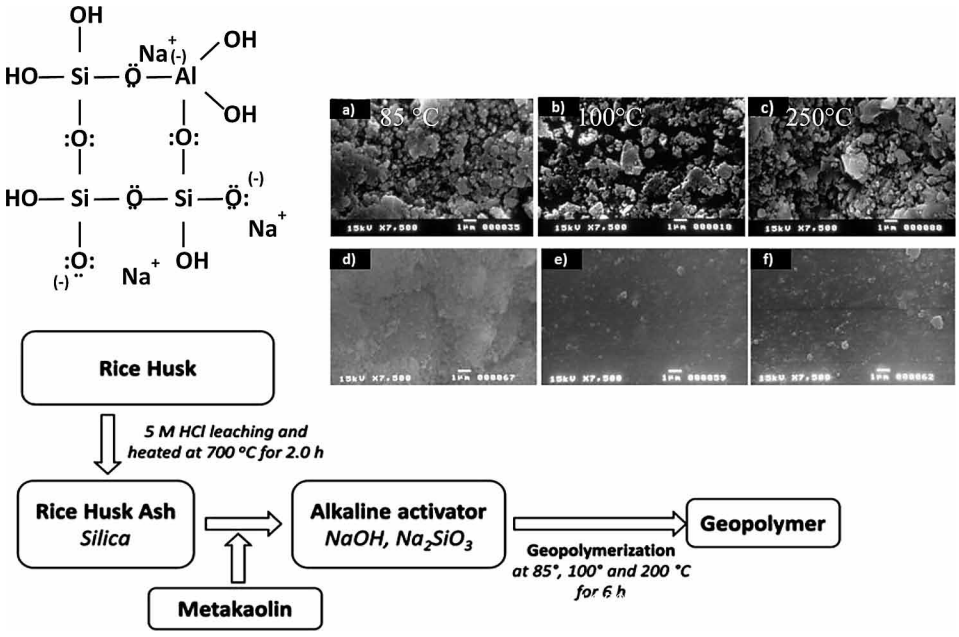
For example, the presence of the toxic metals generated by mineral processing in industries causes a major hazard to the water environment (Matis, Zouboulis, & Lazaridis,1998). Thus, serious regulations are required to establish in many countries to remove effectively the toxic metal ions from the waste waters prior to discharge into natural environment. So, the adsorption techniques present excellent qualities for treating industrial waste waters containing metal ions, when solid adsorbents are employed for recovery of metal ions as lead, copper, cadmium, nickel and zinc (Brauckmann, 1990: Cheng, Lee, Ko, Ueng, & Yang, 2012: Lopez, Sugita, & Kobayashi, 2014). Geopolymers are alkali activated aluminosilicates, consisting of a solid reactive component that contains SiO_2 and Al_2O_3 (Komnitsas & Zaharaki, 2007; Ahmaruzzaman, 2010). By using rice husk, fly ashes, active clays, pozzolanas and slags, decontamination of heavy metal ions were reported as geopolymer adsorbents (Li, Wang, & Zhu, 2006).

GREEN TECHNOLOGIES LEADING FOR SUSTAINABLE SOCIETY

Scientific and technological change brought the human a great benefit until now. By various kinds of harmful chemical substances released abundantly to environment, the various issue of environmental pollution is taking place. To raise the possibility that humanity can continue soundly and to succeed a global environment in a future generation, conservation technologies are necessary. It is essential to purify and have maintenance of environments of air, water and soil. To this end, green technology can prevent the diffusion circulation of the pollutant, causing the environmental damage. The goal is the global environment construction, where people can live under sustainable energy society. Also, the cyclically used technology conserves resources of the earth. The green technique can prevent the cycle.

Figure 8. Protocol of geopolymerization synthesis with rice husk and metakaolin
Source: Lopez, Sugita, Tagaya, & Kobayashi, 2014



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As seen in Figure 5 diffusion circulation of the pollutants, SOx, NOx, hazardous organic chemicals and heavy metal ion takes part in the environmental purification especially in the developed country. The green technology has the following evaluation guidelines:

1. Technology to reduce consumption resources and energy,
2. To produce energy,
3. To make use of unused resources in,
4. To reduce environmental load,
5. To make quality of life and
6. To make economic competitiveness.

The critical technology of the materials enables energy saving. New energy, resource saving recycling, and living environment risk reduction is summarized in Table 2. These technical examples are followed; biodegradable polymers as an environmental ecad chemistry product, a compact detergent as a life-related article, a energy saving chemical products, a quickness diagnosis technology with a small size sensor, the high-performance material in eco-tire, health and medical care with the field of diagnosis. Among others, carbon fibers made of polyacrylonitrile is mainstream and are light weight and high strength in the rainforced materials. These are used for a aeroplane, a car, a golf club, engineering works, construction materials or an inquiry material widely.

Table 2. Lists of critical technologies of the field of materials

Classification	Development Theme	Specific Examples
Energy saving	High strength, lightweight resin composite materials	CFRP, carbon / cellulose nano fiber
	Polyolefin having super heat-resistant, and high strength	Post-metallocene catalysts
	Metal substitute super lightweight materials by the organic inorganic hybrid material	Metal-replaced boad
	Materials having a low friction surface and lubrication	Carbon materials, surface coating, nanolubrication materials
	semiconductor for light source materials	Next-generation LED, organic electroluminescence, inorganic EL
	Heat train conversion materials for the low temperature waste	Peltier element, polymer materials, organic no plane based materials
	high-performance decicant air conditioning by high temperature adsorbent materials	Energy saving de-humidification air conditioner

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Table 2. Continued

Classification	Development Theme	Specific Examples
New energy	Polymer actuator	Micromachine, sensor for the biomaterial
	Super high accumulation of electricity type rechargeable battery materials	Original cathode active substance, carbon electrode, electrolyte, separator (film)
	New battery materials including the lithium substitute	Lightweight small batteries
	Organic radical battery, redox polymer materials	Thin and light devices
	Electrolyte for the high accumulation of electricity	High performance ionic liquid
	High accumulation of electricity energy materials for the movement / fixation power supply	New solid electrolyte, electrolyte membrane, ionic liquid
	New materials for the fuel cell	Pt substitute electrode, fluorine substitute film, CO reduction catalyst, H_2 production device
	Dye sensitization type solar battery materials	Titania dye sensitization type, plastic board type
	Thin film silicon type solar battery materials	Amorphous; crystalline
	Organic semiconduction type solar battery materials	P-type semiconductor polymer, n type fullerene
	High performance organic semiconductor materials	Fullerene type new materials
Resource saving recycling	Substitute materials for the fluorine-based functional chemicals	Refrigerant, blowing agent, jet agent, insulating material, glass for the semiconductor / liquid crystal
	Substitute materials of the laminated film, easy recycling materials	Single-like layer film
	Easy recycling and decomposable adheisive, self-detachment material	Non-epoxy adheisives
	Rare metal, noble metal substitute materials	Ni,Co,Mo,W,Li,In, rare earth elements, Ta, platinum group, boron
	Non-organic solvent-based lithography and patterning technology	Liquid hardening resin nano imprint methods
Life environment risk reduction	Halogen, phosphorus free new incombustible materials	Nanoparticles composite, carbonization layer formation, high density filler composites
	Complete water-based paints	De-VOC (volatile organic compounds)
	Non-VOC component building materials for the residence environment	Material-related industry for building and the residence materials
	Non-VOC component adhesive, ink	Public welfare, assembling processing-related industry
	Safe insect killing, insect repellent, mold agent-proof, sanitization	Photocatalyst, nanocatalytic model antibiotics
	Security deodorization, deodorant materials	Nanocatalytic model deodorant, nanopore type deodorant
	Easy biodegradability surfactant	Natural sourced soap and detergent
	Future model cosmetics materials using a nanotechnique and an interface technique	Anti-aging function, safety
	High functional foods wrapping materials	Materials for detection of cold insulation, oxidization prevention, dehydration, humidity retention, shading and, abnormality
	Self-repairing materials	Organic-inorganic hybrid, plastic
	Insulation materials for sound, heat and electromagnetic wave	New glass, new building materials, insulation paint

Source: Ministry of Economy, Japan, 2010

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CONCLUSION

This chapter accounts environmental materials in the point of view of green chemistry and technology. Sustainability in eco-friendly materials and the related technologies for biomass resource is described especially for biomass fuel, biomass waste and inorganic waste. Also, trials of pollution problems in earth are reviewed in this chapter. As prevention techniques applied, it is described that green technology is suitable for the future sustainable society.

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KEY TERMS AND DEFINITIONS

Biomass: In general, this means plant as the source of supply of the alternative energy. In this chapter, supply to alternative energy and material source of plants.

Biofuel: Fuels derived from biomass; any matter derived from plants or animals.

Biopolymer: Polymers produced by living organisms.

Carbon Neutral: Achievement of a product, service or event being equal to zero, as net greenhouse gas emissions of an organization to earth.

Environmental Material: Materials applied to a serious environmental problem such as an energy problem and the water pollution in a various materials technology.

Geopolymer: Typically inorganic ceramic materials having non-crystalline amorphous networks of silico-oxide (-Si-O-Si-O-), silico-aluminate (-Si-O-Al-O-), ferro-silico-aluminate (-Fe-O-Si-O-Al-O-) and alumino-phosphate (-Al-O-P-O-) by geopolymerization.

Green Chemistry: Chemistry related science to solve problems in energy, a material, an environmental pollution and for development of sustained society.

Green Technology: Technology for clean and sustainable communities.

Remediation: The following technologies, isolation, immobilization, toxicity reduction, separation and extraction remediate contaminant level in soil, water and air.

Sustainable Society: Ensuring the health and vitality of human life and culture and of nature's capital, for present and future generations.

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Toxic Heavy Metal: Heavy metals, particularly cadmium, mercury, lead and arsenic has potential toxicity, especially in environmental contexts. Additionally, the major public concern of other examples includes manganese, chromium, cobalt, nickel, copper, zinc, selenium, silver, antimony and thallium.

Water Cycle: Hydrological cycle occurs continuously in the movement of water in earth through atmosphere, hydrosphere and lithosphere. When water moves, it goes through different phases of liquid, ice and vapor phases.

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Chapter 7
Introduction to Leachate Treatment

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ABSTRACT

Leachate is created while water penetrates through the waste in a landfill, carrying some forms of pollutants. The goal of this chapter is the introduction to leachate treatment. Biological, physical, and chemical treatments of leachate are the most common methods. The biological techniques in leachate treatment are studied. The physical-chemical ways for landfill leachate treatment like chemical precipitation, chemical oxidation, coagulation–flocculation, membrane filtration, ion exchange, adsorption and electrochemical treatment are studied. The landfill leachate properties, technical applicability and constraints, effluent discharge alternatives, cost-effectiveness, regulatory requirements and environmental impact are important factors for selection of the most suitable treatment technique for landfill leachate treatment.

INTRODUCTION

The rapid growth in volume and forms of solid and hazardous wastes as a result of continuous economic development, industrialization, and urbanization is an increasing problem faced by domestic and local governments in ensuring an efficient and sustainable waste management (Mojiri, 2014). Municipal Solid Waste (MSW) has continued to be a major problem in many nations of the world. MSW has gradually become a threat to the environment of developing countries as they progressively move towards industrialization. MSW has become one of the most serious environmental challenges facing many cities in the country (Oloruntade et al., 2013). MSW management is an important aspect of urban planning and development.

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In 2006, the estimated total volume of MSW generated internationally reached 2.02 billion tons, indicating a 7% annual rise since 2003. Between 2007 and 2011, the rise in universal generation of urban waste was estimated at 37.3%, equivalent to an increase of approximately 8% per year (UNEP, 2009).

In most countries, sanitary landfills are a common means of solid waste disposal. Although this method has numerous benefits, one of its drawbacks is leachate production, which must be managed properly. Without proper treatment, landfill leachate greatly increases water pollution as it can penetrate through soil and subsoil. Therefore, the levels of hazardous components in leachate should comply with discharge standards before releasing into landfills to avoid pollution of water sources and to prevent acute and chronic toxicity (Aziz et al., 2011sa). Leachate is created when water penetrates into landfill waste, carrying with it certain forms of pollutants, such as ammoniacal nitrogen (NH_3–N), chemical oxygen demand (COD), color, biological oxygen demand (BOD_5), suspended solids, and metals. Leachate composition depends on deposited waste, landfill age, site hydrology, landfill operation, and landfill type. High concentrations of suspended solids, BOD_5, COD, NH_3–N, and metals are usually present in leachate (Foul et al., 2009). Landfill leachate treatment methods depend on leachate composition, landfill age, and site hydrology, among other factors. The main applicable methods of landfill leachate treatment contain physical/chemical and biological treatment methods. Typically, combinations of physical, chemical, and biological techniques are applied for landfill leachate treatment because of the difficulty in obtaining satisfactory treatment efficiencies by a single method (Aziz, 2011).

BIOLOGICAL TREATMENT

Biological treatments include aerobic treatments, anaerobic treatments, and phytoremedation.

Aerobic Treatment

The word "aerobic" refers to the characteristic of being in the presence of air, which usually implies being in the presence of oxygen. Thus, aerobic treatment methods are performed in the presence of air and utilize microorganisms called "aerobes," which utilize molecular/free oxygen to assimilate organic impurities; that is, aerobes convert these impurities into carbon dioxide, water, and biomass (Mittal, 2011).

Membrane Bioreactor (MBR)

The MBR technique is the combination of activated sludge sewage treatment and microfiltration (MF) or ultrafiltration (UF) membranes, with pore sizes ranging typically from 10 nm to 0.5 μm. In a conventional activated sludge treatment plant, the membrane filtration process replaces the final clarifier step treatment achieved solely by gravity, whereas the activated sludge bioreactor is kept separated from the UF treatment. In addition, the membrane disinfects by eliminating bacteria and viruses as well as by producing high-quality, suspended solid (SS)-free effluent (Battilani et al., 2010). The benefits of MBR include better control of biological activity, effluent that is free of bacteria and pathogens, smaller plant size, and higher organic loading rates (OLR) (Cicek, 2003; Johir et al., 2011). Advantages and disadvantages of the MBR are presented in Table 1.

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Table 1. Advantages and disadvantages of MBR

Advantages	Disadvantages
Better effluent quality	Typically higher capital
Smaller space requirements	Operating costs
Ease of automation	Energy costs

Activated Sludge System

Biological wastewater treatment hastens waste disintegration. Activated sludge is supplemented to wastewater, and the combination of treatment process is aerated and agitated. After a certain period, the activated sludge is allowed to settle by sedimentation and is disposed of or reused by returning it to the aeration tank.

The ability to perform wastewater treatment in the mosteconomical technique is advantageous for a community. The activated sludge method applies microorganisms to feed on organic pollutants in wastewater, producing a high-quality effluent that results in reasonable operating and maintenance costs. The basic principle behind all activated sludge processes is that as microorganisms grow, they form particles that clump together. These particles, known as floc, are allowed to settle to the bottom of the tank, leaving a relatively clear liquid free of organic material. Screened wastewater is blended with various amounts of recycled liquid, including a high proportion of organisms taken from a secondary clarifying tank, becoming a product called mixed liquor. This mixture is stirred and injected with large quantities of air to provide oxygen and keep solids in suspension. Afterward, mixed liquor flows to a clarifier, in which the liquor is allowed to settle. A portion of the bacteria is eliminated as the liquor settles, and the partially cleaned water flows on for further treatment (Pipeline, 2013).

The activated sludge method is extensively applied worldwide for the treatment of domestic and industrial wastewaters in situations where high effluent is necessary and space is limited. However, the activated sludge system is more heavily mechanized than other systems, involving a more sophisticated operation. Another disadvantage is the consumption of electrical energy for aeration (Sperling, 2007). Figure 1 shows the main units in the biological stage of the activated sludge system.

Activated sludge methods come in several forms, such as conventional plug flow activated sludge process, extended aeration activated sludge method (i.e., extended aeration), contact stabilization, step-feed, complete mix, and sequencing batch reactors (SBRs). Advantages and disadvantages of the activated sludge system are presented in Table 2.

Table 2. Advantages and disadvantages of activated sludge System

Advantages	Disadvantages
Efficient removal of BOD, COD and nutrients	Larger volume, high aeration costs
Flexibility and numerous modifications	Associated with biomass instabilities like sludge bulking

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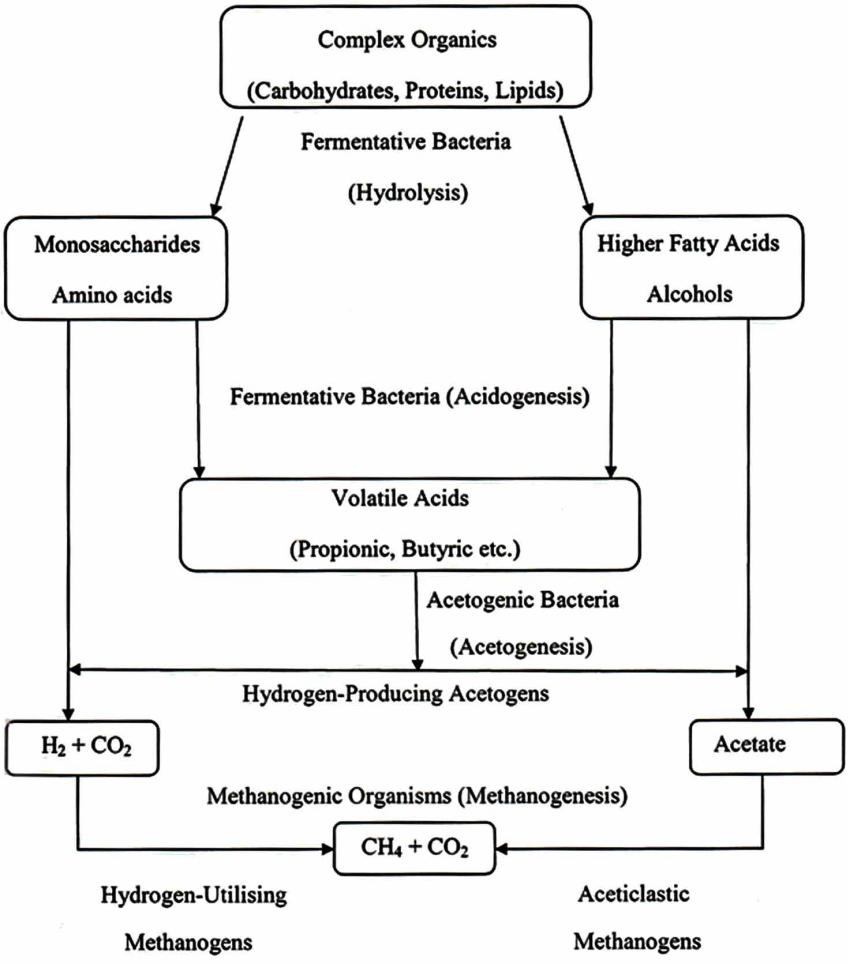
Figure 1. Representation of the main units in the biological stage of the activated sludge system
(Source: Sperling, 2007)



Conventional Plug Flow Activated Sludge Method

In the conventional plug flow activated sludge (Figure 2), the influent and the returned activated sludge enter at the head of the aeration tank and travel through the tank at a constant rate. The sludge age is commonly less than 15 days, and the optimal age is usually between 3 and 10 days (Water/Wastewater Distance Learning, 2014).

Extended Aeration Activated Sludge Process (Extended Aeration)

The extended aeration uses conventional plug flow patterns. However, aeration tanks are large and allow 15 hours of hydraulic retention times (HRT). The sludge age is normally greater than 15 days, and the optimum age is between 15 and 30 days. As such, the effluent is thoroughly treated, and less waste-activated sludge is produced. The oxidation ditch (Figure 3) is a variation of the extended aeration process (Water/Wastewater Distance Learning, 2014).

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Figure 2. Flow diagram for the plug flow of the activated sludge process
(Source: Water/Wastewater Distance Learning, 2014)

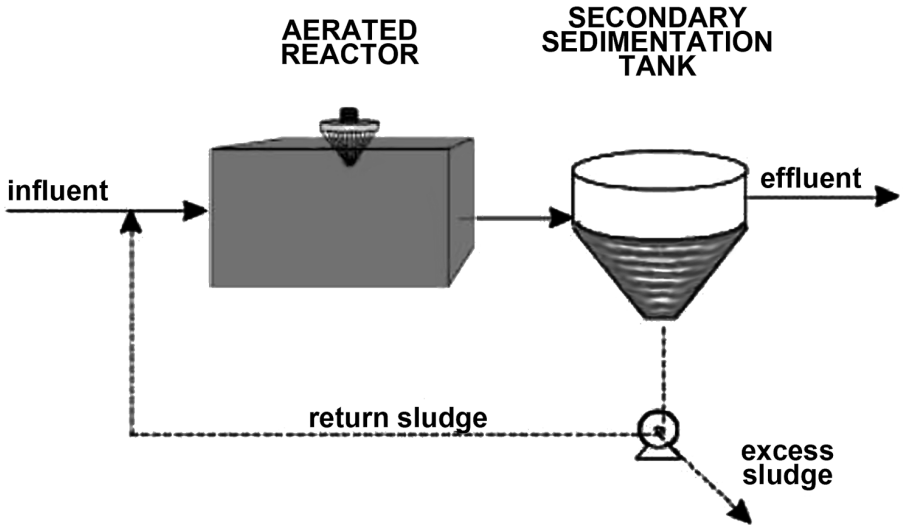
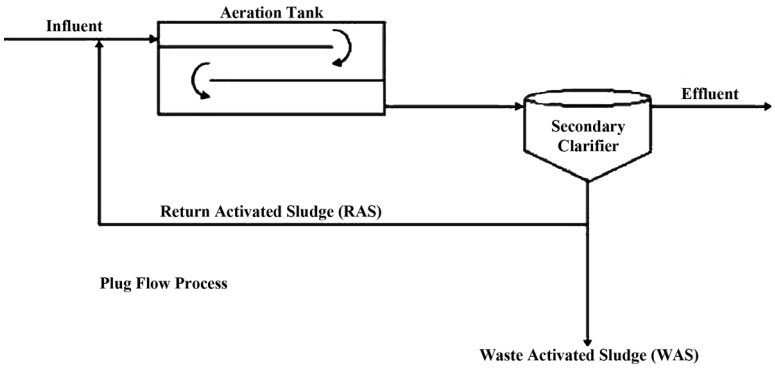


Figure 3. Flow diagram for the extended aeration of the activated sludge process
(Source: Water/Wastewater Distance Learning, 2014)



Contact Stabilization

This type of activated sludge process has several properties:

1. Microorganisms employ organics in the contact tank.
2. Fresh wastewater flows into the contact tank where it is aerated and blended with bacteria.
3. Soluble materials pass through bacterial cell walls, whereas insoluble materials stick to the outside of the cells.
4. Solids settle out later and are ejected from the tank or returned to a stabilization tank.
5. Microbes digest organics in the stabilization tank and are then recycled back to the contact tank as the organics are consumed.
6. Retention time is minimized; thus, the size of the contact tank can be decreased.

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7. The volume requirements for the stabilization tank are also smaller because the basin receives only concentrated return sludge. Moreover, no raw wastewater enters the tank.
8. Normally, primary clarification is not conducted before the wastewater goes into the contact tank because of the rapid uptake of soluble and insoluble food (Dohse and Heywood, 1999).

Step-Feed

In the step-feed method, the primary effluent is added at two or more points along the aeration tank length (Figure 4). This configuration allows for better control in handling shock loads and lowers the amount of mixed-liquor SSs to the secondary clarifiers. This configuration spreads out the organic load and evens out the rate of oxygen uptake throughout the basin length (Water/Wastewater Distance Learning, 2014).

Complete Mix

Complete mix method is currently the most commonly used approach in leachate treatment. In this method, the concentration of volatile-SSs and oxygen demand are the same throughout the tank because the wastewater is completely mixed with bacteria and oxygen (Dohse and Heywood, 1999).

Sequencing Batch Reactor

An SBR is a comprehensive mix-activated sludge method without a secondary clarifier. A number of different sequences are completed within the aeration basin. Aeration and clarification are also accomplished in one tank (Alkhaddar et al., 2005). Research on SBRs started in the 1970s, along with the development of other discontinuous processes. One of the benefits of these batch systems is that they can be merged for numerous variations of contaminant concentrations (Liermann, 2009). In the literature, different methods of biological treatment were used for the treatment of wastewater and leachate. SBR is a type of biological treatment that is different from activated sludge plants. Specifically, SBRs band all treatment phases and processes into a single basin, whereas conventional methods rely on different tanks. The treatment phases of SBR are fill, react, settle, draw, and idle. In many investigations, SBR was used to treat domestic, urban, dairy, industrial, synthetic, and slaughterhouse wastewaters and landfill leachate, as shown in Table 3 (Aziz et al., 2011c). Figure 5 shows the phases of SBRs.

Figure 4. Flow diagram for the step feed process of the activated sludge process
(Source: Water/Wastewater Distance Learning, 2014)

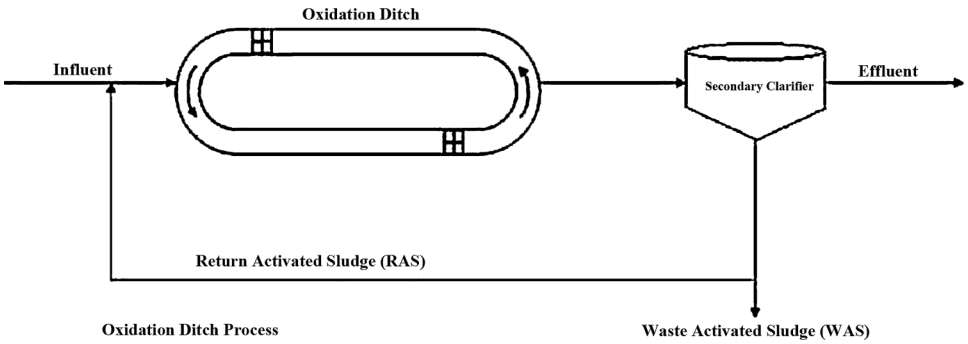

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Table 3. Treatment of different types of wastewaters by using the SBR process

No.	Type	Contaminants	Removal (%)
1	Landfill leachate	COD	75
		Ammonium	44
		Phosphate	44
2	Landfill leachate	COD	<83
3	Municipal wastewater	Biochemical oxygen demand	98
		Total SS	90
		Ammonia	89
4	Dairy wastewater	COD	80.2
		Total solids	63.4
		Volatile solids	66.3
		Total nitrogen	38.3
5	Textile effluent	Total organic carbon	66
		Color	94
6	Wool dyeing effluents	COD	79 to 91
		Biochemical oxygen demand	91 to 99
7	Slaughter house wastewater	COD	96
		Total nitrogen	96
		Total phosphorus	99
8	Abattoir effluent	Nitrogen	85.5
		Phosphorus	90
9	Tannery wastewater	COD	80 to 82
		Ammonia	83 to 89
10	Synthetic wastewater	Biochemical oxygen demand	97.7
		COD	94.9
		Total nitrogen	71.4
		Total phosphorus	55.9

(Source: Aziz et al., 2011c)

Advantages and Disadvantages of SBR

The main advantages of the SBR process are as follows:

1. Simple construction,
2. Flexible plant setup,
3. Flow through plants require regular-shaped sites,
4. Fewer channels and pipe work,
5. Easily scalable, and
6. Can be adapted to nitrification and denitrification.

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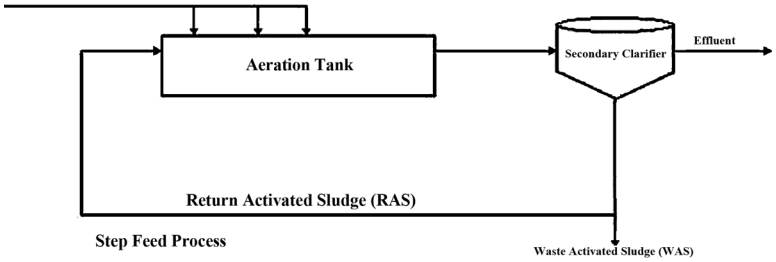
Figure 5. Phases of normal SBR
(Source: Mahvi, 2008)



The main difficulties of the SBR methods are as follows (Mace and Alvarez, 2002; USEPA, 1999):

1. A higher level of sophistication is required compared with conventional systems for timing units and controls, especially for larger structures;
2. A higher level of preservation is achieved compared with conventional systems associated with more sophisticated controls, automated switches, and automated valves required;
3. Floating or settled sludge is potentially discharged during the draw or decant phase with certain SBR configurations;
4. Equalization is potentially required after SBR, depending on the downstream processes; and
5. Batch feeding from storage or bioselectors is required to control bulking.

Additional Information on SBR

Janczukowicz et al. (2001) investigated the settling properties of activated sludge from an SBR, and their results showed good settling properties of the sludge. Low sludge volume index (SVI) (30 mL/g to 60 mL/g SS) caused severe and rapid sedimentation, which shortened the settling phase to less than 1 hour. Moreover, low SVI prevented the sludge from bulking. High dissolved oxygen concentrations in the aeration tank during the reacting phase resulted in minimal sludge biomass growth, which is vital in terms of sludge dumping at a wastewater treatment plant.

Mahvi et al. (2005) investigated the feasibility of continuous flow SBR in synthetic wastewater treatment. The results showed that the removal efficiencies achieved by the system were 97.7%, 94.9%, 85.4%, 71.4%, and 55.9% for BOD_5, COD, TKN, total N, and total P, respectively.

In many investigations, the SBR has been applied in the treatment of leachate with low BOD_5/COD ratios ranging from 0.09 to 0.37. The capability of SBR in leachate treatment was lower than that for municipal and industrial wastes because of the low biodegradability ratio and high concentration of heavy metals, COD, NH_3–N, and other compounds in landfill leachate. In the reported studies, the adsorption method improved the SBR process and increased the elimination efficiencies of organic matter, heavy metals, NH_3–N, and other pollutants. Aziz et al. (2011b) investigated landfill leachate treatment by powdered activated carbon SBR (PAC-SBR) method and optimization by response surface methodology. This result indicated that PAC-SBR showed superior performance in terms of removal efficiencies compared with the SBR Anaerobic Treatment.

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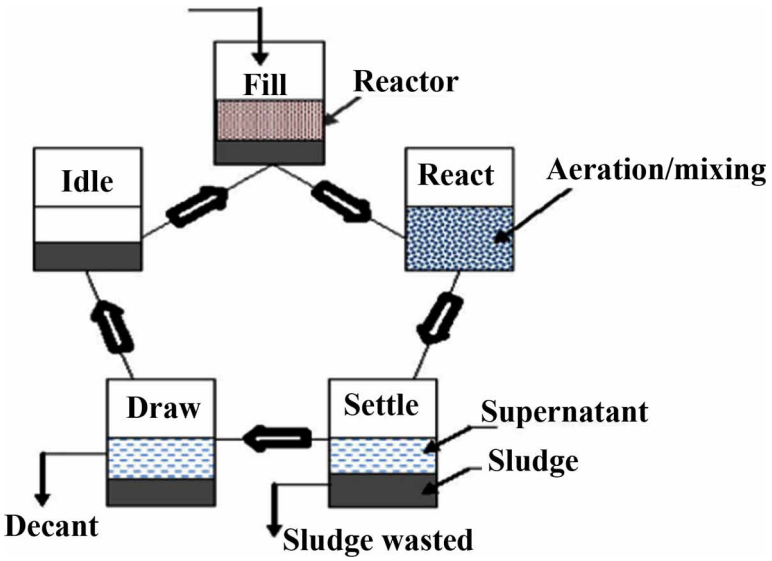
This part describes several anaerobic methods, such as anaerobic hybrid reactors and other anaerobic bioreactors. Anaerobic treatment is a sustainable wastewater treatment system for developing countries and is already gaining acceptance as a simple and cost-effective technology for the treatment of a variety of wastewaters (Alptekin, 2008). Anaerobic digestion (AD) is a biological process that occurs when bacteria breaks down organic matter in environments with minimal or no oxygen. AD is an efficiently controlled and enclosed version of the anaerobic breakdown of organic waste in a landfill that releases methane (Friends of the Earth, 2007). Figure 6 shows the metabolic pathways and microbial groups involved in AD.

Upflow Anaerobic Sludge Blanket

The upflow anaerobic sludge blanket (UASB) reactor was established in the Netherlands in the early 1970s (Lettinga et al., 1980). Originally proposed by Lettinga, this reactor was one of the earliest systems in which the development of a granular biomass was observed. Excellent sludge retention is ensured in this reactor system as a result of the excellent settling characteristics of this granular biomass and the presence of a specially designed three-phase (biogas, water, and biomass) separator device in the upper part of the UASB reactor. The major disadvantage of the UASB process is the relatively long start-up period, although this occurs merely in cases where proper seed sludge is not available in sufficient quantities. A significant washout of sludge generally manifests during the initial phase of the start-up process of a UASB reactor inoculated with flocculent seed sludge. Therefore, the first reactor start-up would highly benefit from skilled operation (Mai, 2006).

Figure 6. Metabolic pathways and microbial groups involved in AD
(Source: Lettina et al., 1996; Hampannavar, 2010)



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Upflow Anaerobic Filter

Anaerobic filters have been used successfully for the treatment of dilute wastewater with COD removal efficiencies between 60% and 80%, depending on the HRT used (Alptekin, 2008). The upflow anaerobic filter (UAF) maintains the biomass immobilized over a fixed support, thereby retaining high cellular retention times even when operating at low HRT. The UAF also tolerates low and variable OLR and pH. These features enable a reduction in the dimensions of the reactor.

Anaerobic Hybrid Reactor

The anaerobic hybrid reactor (AHR) combines the sludge blanket in the lower portion and the filter in the upper part; the AHR has been reported to enhance the advantages of the UASB and upflow filter while minimizing their limitations (Kumar et al., 2007). The AHR is a combination of the UASB reactor and an anaerobic filter. A layer of biomass carrier is placed in the upper part of the AHR instead of the gas–liquid–solid phase separator. This layer separates the bubbles of the biogas from the biomass and functions as a support material for biomass growth. In addition, the layer has a notable efficiency as a SS separator (Hutnan et al., 1999).

Phytoremediation

The use of plants for the remediation of polluted soils and waters has gained acceptance in the past two decades as a cost-effective and non-invasive method (Mojiri et al., 2013). Phytoremediation is a new approach that offers more ecological benefits and a cost-efficient alternative. Although this method is less expensive than other techniques, it requires technical strategy and expert project designers with field experience to choose the proper species and cultivars for specific metals and regions. Phytoremediation presents many advantages compared with other remediation techniques; for instance, phytoremediation can be performed with minimal environmental disturbance (Mojiri, 2012 & 2011a). The most vital factor in implementing phytoremediation is the selection of a suitable plant. A list of potentially beneficial plants for remediation must be prepared first to select the most appropriate plant (Kutty et al., 2009). Several investigations on wastewater treatment by phytoremediation can be found in literature (Mojiri et al., 2013; Mojiri et al., 2012; Khider et al., 2012).

PHYSICAL/CHEMICAL TREATMENT

Reduction of floating material, colloidal particles, color, and toxic compounds using flotation, coagulation/flocculation, adsorption, chemical oxidation, and air stripping are considered physical and chemical processes. Physical/chemical treatments for the landfill leachate are employed in addition to the treatment line (pretreatment or last purification) or treatment of a specific contaminant (e.g., stripping for ammonia) (Renou et al., 2008).

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Chemical Precipitation

Chemical precipitation is employed as pretreatment to eliminate high-strength ammonium nitrogen in leachate treatment (Renou et al., 2008). Given its efficiency, simplicity, and low cost, chemical precipitation has been used to remove non-biodegradable organic combinations, NH_3–N, and heavy metals from landfill leachate. During chemical precipitation, dissolved ions in the solution are converted to an insoluble solid phase via chemical reactions. The removal of ammoniacal–nitrogen from anaerobically pre-treated leachate was studied using struvite (magnesium ammonium phosphate) precipitation in the Odayeri landfill (Turkey). Using this method, ammonia was converted into a nitrogen fertilizer, such as urea. Approximately 50% COD and 90% NH_3–N, with an initial COD concentration of 4,024 mg/L and NH3–N concentration of 2,240 mg/L, were removed (Kurniawan et al., 2006). Table 4 shows advantages and disadvantages of this method.

Chemical Oxidation

Chemical oxidation processes have been developed at different sites over the past few years. A mixture of oxidation agents, such as ozone or hydrogen peroxide and ultraviolet (UV) light, is applied. This mixture displays high oxidation rates for leachate COD. The method involves a mixing chamber, which is used to combine the influent leachate and oxidation agent. This mixture then goes into a chamber with UV lamps. Flows are recirculated to increase the elimination rates of leachate manifold. Mixing gaseous ozone and water is more difficult than mixing hydrogen peroxide and water.

Inorganic compounds may also be oxidized during chemical oxidation. A biological pretreatment, e.g., nitrification/denitrification, should be considered to prevent the expensive oxidation of easily biodegradable components. During chemical oxidation, not all organics are oxidized to carbon dioxide and water. Some organics are only partly oxidized, often to biodegradable intermediates. These so-called "new" biodegradable organics should be reduced by biological treatment. A fixed film reactor may be an option for the reduction of these relatively low concentrations of organics. Feeding the effluent of the chemical oxidation plant back to the influent of the biological reactor may also be considered (Stegmann et al., 2005). Table 5 shows advantages and disadvantages of this method.

Fenton Treatment

The Fenton process has been widely studied in recent years, and analyses indicate that the Fenton method is one of the most cost-effective alternatives among potential physicochemical technologies for leachate treatment (Deng, 2007). Fenton oxidation is one of the advanced oxidation processes with high efficiency

Table 4. Advantages and disadvantages of chemical precipitation

Advantages	Disadvantages
Chemical precipitation is a well-established technology with ready availability of equipment and many chemicals	Chemical precipitation may require working with corrosive chemicals, increasing operator safety concerns.
Some treatment chemicals, especially lime, are very inexpensive.	Large amounts of chemicals may need to be transported to the treatment location

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Table 5. Advantages and disadvantages of chemical oxidation

Advantages	Disadvantages
Contaminant mass can be destroyed in-situ	Potentially higher initial and overall costs relative to other source area solutions
Rapid destruction/degradation of contaminants (measurable reductions in weeks or months)	Contamination in low permeability soils may not be readily contacted and destroyed by chemical oxidants.
Reduced operation and monitoring costs.	Dissolved contaminant concentrations may rebound weeks or months following chemical oxidation treatment.

and low capital costs. Fenton oxidation involves a mixture of H_2O_2 and ferrous salts, which can generate aggressive hydroxyl radicals at ambient temperatures. The generated radicals are able to oxidize an extensive range of chemicals in aquatic medium, theoretically, all organic compounds containing hydrogen (R–H). The Fenton procedure can effectively achieve not only good oxidation of organics, but also their removal because of coagulation in the presence of ferrous salts (Gotvajn et al., 2011).

Coagulation–Flocculation or Flocculation–Precipitation

Table 6 shows that coagulation–flocculation has been used to remove non-biodegradable organic compounds and heavy metals from landfill leachate. The coagulation process destabilizes colloidal particles through the addition of a coagulant. Coagulation is usually followed by flocculation of the unstable particles into bulky floccules so that they can settle more easily and increase the particle size. This method facilitates the removal of SS and colloid particles from a solution. The general approach for this method involves pH adjustment and the addition of ferric/alum salts as coagulant to overcome the repulsive forces between the particles (Kurniawan et al., 2006).

Table 6. Removal of recalcitrant compounds using coagulation-flocculation (Source: Kurniawan et al., 2006)

Location of Landfill	Process	Precipitant / Coagulant	Dosages	BOD/COD	pH	Removal Rate (%)		
						COD	NH_3-N	Metals
NA (Non Available)	Cd(II) Ca(II) Ni(II) Pb(II) Zn(II) Cr(VI)	$FeCl_3$	0.3	NA	9.0	NA	NA	97 74 82 98 95 87
France	NA NA	$FeCl_3$ $Al_2(SO_4)_3$	2 0.9	0.05	4.5-5.0	55 42	NA	NA
Greece	NA NA	$FeCl_3$ $Al_2(SO_4)_3$	0.8 0.4	0.1	4.8	56 39	NA	NA
Greece	NA NA	$FeCl_3$ $Al_2(SO_4)_3$	1.5 5.5 1.5 3.0	0.20 0.38 0.20 0.38	10.0 6.2 10.0 6.2	80 30 38 40	- - - -	- - - -
Turkey	NA	$Ca(OH)_2$	2.0	NA	12.0	86	-	-

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Membrane Filtration

A membrane is a material that creates a thin barrier that can selectively resist the movement of different constituents of a fluid, thereby affecting the separation of the constituents (Visvanathan et al., 2000). Usually, a thin layer of material with high surface porosity and a narrow pore size affects the physical structure of the membrane. Different membrane filtration techniques, namely, microfiltration(MF), ultrafiltration(UF), nanofiltration(NF), and reverse osmosis(RO), are employed in landfill leachate treatment.

Microfiltration

MF with pore sizes of 0.05 μm to 10 μm is used to capture microbial cells, small particles, and large colloidal particles. Based on landfill leachate treatment, this method is unsuitable to be used by itself. MF is used as a pretreatment process with other membrane processes (i.e., UF, NF, or RO) or in combination with 10 chemical treatment processes to remove suspended matter and colloids. Piatkiewicz et al. (2001) used this method in the prefiltration stage and obtained COD removal rates of 25% to 35%.

Ultrafiltration

UF is a selective method that utilizes pressures of up to 10 bar. This technique efficiently removes suspended matter either by direct filtration or with biological treatment to replace the sedimentation unit. UF is significantly dependent on the material that constitutes the membrane. Syzdek and Ahlert (1984) proposed that this process might prove useful as a pretreatment method for RO. UF eliminates the larger molecular weight components of leachate that tend to foul RO membranes (Bohdziewicz et al., 2001; Rautenbach et al., 1997). A COD removal rate of 50% was obtained by using UF alone (Bohdziewicz et al., 2001). Tabet et al. (2002) reported that UF membranes have been successfully used in full-scale MBR plants by combining bioreactors and membrane technology. High level of landfill leachate treatment have also been obtained using this method.

Nanofiltration

NF has been used to remove recalcitrant organic compounds and heavy metals from landfill leachate because of its unique properties. NF also has the ability to remove particles with molecular weights greater than 300 Da and inorganic substances through electrostatic interactions between ions and membranes. The significance of this membrane lies in its surface charges, which permit charged solutes smaller than the membrane pores to be rejected, along with larger neutral solutes and salts. Table 7 shows that NF is also effective in removing heavy metals because of the negatively charged groups on the membrane. The application of NF enables material dissolved in water to be separated into monovalent and divalent ions (Kurniawan et al., 2006).

Reverse Osmosis

RO is one of the developments in leachate treatment over the past decade. However, in contrast to biological treatment, RO separates leachate into two streams: a barely contaminated permeate stream and

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Table 7. Removal of recalcitrant compounds Using NF and RO (Source: Kurniawan et al., 2006)

Location of Landfill	Process	Type of Membrane	Species	Pressure (Bar)	BOD/COD	pH	Removal Rate (%)		
							COD	NH_3-N	Metals
NA (Non Available)	NF	NTR-7250	Cr(III) Cu(II) Pb(II)	3	NA	NA	NA	NA	100 99 93
Odayeri (Turkey) Mustankorkea (Finland)	NF NF	SW Desal-5-DL	NA NA	25 6-8	NA 0.40	NA 7.6	89 66	75 50	NA NA
Spilepeng (Sweden)	NF	AFC-30	Pb(II) Zn(II) Cd(II)	20	NA	NA	NA	NA	97 88 94
Chung Nam (S. Korea) Yachiyo (Japan)	RO RO	SW-40-10 DT	NA Mn(II)	NA 9-11	0.30 0.05	NA 6.0	97 100	96 98	NA 100
Pietramelina (Italy)	RO	SW30-2521	Cd(II) Zn(II) Cu(II)	52	0.31	6.0	98	NA	100 97 99
Hedeskogn (Sweden) Spillepeng (Sweden) Wijster (Holland)	RO RO RO	AFC99 NA NA	Cr(III) NA NA	40 30 40	0.10 NA NA	7.0 6.5 6.5	95 98 98	82 98 98	NA NA NA
Ihlenberg (Germany)	NF	NA	NA	36-60	0.03 0.03	7.7 6.4	99 96	100 58	98 NA
Lipoka (Poland)	RO	SS	NA	27.6	0.28	7-8	97	NA	NA

a highly contaminated concentrate stream. Biological pretreatment may be necessary when leachate from the acetic phase is treated. Ammonium separation is often insufficient during RO. Reduction of ammonia concentrations in permeate may be improved through a two- or multiple-step RO. In various cases, ammonium is eliminated through a prestripping process or through a biological nitrification and denitrification steps. However, a disadvantage of RO is the production of liquid concentrate that is approximately 20% of the leachate. The method of back passing the concentrate into the landfill is a suggestion of researchers and may not be the best option (Stegmann et al., 2005). In contrast to RO, NF has a looser membrane structure, thus enabling higher fluxes and lower operating pressure for lecheate treatment (Kurniawan et al., 2006).

Electrochemical Treatment

In recent years, electrochemical methods have been used to treat organic materials with high toxicity and low biological degradability. Electrochemical methods, such as electrocoagulation, electrooxidation, and electro-photooxidation, have been frequently used to treat wastewaters from textile, tannery, and oil industries. Treatment of landfill leachate by electrochemical methods is another important research area. Electrooxidation was specifically examined in most of the studies in this field (Deng, 2007).

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Electrooxidation

In recent years, the electrochemical oxidation process has shown promise in wastewater treatment mainly because of its effectiveness and ease in operation. This process has significant efficacy in destroying refractory pollutants, such as cyanide, EDTA, and aniline, as well as for color removal (Chiang et al., 1995).

Ion Exchange

Ion exchange is a reversible interchange of ions between solid and fluid phases without changing the structure of the solid. This treatment can effectively eliminate traces of metal impurities to meet the increasingly strict discharge standards in developed countries. The leachate should be subjected to biological treatment prior to ion exchange (Kurniawan et al., 2006).

Solid ion exchange particles can be classified as natural inorganic particles (e.g., zeolites) and synthetic organic resins developed from high-molecular-weight polyelectrolytes (Bashir et al., 2010). Development of ion exchange resins and characterization of naturally occurring ion exchange materials have demonstrated that ion-exchange technique has numerous possible applications in water and wastewater treatment (Wang & Peng, 2010).

The ion-exchange technique offers many benefits, including the ability to handle shock loadings and the ability to operate under a wide range of temperatures. Some of the most popular and widely available natural ion exchangers are zeolites, which consist of an aluminosilicate molecular structure with weak cationic bonding sites. Natural zeolites have been avoided in high purity processes, or where consistency is vital, because of their irregularities and impurities. Zeolites are hydrated aluminosilicates comprising silica and aluminum tetrahedra that are mutually bound by chemical covalent bonds with common oxygen atoms (Mojiri, 2011b). Table 8 shows advantages and disadvantages of ion exchange.

Adsorption

Among all techniques, adsorption is the most widely used in the removal of recalcitrant organic compounds from landfill leachate. In this process, a substance is transferred from the liquid phase to the surface of a solid and then bound by physical and/or chemical interactions (Kurniawan et al., 2006). Regardless of the initial organic matter concentration, adsorption of contaminants onto activated carbon in columns or in powder form results in better reduction in COD levels than that in the chemical methods. However, adsorption requires frequent regeneration of columns or an equivalently high consumption of PAC. Along with biological treatment, adsorption by activated carbon has been used for the effective treatment of landfill leachate. Non-biodegradable organics, inert COD, and color may be reduced to acceptable levels for biologically treated landfill leachate (Renou et al., 2008).

Table 8. Advantages and disadvantages of ion exchange

Advantages	Disadvantages
An advantage of the ion exchange treatment process is that it does not change the pH or alkalinity of the water.	First is the increase of total dissolved solids (TDS) in the treated water due to the release of sodium
Excellent process reliability, process stability, and chemical safety	Second is the cost of disposing of the regeneration cycle's salt brine.

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Adsorption technique is an efficient and a promising straightforward approach in wastewater treatment processes (Foo & Hameed, 2009). This technique is employed as a phase of integrated chemical–physical–biological method for leachate treatment or performed simultaneously with a biological process. The most commonly applied adsorbent is granular-activated carbon (GAC) or PAC (Mojiri, 2011b).

Adsorption using GAC or PAC has been widely used in the removal of organic and inorganic contaminants from polluted wastewater because of its inherent physical properties, large surface area, microporous structure, high adsorption capacity, and surface reactivity (Kurniawan et al., 2006).

Rodriguez et al. (2004) studied the efficiency of PAC and different resins in reducing non-biodegradable organic matter from landfill leachate. Activated carbon presented the highest adsorption capacity, with 85% COD decrease and a residual COD of 200 mg/L (Renou et al., 2008).

CONCLUSION

The main landfill leachate treatment methods are the physical, chemical, and biological methods. Each method has benefits and disadvantages based on the purpose of the research. Landfill leachate properties, technical applicability and constraints, effluent discharge alternatives, cost-effectiveness, regulatory requirements, and environmental impact are important factors in selecting the most suitable treatment technique for landfill leachate treatment. Physical/chemical treatments such as chemical precipitation, chemical oxidation, coagulation–flocculation, membrane filtration, ion exchange, adsorption, and electrochemical treatments were described in this manuscript. Physical/chemical treatments for landfill leachate are used in addition to pretreatment or final purification to treat a specific pollutant. Physical/chemical methods have been mostly used to remove metals from leachate. Biological methods, such as aerobic and anaerobic methods, were also discussed in this chapter. These methods have been used to reduce contaminations, such as COD, BOD, ammonia, color, and metals, from leachate.

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Chapter 8
A Review of Emerging Contaminants in Water:
Classification, Sources, and Potential Risks

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ABSTRACT

Contaminants of emerging concern or, simply, emerging contaminants represent a newly discovered group of chemicals present in surface and groundwater. It was only the improvements in analytical instrumentation that allowed for the detection of these contaminants even at trace levels. The continuous detection of new chemicals with time raises questions concerning their source pathways, their fate, transport, transformations and impact on aquatic environments. The scope of this chapter is to present an overview of the contaminants classified as "emerging", their sources and introduction pathways to the environment and the related risks to human health and aquatic life.

INTRODUCTION

Current practice and experience dictates that investments in detection, prevention, control and elimination strategies of environmental pollution by chemical pollutants will continue to rise. However, given the huge number of pollutants occurring in the environment due to the combined effects of both natural processes and human activities, it seems that the range of currently regulated chemical pollutants represents only a small fraction of the total chemical pollution. To this, the gradual detection and identification of new emerging pollutants further increases the long list of chemical pollutants. It is then unavoidable that national and international lists of regulated chemicals will ignore the majority of other chemicals occurrence based on the assumption that the chemicals considered by the regulatory processes are the most significant and that they possess the greatest risk to the environment, human

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health and the economy. However, questions will still remain concerning the right (or not) selection of the most dangerous chemical pollutants. Additionally, developments of the last 10-15 years imply that there is a large chemical universe still unidentified that will be possibly determined in the near future.

Contaminants of emerging concern or emerging contaminants (ECs) represent relatively newly discovered groups of unregulated contaminants which occur in surface and groundwater, such as pharmaceuticals and personal care compounds, and generally include compounds used in everyday life and various industrial additives. Most of these pollutants were previously (e.g., 15-20 years ago) unknown or simply unrecognized or unidentified and have recently emerged as contaminants associated with potential environmental risks. Their fate in water/wastewater treatment plants, in engineered systems and generally in the environment still remains relatively unknown. At the same time, potential impact and risks to human health, wildlife, aquatic life and ecosystems is another important topic of great interest which needs further investigation. These pollutants are usually bioactive and bioaccumulative and can have a widespread occurrence and persistence. The vast majority of ECs is currently not regulated which means that a continuous monitoring and reporting of their possible presence in water supplies and effluent discharges is required. Today, it is clear that an integrated research and approach to these contaminant groups should be multidisciplinary, involving disciplines such as chemistry, biology and engineering.

Background

ECs are not necessarily newly created chemicals. It could be stated that term refers to three general categories. The first category includes compounds which are recently introduced into the environment (e.g., industrial additives). The second category consists of compounds that might have been present in the environment in the past for many years, but it is only during the last years that their presence was detected and their significance started to attract interest (e.g., pharmaceuticals). The third category includes compounds that are known for a longer time but their potential negative impact on humans and the environment was only recently realized (e.g., hormones). The main problem with ECs is that available data for most of these contaminants are scarce and relatively limited and respective detecting methods and instrumentation either do not yet exist or are at the early development stage. This is why only with the gradual progress in analytical detecting and measuring techniques became possible the detection of these micro-contaminants in the environment. In other words, for many ECs it is not yet clarified the level of risk they represent for the environment and human health, while the techniques to monitor them and the effective technologies to further mitigate contamination are still in development. Only advances in analytical chemistry and instrumentation, as well as in engineering, made it possible to identify ECs in the environment. Analytical capabilities have significantly improved during the last two decades from parts per thousand to parts per trillion (ppt) or even parts per quadrillion (ppq) in some cases, which allowed for the detection and investigation of these contaminants in environmental samples.

The goal of this chapter is to present an overview of these newly discovered contaminant groups, mainly of the organic chemicals detected in surface and groundwaters. The chapter includes their classification, sources and related environmental and human risks, along with a brief analysis of the current legislative status in Europe.

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CLASSIFICATION OF EMERGING CONTAMINANTS

ECs include a large variety of natural and synthetic chemical compounds which are considered as potential hazards, although sufficient knowledge for all the various ECs is still not available. ECs include compounds such as pharmaceuticals, personal care products (PCPs), Endocrine Disrupting Chemicals (EDCs), steroids, hormones, surfactants and surfactant metabolites, flame retardants, pesticides, industrial additives, nanomaterials and gasoline additives. Table 1 presents a general overview of the various contaminant groups that are considered as emerging.

Pharmaceuticals and PCPs are typical examples of emerging contaminants present in surface water for a long time now but whose presence was only recently identified. As Table 1 shows, the term "ECs" is rather extended and includes a large variety of chemical contaminants, which sometimes could be confusing concerning the different categorization of chemical pollutants (Daughton, 2005). Thus, chemical pollution could also be categorized in the following groups based on different properties:

- CMR: carcinogenic, mutagenic, toxic to reproduction,
- EDCs (toxic contaminants)

Table 1. List of major emerging contaminant groups.

Emerging Contaminant groups	Examples
Pharmaceuticals	
Human antibiotics and veterinary	Trimethoprim, erytromycine, amoxicillin, lincomycin, sulfamethaxozole, chloramphenicol
Analgesics, anti-inflammatory drugs	Ibuprofene, diclofenac, paracetamol, codein, acetaminophen, acetylsalicilyc acid, fenoprofen
Psychiatric drugs	Diazepam, carbamazepine, primidone, salbutamol
β-blockers	Metoprolol, propanolol, timolol, atenolol, sotalol
Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid, etofibrate, gemfibrozil
X-ray contrasts	Iopromide, iopamidol, diatrizoate
Personal care products (PCPs)	
Fragrances	Nitro, polycyclic and macrocyclic musks, phthalates
Sun-screen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	N,N-diethyltoluamide
Endocrine Disrupting Chemicals (EDCs)	Octylphenols, nonylphenols, Di(2-ethylhexyl)phthalate (DEHP)
Hormones and steroids	Estradiol, estrone, estriol, diethylstilbestrol (DES)
Perfluoronated compounds	Perfluorotoctane sulfonates (PFOs), perfluoroctanoic acid (PFOA)
Surfactants and surfactant metabolites	Alkylphenol ethoxylates, 4-nonylphnol, 4-octylphenol, alkylphenol carboxylates
Flame retardants	Polybrominated diphenyl ethers (PBDEs): polybromonated biphenyls (PBBs) – polybromonated dibenzo-*p*-dioxins (PBDDs) – polybromonated dibenzofurans (PBDFs), Tetrabromo bisphenol A, C10-C13 chloroalkanes, Tris (2-chloroethyl)phosphate, Hexabromocyclododecanes (HBCDs)
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates
Gasoline additives	Dialkyl ethers, Methyl-t-butyl ether (MTBE)
Antiseptics	Triclosan, chlorophene

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- PBT: persistent, bioaccumulative, toxic,
- vPvB: very persistent, very bioaccumulative,
- POP: persistent organic pollutant (based on their environmental properties)
- PPCPs: pharmaceuticals and personal care products (based on their usage)
- Priority pollutants (regulated)
- Xenobiotics, exotics (foreign vs endogenous pollutants)
- Toxicants, toxins, toxics (based on the overall toxicity)
- HPV: high production volume chemicals

Most of these substances exist in the environment and persist to a greater extent, not only in industrialized regions but even in remote areas. Table 2 contains examples of common contaminants and their main properties. Some pollutants are conservative and do not degrade in the environment (e.g., heavy metals). Persistent organic pollutants (e.g., DDT, EDTA, perfluorinated compounds) are degradable but at a very slow rate, as many pharmaceuticals too (e.g., carbamazepine, sulfamethoxazole). Polar persistent water-soluble chemicals can easily infiltrate into waters (Schwarzenbach et al., 2006). It should be noted that although some contaminants are not persistent in the environment and they can be transformed/removed through natural processes, their continuous introduction from various sources (e.g., wastewater treatment plant outflows) prolongs and maintains their presence in waters and the possible negative impacts on the aquatic life (Vera-Candioti, García, Galera, & Goicoechea, 2008). In an interesting study, Loos et al. (2009) analyzed samples from 100 rivers in 27 different European countries for 35 compounds, including pharmaceuticals, pesticides, PFOs, PFOA, benzotriazoles, hormones, triclosan and EDCs. The most frequently detected compounds and at the highest concentrations were benzotriazole, ceaffeine, carbamazepine, tolyltriazole and nonyl-phenoxy acetic acid (NPE1C). It is also interesting that among the monitored rivers, only 10% could be classified as "very clean" in terms of chemical pollution.

Pharmaceuticals and Personal Care Products (PPCPs)

These substances are natural or man-made chemicals used in prescription medicines and veterinary drugs. To better understand their potential level of presence in the environment, we should consider the annual global mean consumption of pharmaceuticals of 15 g per capita, which rises up to 50-150 g in developed countries (Zhang, Geiβen, & Gal, 2008). Nowadays, more than 3,000 known pharmaceutical compounds are produced (Davis, 2008). Of course, consumption rates vary from country to country according to national legislation and prescription lists. Latest developments in analytical techniques and improvements in analytical instrumentation allowed for the detection of these substances at trace levels. The transformation products of these substances can also be persistent in the environment (Fent, Weston, & Caminada, 2006).

Table 3 presents examples of different analytical techniques used to detect various pharmaceutical compounds in the water cycle (surface water, groundwater, treated wastewater, drinking water). Advanced technologies such as gas chromatography with mass spectrometry (GC-MS) or tandem mass spectrometry (GC-MS/MS) and liquid chromatography with mass spectrometry (LC-MS) or tandem mass spectrometry (LC-MS/MS) can detect pharmaceuticals in water at very low concentrations (down to ng/L). For more polar and water soluble substances LC-MS/MS is more appropriate, while for more volatile substances

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Table 2. Examples of common emerging contaminants and their properties.

Contaminant	Source/origin	Persistence and Bioaccumulation	Occurrence in the environment
Nonylphenol	Degradation of non-ionic surfactants	Medium persistent, bioaccumulative	Soil, sediment, sludge, water
Bisphenol A	Plastics and epoxy resins	Not bioaccumulative	Surface water, groundwater
Veterinary medicine	Use in aquaculture, release from animals at pasture	Persistent, bioaccumulative	Water, soil, sediment
Phthalates	Plastics	Low to medium persistent, atmospheric deposition	Water, sediment, sludge
PBDE	Flame retardant	Persistent/highly bioaccumulative, atmospheric deposition	Soil, sediment, sludge
Nanomaterials	Use of nanopesticides in agriculture, release of nanomedicnes in livestock, waste landfill disposal	Persistent, nioaccumulative	Surface water, soil, sludge
C_{10}-C_{13} chloroalkanes	Flame retardant	Persistent, bioaccumulative	Surface water
Sulphonamides	Human and veterinary drugs	Slightly-very persistent	Groundwater
Tetracyclines	Human and veterinary drugs	Moderately-very persistent	Groundwater, soil, sludge
Steroid sex hormones	Contraceptives	Moderately persistent	Water, sediment, sludge
MTBE	Gasoline additive	Persistent, not bioaccumulative, ubiquitous in the atmosphere	Groundwater

GC-MS/MS is better (Fatta, Nikolaou, Achilleos, & Meriç, 2007). It should be noticed that currently there is no standardized protocol for the sampling and determination of pharmaceutical compounds in water to provide proven comparability and quality of the obtained data.

Pharmaceuticals and their related metabolites are subjected to natural transformation/removal processes in the environment (e.g., dilution, degradation, sorption), based on their hydrophobicity, biodegradability and the environmental conditions, which explains their presence at trace levels in water sources and drinking water. Pharmaceuticals can be classified based on their purpose and biological activity to antibiotics, analgesics, anti-neoplastics, disinfectants, anti-flammatory compounds, X-ray contrast media etc. Another classification can be made based on the mode of action, e.g., anti-metabolites, alkylating agents, etc. Due to the large variety of compounds, pharmaceuticals have varying biological and physicochemical characteristics. Typical concentrations of these compounds vary within the range of microgram per litre (μg/L) down to nanogram per litre (ng/L), which explains why they are also called as micro-pollutants. Pharmaceutical compounds (as most of chemicals) are subjected to various biotic and abiotic processes which might change their structure, once introduced into the environment. Human and animal metabolism activities also result in structural changes of many pharmaceuticals caused by biological and non-biological transformations (processes initiated by human enzymes, fungi, bacteria as well as processes including oxidation, hydrolysis and photolysis; Kümmerer, 2009), which are the production processes of pharmaceutical metabolites.

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Table 3. Analytical methods and instrumentation used for the detection of pharmaceutical substances in water and wastewater (Fatta et al., 2007).

GC-MS or GC-MS/MS without derivatization	**GC-MS or GC-MS/MS after derivatization**	**LC-MS or LC-MS/MS**		
Aspirin	Aspirin	17α-Ethinylestradiol	Hydrochlorothiazide	Penicillin G
Codeine	Etofibrate	7β-Estradiol	Iopamidol	Penicillin V
Cyclophosphamide	Etofyllinclofibrat	Acetyl-sulfamethoxazole	Lofepramine	Pindolol
Galaxolide	Flurbiprofen	Amidotrizoic acid	Metronidazole	Piroxicam
Pentoxyfylline	Ketoprofen	Aminopyrine	Ofloxacin	Ranitidine
Tonalide	Nadolol	Amoxycillin	Enalapril	Ronidazole
Triclosan	Tolfenamic acid	Anhydro-erythromycin	Furazolidone	Spiramycin
		Atenolol	Ifosfamide	Sulfacetamide
		Betaxolol	Ketorolac	Sulfadiazine
		Bisoprolol	Methicillin	Sulfadimethoxine
		Chloramphenicol	Nafcillin	Sulfadimidine
		Chlortetracycline	Erythromycin	Sulfaguanidine
		Ciprofloxacin	Furosemide	Sulfamethazine
		Clarithromycin	Iomeprol	Sulfapyridine
		Clenbuterol	Lincomycin	Sulfasalazine
		Cloxacillin	Methotrexate	Sulfathiazine
		Cyclophosphamide	Norfloxacin	Tamoxifen
		Dapsone	Oleandomycin	Terbutaline
		Demethyl diazepam	Simvastatin	Tetracycline
		Dextropropoxyphene	Sotalol	Tilmicosin
		Dicloxacillin	Omeprazole	Trimethoprim
		Doxycycline	Oxacillin	Tylosin
		Estrone	Oxytetracycline	Virginiamyci
	Bezafibrate, Clofibrate, Diclofenac, Fenofibrate, Fenoprofen, Gemfibrozil, Indomethacine, Iopromide, Mefenamic acid, Metoprolol, Naproxen, Propranolol, Propyphenazone, Roxithromycin, Salbutamol, Sulfamethoxazole			
Carbamazepine, Diazepam, Ibuprofen, Paracetamol, Phenazone				

Personal care products (PCPs) detected in waters include:

- DEET – N,N-diethyl-meta-toluamide, which is the most frequently used active ingredient in insect repellents,
- Parabens – alkyl esters of p-hydroxybenzoic acid, which are used for decades as bacteriostatic and fungistatic agents in cosmetics, drugs and foods,
- Triclosan, a bacteriocide and antifungal agent used in household products (e.g., toothpaste, soap),
- Polycyclic musks, such as tonalide and galaxolide which are used as fragnances in washing and cleaning agents and PCPs,

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- UV filters/sunscreen, including benzophenones and methoxycinnamates,
- Caffeine and nicotine: substances connected with the modern lifestyle and way of living.

Pharmaceuticals and PCPs are the more frequently detected groups of ECs in surface and groundwater (Lapworth, Baran, Stuart, & Ward, 2012). Among them, common substances in groundwater are anti-inflammatory drugs (ibuprofen, ketoprofen, diclofenac), three antibiotics (triclosan, sulfamethoxazole, lincomycin and partially erythromycin), five analgesics (paracetamol, ibuprofen, phenazone, propyphenazone and salicyclic acid), one anti-epileptic (carbamazepine), one barbiturate (primidone), a commonly used insecticide (DEET), an X-ray contrast agent (iopamidol) and clofibric acid (a metabolite of the lipid regulator clofibrate).

Caffeine and nicotine are probably the two most commonly detected lifestyle compounds in water produced by human activities (Loos et al., 2010). Sulfamethoxazole, ibuprofen, carbamazepine and caffeine are more frequently detected in Europe than in the USA (Lapworth et al., 2012). Other common compounds are fragrances (e.g., galaxolide and tonalide) and non-steroidal pharmaceuticals such as ibuprofen, paracetamol, naproxen, diclofenac, clofibric acid and fluoxetine (Caliman & Gavirilescu, 2009). It should be mentioned that this group of pharmaceuticals also contains drugs used for non-medical applications, ie., cocaine, heroin, cannabinoids (marijuana, hashish) and amphetamine-like stimulants (Castiglioni, Zuccato, Chiabrando, Fanelli, & Bagnati, 2008). These compounds have not been studied extensively and little is known concerning their presence in the environment. Veterinary drugs group includes medicines used exclusively for veterinary purposes. Examples of these drugs are sulfamethazine, which is often detected in groundwaters in Europe and in the USA, as well as monensin and tylosin (Lapworth et al., 2012).

Hormones and Steroids

This category of ECs includes natural endogenous steroids, such as sex hormones (androgens such as androstenedione and testosterone, oestrogens such as oestrone, oestriol and progesterone), phytoestrogens, faecal indicators and plant sterols, which are excreted from the human body. Synthetic androgens include oxandrolone, nandrolone and synthetic oestrogens (xenoestrogens) such as diethylstilbestrol, which are used as contraceptives. Natural and synthetic steroids and hormones occur in wastewater influents and effluents as free active steroids. Most of these compounds are considered as EDCs. Estrone, E2, NP and bisphenol A are the four most frequently detected compounds in groundwaters (Lapworth et al., 2012).

Perfluorochemicals (PFCs)

Perfluorochemicals are anthropogenic chemical compounds used for the manufacturing of products resistant to oil, grease, heat, water and stains. PFCs surfactants are bioaccumulative, persistent, toxic, and ubiquitous contaminants (Nguyen, Reinhard, & Karina, 2011). Their basic chemical bond (C-F) is one of the strongest chemical bonds. These compounds have been detected in many environmental samples including surface waters, groundwater, drinking water, wastewater and sediments. Their impact on human health and ecotoxicological effects are not yet well known, although they are suspected as EDCs (Clarke & Smith, 2011). The most common substances in the environment are perfluoroalkyl sulphonates (PFASs) (e.g., perfluorooctane sulphonate – PFOS) and perfluoroalkyl carboxylates (PFACs) (e.g., perfluorooctanoic acid – PFOA), both synthetic chemicals. It is reported that effluent concentrations of

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PFOA and PFOS were higher than influent ones in wastewater treatment plants, which indicates possible degradation of other fluorinated organic compounds into PFOA and PFOS during the treatment processes (Clarke & Smith, 2011).

Nanomaterials

Nanomaterials are materials with a structure designed at the nanoscale or sub-microscale (1-100 nm) with high strength, low permeability, thermal stability and high conductivity. Their chemical composition varies and may include nanotubes, metal oxanes, nanosliver, TiO_2 nanoparticles, nanogold and quantum dots. Engineered nanomaterials are used in PCPs, e.g., in cosmetics for sun protection and in hip replacement materials (Colvin, 2003). Although nanotechnology could bring significant societal benefits, there is a certain risk associated with the release of nanoparticles to the environment and questions arise concerning their possible effects on human health. These materials have relatively large active surface and high chemical reactivity and biological activity which means that they can enter the body and the cells easier than other larger particles. However, related information about their potential toxicity or the damages they can cause is still limited (Wiesner et al., 2009).

Flame Retardants

These compounds are used in plastics, textiles and furnishing foam in order to reduce their flammability by interfering with polymer combustion. They can be halogenated or brominated compounds. Polybrominated diphenyl ethers (PBDEs) flame retardants are bioaccumulative and are considered as EDCs (Rahman, Langford, Scrimshaw, & Lester, 2001). PBDEs have been used in plastics, textiles, electronic circuitry among other materials.

Pesticides

Pesticides are often detected in groundwater at trace concentrations for many years now. They can be synthetic chemicals or natural compounds. They are used in agriculture to control weeds, pests and diseases in crops. Over the last years, compounds such as atrazine which were considered to pose a high risk to the environment are no longer in use, although the compounds used to replace them (e.g., diuron) could also have a negative impact. Currently, pesticides of special interest are metaldehyde which in some cases has been detected above the EU drinking water limit for pesticides (Environmental Agency, 2010).

Industrial Compounds

This group includes substances used in industrial processes and production, especially in the chemical industry. Two known EDCs, bisphenol A and the metabolite NP, the fire retardant (tri(2-chloroethyl) phosphate) and the musk galaxolide are among the most frequently detected substances, especially in groundwaters (Lapworth et al., 2012). Nonylphenol and bisphenol A present the highest detection frequency in Europe (11% and 39.6%, respectively) compared to the USA in wastewater influents and effluents and in sewage sludge, with higher values occurring in Austria for both compounds. It is reported that wastewater treatment processes achieve high removal rates of bisphenol A (up to 99%) through biodegradation (Clarke & Smith, 2011). Polychlorinated alkanes (PCAs) are industrial chemicals detected

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in treated wastewater effluents at trace levels, as well as in sewage sludge. However, little is known concerning their impact on human health and the environment. MTBE (methyl tertiary-butyl ether) and BTEX compounds (benzene, toluene, ethylbenzene, m-, o-, and p-xylene) are frequently detected in groundwater (van Afferden et al., 2011; Stefanakis et al., 2013). They are considered as posing potential risks for human health and drinking water contamination and MTBE is classified as a potential carcinogen.

SOURCES OF EMERGING CONTAMINANTS

Currently, the role, the importance and the related contribution of the various sources to the occurrence and transport of ECs in the environment are under investigation and many related projects are running to determine the concentrations and fate of various ECs. Most of the available information in the literature has to do with the so-called priority pollutants such as pesticides, heavy metals and other regulated priority organic pollutants, thus, respective information for emerging contaminants is relatively limited, although information about some pharmaceuticals and other ECs was published during the last 10 years. ECs can be found in water in relatively low concentrations (ng/L to μg/L). This means that the detection of ECs could be challenging in practice, given that analytical measurements are still time consuming, expensive and require the use of sophisticated advanced equipment. However, currently available techniques such as liquid chromatography and mass spectrometry allow the detection and study of many ECs in the environment, mainly in surface waters and treated wastewaters

ECs have been detected in both surface and groundwaters. Their concentrations in surface waters is usually lower than those measured directly at the outflow of wastewater and sewage treatment plants, due to dilution and natural attenuation processes (biodegradation, photolysis, volatilization, sorption) or combination of all of them (Gurr & Reinhard, 2006; Pal, Gin, Lin, & Reinhard, 2010). Local and regional usage frequency and dosage of pharmaceuticals and PCPs, as well as the effectiveness of wastewater treatment plants affects the concentration level that reaches the surface water body. Range and concentrations of ECs measured in surface waters are usually higher than respective ones in groundwaters, since surface waters are the direct receiver of effluents from wastewater treatment plants and the residence times occurring in surface waters are shorter than in groundwaters (Barnes et al., 2008). Generally, current knowledge and data show that the levels of ECs concentrations in groundwater are low enough so that their presence would not have any toxic or other harmful effects on the environment, due to natural attenuation processes and dilution mechanism. However, it should be noted that increased concentrations could be found in groundwater if the aquifer is close to pollution sources. It is reported that the most frequently substances detected in groundwater are carbamazepine, sulfamethoxazole, ibuprofen, caffeine, diclofenac and bisphenol A (Lapworth et al., 2012).

The presence, distribution and fate of the various ECs in the environment and the aquatic ecosystems are affected by many factors. The source type controls the exposure levels and the properties of the substance. Physicochemical characteristics including water solubility, polarity, volatility etc., as also environmental parameters such as temperature, pH, organic matter content, precipitation and altitude-latitude among others, also play an important role in the transport and transformation of ECs. These properties are crucial since they define the life time of an EC in the environment. ECs can be soluble in water, which means that they can be introduced in the aquatic environment through run-off. Polarity expresses the tendency of a chemical compounds to be in the organic or aqueous phase, thus, compounds with high octanol-water partition coefficient (K_{ow}) tend to bioaccumulate in organisms.

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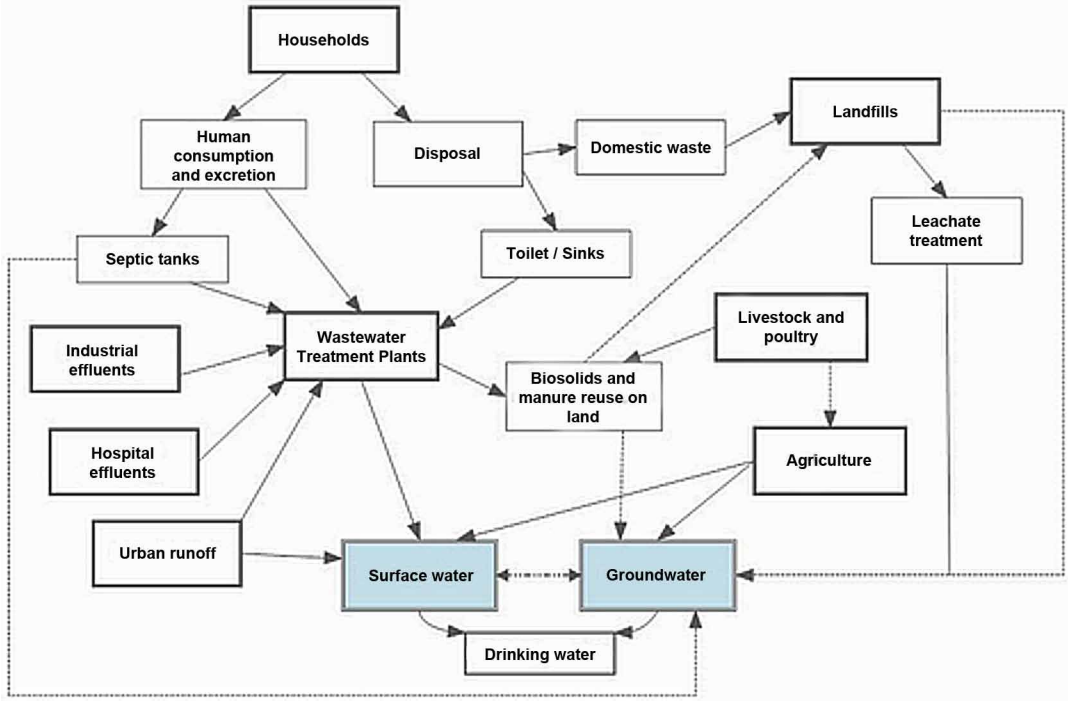
Figure 1. Sources and pathways of emerging contaminants in the environment.



Point Sources

ECs sources vary in both number and nature. They can be classified into point-sources and diffuse pollution sources (Lapworth et al., 2012). Figure 1 presents schematically the various point and non-point sources of ECs.

Point sources include excretion in human and animal urine and feces, flushing of unused drugs, household uses and bathing. The major pollution point source is treated municipal and industrial wastewater at the outflow of wastewater treatment plants in urban, industrial as also in agricultural areas (Glassmeyer et al., 2005; Pal et al., 2010; Lapwoth et al., 2012). Due to their high solubility, low volatility and – for many of them – low degradability, ECs can pass through the different treatment processes. Conventional biological wastewater treatment plants (e.g., activated sludge systems) and combined sewage-stormwater overflows treatment facilities have been proved to provide inadequate level of treatment for most of these contaminants, which means that ECs are still present – at low concentrations – in the effluent of these treatment facilities (Asano, Burton, Leverenz, Tsuchihashi, & Tchobanoglous, 2007; Stefanakis et al., 2014). Many parameters of ECs including their treatability in wastewater treatment plants, their persistence or their mobility are defined by their chemical properties (Clarke & Smith, 2011). Other ECs point sources are industrial facilities such as manufacturing factories, food processing plants, mining activities and landfill sites. Related data such as mass balance, flow levels and fate in the environment for most of the ECs are still limited. Generally, ECs sources could be summarized as follows (Kümmerer, 2009; Pal et al., 2010):

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- *Wastewater and sewage treatment plants*: residual concentrations containing hormones and drugs
- *Drug manufacturing industries*: industrial wastes containing residual drug concentrations and stormwater runoff carrying powdered drugs
- *Hospitals*: waste discharge and expired drugs
- *Livestock farms*: drugs and hormones injection to poultry and cattle
- *Aquaculture:* hormones used to feed fish and antibiotics added to food and water
- *Household outflows:* effluents containing used and expired drugs

Households are considered as important point sources of many ECs, especially of pharmaceuticals and PCPs (e.g., natural hormones, synthetic steroids). Expired or unused drugs in Europe are usually disposed via household solid waste or are flushed down in the toilet (Vollmer, 2010; Khan, 2012); for example, it is estimated that more than 30% of the pharmaceuticals sold in Germany and 25% in Austria are disposed this way (Kümmerer, 2008; 2009). Same results were also obtained in the UK and in the USA (Bound & Voulvoulis, 2005; Glassmeyer et al., 2009). In the UK, the disposal of unused and expired pharmaceuticals with household waste or through the sink/toilet was the dominant disposal route, while in the USA more than half of patients participated in a study flushed them in the toilet. Table 4 presents common pharmaceutical compounds found in wastewater in the UK, mainly originated from household effluents. These facts clearly show that introduction of ECs through households should be taken into account. In Europe, the EU Directive 2004/27 (European Commission, 2004) mentions that all EU member States should ensure the installation of appropriate collection systems for unused or expired pharmaceutical products, although household disposal routes are not yet illegal in Europe. Disposal of pharmaceuticals with household waste usually results in the occurrence of these compounds in leachates produced in landfill sites and, thus, contaminate groundwater if no treatment takes place.

Artificial recharge for maintaining and increase groundwater levels is considered as an effective strategy to counterbalance water losses through intensive abstraction of groundwater. However, recharge with treated wastewater (of both domestic and industrial origin) or urban and stormwater runoff poses the risk of re-introducing to the environment various chemical contaminants that might be still present in these waters (Díaz-Cruz & Barceló, 2008). Thus, this strategy may have adverse impact on the groundwater

Table 4. Excretions rates of unmetabolized active pharmaceutical compounds (DWI, 2007).

Compound	Pharmaceutical group	Parent compound excreted (%)
Atenolol	β-blocker	90
Amoxycillin	antibiotic	60
Bezafibrate	lipid regulator	50
Cetirizine	antihistamine	50
Felbamate	antiepileptic	40-50
Erythromycin	antibiotic	25
Diclofenac	anti-inflammatory	15
Ibuprofen	analgesic	10
Clofibric acid	active metabolite	6
Carbamazepine	antiepileptic	3

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quality and followingly on human health, since groundwater is often used as drinking water source. Furthermore, excess drinking water is also often used for recharge purposes. In this case and given that drinking water is usually pre-treated to reach drinking water standards, disinfection products such as trihalomethanes (THMs) and haloacetic acids which are formed during chlorination process can also reach surface and groundwater. It has been proved that some pharmaceuticals and other organic chemicals present in treated wastewater effluents such as carbamazepine, sulfamethoxazole, benzophenone, 5-methyl-1H-benzotriazole, N,N-diethyltoluamide, tributylphosphate, tri(2-chloroethyl)phosphate and cholesterol, can reach the aquifer when used for recharge (Cordy et al., 2004).

The same risk also exists even then surface waters are used for recharge purposes (Díaz-Cruz & Barceló, 2008). A study in Berlin, Germany showed that pharmaceuticals such as carbamazepine, primidone, bezafibrate, indomethacine, diclofenac and propyphenazone, and two drug metabolites (clofibric acid and 1-acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide (AMDOPH)), were detected in water from recharging ponds and wells, while six of them were found to be persistent in a water recharge plant of the lake Tegel (Heberer & Adam, 2004; Heberer, Verstraeten, Meyer, Mechlinski, & Reddersen, 2011).

Hospital wastewater outflows are another source of ECs including residual concentrations of typical prescription medicines as well as pharmaceutical substances, X-ray contrast media, which represent the main fraction of the adsorbable organic iodine in waters, solvents and disinfectants (Ternes & Hirsch, 2000; Verlicchi, Galletti, Petrovic, & Barceló, 2010). Hospital wastewater contains higher concentrations of pharmaceutical compounds than municipal wastewater, but the volumetric flow of this wastewater source is far smaller. X-ray contrast agent was detected in extracted raw water from local wells in lake Tegel in Berlin, Germany where artificial recharge of the aquifer takes place (Grünheid, Amy, & Jekel, 2005). Some substances present in hospital wastewater (e.g., iopromide, iopamidol, diatrizoate) are very persistent in the aquatic environment and have also been detected in groundwater (Ternes & Hirsch, 2000; Sacher, Lange, Brauch, & Blankenhorn, 2001; Schulz, Loffler, Wagner, & Ternes, 2008).

Landfill sites are also important sources of ECs (e.g., polychlorinated compounds), specifically of those found in groundwater. Contamination of local aquifers in landfill sites is known for many years now due to parameters such as false choice of the location or bad design, although today the vast majority of landfills in western countries do not raise such issues. However, such problems still occur in many countries. For example, groundwater contamination with pharmaceutical substances in landfill areas has been detected in Croatia (Ahel, Mikac, Cosovic, Prohic, & Soukup, 1998) and in Denmark (Holm, Rügge, Bjerg, & Christensen, 1995), as well in the USA (Buszka et al., 2009).

Swine farms and livestock farms represent point sources for estrogenic compounds in the environment. It is reported that the effluent of a treatment plant for swine and dairy wastewater contains estrogens (e.g., E1, E2, oestrone, testosterone, androstenedione) at levels higher than the respective ones in municipal wastewater treatment plants (Kolodziej, Harter, & Sedlak, 2004; Furuichi et al., 2006). Concentrated animal feeding operations (CAFOs) also produce contaminants such as veterinary antibiotics due to waste production and waste storage in lagoons or waste land application, which poses the risk of leakage to the groundwater (Bradford, Segal, Zheng, Wang, & Hutchins, 2008; Bartelt-Hunt, Snow, Damon-Powell, & Miesbach, 2010).

Although often disregarded, water contamination from onsite wastewater disposal systems – mainly septic tanks – also takes place, especially in areas where the groundwater level is high enough. Septic tanks are widely used which makes it difficult to monitor and estimate the actual contamination risk posed from these point sources (Pal et al., 2010). A Canadian study reported that pharmaceutical substances (i.e., gemfibrozil, ibuprofen and naproxen) were detected in samples taken from septic tanks

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at elevated concentrations (Carrara et al., 2008). This means that leakage from septic tanks may result in groundwater contamination with ECs. PCPs concentrations have also been related with septic tanks leakage (Swartz et al., 2006). However, sampling close to the sources (i.e., households) could partially explain the relatively high concentrations, while the general low leakage volumes of septic tanks probably do not produce high loads of ECs.

Non-Point Sources

Diffuse pollution sources of ECs are more difficult to be identified since they can be extended over large geographical areas, which means that the actual definition of the exact sources is difficult (Lapworth et al., 2012). This category includes sources such as stormwater runoff, terrestrial runoff from roads, urban areas, highways and agricultural land. Compared to point-sources, diffuse sources usually discharge to the environment lighter loads of pollutants (Lapworth et al., 2012).

The use of pesticides in agriculture is considered as the major contamination source. For example, pesticides (two metabolites of DDT) and herbicides (bentazone and mecocrop), as well as flame retardant compounds (tris(2-chloroethyl)-phosphate and tris(2-chloroisopropyl)-9-phosphate) were detected in Lakes Tegel and Wannsee in Berlin, Germany, whose water were used for artificial recharge of the local aquifer (Heberer et al., 2004). Agricultural activities also account for various ECs including veterinary medicines, hormones, natural toxins and transformation products of synthetic chemical substances which are used in agriculture.

Chemical contaminants can stick to sludge particles in the activated sludge system. Since a portion of the daily sludge production in wastewater treatment plants is removed at a daily basis and it is often reused in many areas as a fertilizer in agricultural land, ECs can be re-introduced this way to the environment. When biosolids from wastewater treatment plants are used for land application, ECs in biosolids can potentially reach and contaminate groundwater (Topp et al., 2008; Clarke & Smith, 2011). Two halogenated hydrocarbons (polychlorinated alkanes and perflurochemicals) are reported as potential important groundwater contaminants due to biosolids application to soils and surface runoff (Clarke & Smith, 2011).

Impacts of Emerging Contaminants Presence in the Environment

The development of analytical instrumentation for the detection of ECs in surface and groundwater allowed for the improvement of ECs measurement and assessment in the environment. It has been shown that surface and groundwater are contaminated with a large variety of ECs often at significant concentrations which could potentially represent major environmental risks. Despite the advances in water and wastewater treatment processes and methods, complete elimination of ECs does not take place in water/wastewater treatment facilities, thus, ECs concentrations are still reaching the water bodies (Kümmerer, 2009; Houtman, 2010).

Chronic effects of certain ECs have been studied in the past, e.g., short-term effects of pharmaceuticals on anthropods, but the concentrations tested were usually higher enough that the typical ones found in environmental samples. Thus, in order to obtain more realistic results, concentrations closer to the ones measured in the environment are today more often used. In such tests the species used and their respective sensitivity is also important. For most of the ECs, related risk assessment and ecotoxicological effects are not precisely identified due to the lack of data, although during the last 10 years the investigation of

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the ecotoxicological effects of ECs was significantly increased. As already mentioned, until today only 8 pharmaceutical compounds are under review for their characterization as possible priority substances or priority hazardous substances; a number very small compared to the total number of pharmaceutical compounds or other contaminant groups under review process. The EU has published guidelines for the environmental risk assessment (ERA) of human medicinal products, which is required by all manufacturing companies during the medicine production (EMA, 2006; 2013). ERA in Europe includes three phases: initial screening (estimation of the exposure levels for a trigger value of 0.01 μg/L), fate evaluation of the medicinal product and potential effects on the aquatic environment and refinements and extended risk assessment.

A web-based database has been created which summarizes ecotoxicological data of the most common ECs (Molander, Agerstrand, & Ruden, 2009). A preliminary risk assessment database for the most common pharmaceuticals and related risks to the environment is also reported in the literature (Cooper, Siewicki, & Phillips, 2008). Physicochemical and toxicological data, as well as the level and extent of environmental transport, fate and aquatic toxicity were used to identify potential risks. This study showed that drugs from the central nervous system, cardiovascular and anti-infective classes possess the highest risk to the environment. Anti-infectives are the most toxic compounds, thus, respective risks from these substances are on top. However, there are still uncertainties concerning the long-term impact of ECs on human health, aquatic and terrestrial wildlife and ecosystems, especially for long-term exposure even at low concentrations (Li, Zhu, Ng, & Tan, 2014). Furthermore, most of respective scientific studies focus on certain groups such as antibiotics, hormones or antineoplastics, but other groups such as antiulcerants and non-prescribed drugs also possess potential negative impact on the environment.

It is known that some ECs can have biological effects on ecosystems and aquatic life. The aquatic toxicity of four different ECs groups (antibiotics, antineoplastics, cardiovascular drugs and sex hormones such as estrogens and androgens) has been evaluated and it was found that daphnids fish and algae were susceptible to these pharmaceutical compounds, while antibiotics and sex hormones were reported as the most dangerous substances for human health and aquatic life (Sanderson, Brain, Johnson, Wilson, & Solomon, 2004). Aquatic organisms can be more sensitive than humans to the presence of ECs in water, since many chemical contaminants can interfere with the normal function of the endocrine system of many aquatic and terrestrial organisms. This interference can have negative impacts on the wellbeing of the organisms including reduced fertility, reproductive dysfunction and population decline (Falconer, Chapman, Moore, & Ranmuthugala, 2006).

It is believed that the presence of ECs in the environment poses a risk mainly for the natural water bodies and the respective ecosystems and aquatic life rather than for human health. Aquatic organisms can be more sensitive than humans to the presence of ECs in water, since many chemical contaminants can interfere with the normal function of the endocrine system of many aquatic and terrestrial organisms. Some pharmaceuticals, PCPs, domestic and industrial cleaning agents, fire-retardants and pesticides are considered as EDCs. Pharmaceuticals such as sex hormones, veterinary growth hormones and antibiotics and glucocorticoids are known for their endocrine disrupting properties, although tests for more pharmaceutical compounds are still ongoing to identify other substances with these properties. EDCs can interfere with the "*synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behavior*" (USEPA, 1998). According to the Endocrine Society, EDCs are "*exogenous chemicals or mixture of chemicals that interfere with any aspect of hormone action*" (Zoeller et al., 2012). However,

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EDCs may have impact on humans as well, with suspected effects being malformations of newborn infants, abnormal and/or low sperm counts, disorder of the thyroid functions and possible breast-testicular or prostate cancer.

Antibiotics presence in treated wastewater effluents and, generally, in aquatic environments may enhance the resistance among microorganisms and can have a significant impact on the microbial ecosystems. They can interfere with the microbial community structure and affect this way the microbial populations and the ecological function of the aquatic ecosystem (Baquero, Martínez, & Cantón, 2008). It is reported that the presence of ECs in the environment could enhance the bacterial antibiotic resistance due to the continuous antibiotics release to waters (Guardabassi, Petersen, Olsen, & Dalsgaard, 1998). Antibiotic resistant bacteria and antibiotic resistant genes are often detected in wastewater, even at higher concentrations than in surface water, which means that wastewater treatment facilities contribute to the dissemination of these antibiotic resistant bacteria (Bouki, Venieri, & Diamadopoulos, 2013). Bacterial organisms of different origin (e.g., human or animal) in water can be mixed and develop resistance through the exchange of genes and different genetic platforms (Baquero et al., 2008). Antibiotic resistant bacteria such as enterococci, *Klebsiella pneumonia* and *Pseudomonas* spp, represent potential threat for human and animal health and can create problems in infection control. Studies have shown that even pathogenic bacteria such as *Aeromonas* and *Pseudomonas* spp can develop resistance to one or more antibiotics (Blasco, Esteve, & Alcaide, 2008). Incidents such as clinical infections, diseases and even death have been associated with resistant bacteria (Bouki et al., 2013). For example, few years ago where was an outbreak in Europe, mainly in Germany, of bloody diarrhea and haemolytic uraemic syndrome (HUS) due to the multi-resistant enterohaemorrhagic *E. coli* (EHEC), which resulted in the infection of thousands of people (877 HUS case with 32 deaths and 3,043 cases of EHEC with 16 deaths) (Rubino, Cappuccinelli,& Kelvin, 2011).

The presence of pharmaceuticals and PCPs in drinking water appears to be a crucial issue. Contamination of water supplies (surface water bodies and groundwater) is directly connected with the drinking water quality. It is not yet clearly and unanimously accepted that these compounds represent a risk for human health. Typical pharmaceuticals concentrations detected in drinking water are usually lower than 0.05 μg/L, lower enough than the lowest therapeutic doses. Thus, exposure levels to individual compounds in drinking water are not considered as a direct threat to human health and there are not regulated guidelines for these compounds (WHO, 2011), although there is an increasing concern due to the continuous and unlimited exposure to pharmaceuticals. However, regular monitoring of pharmaceuticals should not be neglected, especially in regions where local conditions may imply possible higher concentrations in local waters. Although pharmaceuticals, PCPs and EDCs are widespread substances, their concentrations in drinking waters (usually at the level of ng/L) might not be of significant risk for human health (Snyder, 2008; Kümmerer, 2009). On the other hand, potential environmental effects of pharmaceutical metabolites are not known (Hernando, Rodríguez, Vaquero, Fernández-Alba, & García, 2011). However, given that the exact fate of these numerous compounds in water and during water treatment processes are not yet known in detail and that the existence of new chemicals is continuously reported, precaution measures should not be neglected. In addition, possible interactions and respective combined effects of multi-component mixtures of ECs in the environment should be further investigated, since combined presence might have different effects than the presence of single compounds. It is practically impossible to estimate and evaluate the risk for each one of the thousands of chemical compounds and medicines that have been detected in waters, thus, the focus should be given to those substances that are known for their harmful effects. This is why risk management and risk assessment studies are of high importance.

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Current European Legislation

The main issue with emerging contaminants is that the majority of them still remain unregulated. It is only during the last years that steps forward were taken for the regulation of these substances in national and international legislation. The Water Framework Directive (WFD) published in 2000 (European Commission, 2000) is the main European Water Policy Instrument for the protection of European waters and aims at achieving good surface water chemical status. This Directive includes strategies and measures for the mitigation of pollution caused by chemical compounds listed as priority substances. The Decision 2455/2001 (European Commission, 2001) presents the first list of priority substances which were considered as the most dangerous for the aquatic environment. The Directive on Environmental Quality Standards 2008/105 (known as the Priority Substances Directive; European Commission, 2008) set the quality standards for 33 priority substances and 8 other pollutants that are persistent, bioaccumulative and toxic.

However, gradual realization of the new compounds that are detected in waters resulted first in the review of the above mentioned list in 2012 and then in a proposal for the addition of 15 new compounds to this priority list (European Commission, 2012), while for the first time three pharmaceutical compounds (from oral contraceptives to hormone medications) were included among the regulated substances in EU countries: the endocrine disruptors 17 alpha-ethinylestradiol (EE2), 17 beta-estradiol (E2) and diclofenac, which are used in the drug manufacturing, were regulated as potential hazards for humans and fish reproduction. Current and continuous pressure towards the regulation of more toxic chemicals and substances is expected to result in the regulation of additional chemicals in the near future. Other proposed substances to be included in the regulated list are:

- Aclonifen, bifenox, cypermethrin, dicofol, heptachlor and quinoxyfen, which are used for crop and plant protection,
- Cybutryne, dichlorvos and terbutryn, which are used for coastings and surface protection,
- Perfluorooctane sulfonic acid (PFOS) and hexabromocyclododecane (HBCDD), which are chemicals used in the industry,
- Dioxin and dioxin-like PCBs, which were used in the past in electronic equipment and now are produced from combustion.

EU is willing to adopt stricter environmental standards for newly-identified compounds by 2018. Each member state is required to submit a monitoring and measuring program to the European Commission, in order to achieve a good chemical status of the surface water by 2012 for the currently known substances and by 2027 for newly-identified substances. Given that the risk levels related with ECs are varying from growing risk (for recognized substances) to future/unidentified risk (for new chemicals-drugs), the need for additional monitoring programs is necessary. The WFD priority list of the 33 substances aims at exactly that point.

The significance of these pollutants surely is today better understood than it used to be 10-15 years ago. It is not accidental that the EU launched last year a new program on emerging water contaminants aiming at the development and improvement of regulatory issues concerning water quality and use and the promotion of research towards the data collection and future implementations of new directives for water pollution prevention. It is reported that in the EU the number of registered chemicals exceeds 100,000 and 30-70,000 of them are used on a daily basis (EINECS, European Inventory of Exist-

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ing Chemical Substances; URL1; Loos et al., 2009). The new European Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH; REACH, 2006), which is in force since 2007, aims at providing a deeper understanding of the chemical pollution in Europe by making the industry responsible for the assessment and management of risks related with chemicals through the implementation of environmental risk assessments (URL2). The REACH regulation dictates that compounds associated with serious and irreversible health impacts (e.g., carcinogenicity, mutagenicity and reproductive health effects) should be categorized as Substances of Very High Concern (SVHC), subjected to formal authorization and high levels of control. The required criteria for assignment as SVHC include considerations of severity of adverse health effects, their reversibility, the latent period between exposure and the manifestation of adverse effects, the impact on life quality and the ability to identify a safe exposure level. Also, the societal cost of the anticipated adverse health effects is taken into consideration. It should be noted that pharmaceuticals release to the environment from manufacturing industries is already regulated in the United States and is not considered as a major contributor to the environmental pollution in this country (Bell et al., 2011).

A specific environmental assessment system for pharmaceutical substances was developed in Sweden by the Environmental Department of the Stockholm County Council in 2003. By 2005, the classification included an environmental risk assessment carried out by the Swedish Association of the Pharmaceutical Industry. According to the Swedish model, the pharmaceuticals are classified based on their inherent capacity to affect the environment (environmental hazard) and on the toxicity risk to the aquatic (environmental risk). This classification is used in considering the environmental impact of the pharmaceuticals on the so called Wise List, a list of recommended pharmaceuticals for common diseases in Stockholm County Council, issued by the Drug and Therapeutics Committee.

Increasing focus is gradually given on the endocrine disrupting compounds (EDCs), a group which includes a wide range of emerging contaminants. Since November 2011, a special group (Endocrine Disrupters Expert Advisory Group) of the European Commission deals with the scientific aspects and the identification of EDCs, in order to support and provide information to the European Commission concerning the criteria adoption for EDCs identification and assessment for any future regulatory framework (Munn & Goumenou, 2013). The EU introduced a priority list of chemicals, under the frame of the EU-Strategy for Endocrine Disrupters, which includes 564 chemicals suspected for endocrine disrupting activity. Out of them, 147 compounds are likely to be persistent in the environment and of these, 66 chemicals have a proven endocrine disrupting activity, including 60 chemicals that considered likely to be exposed to humans. Further 52 chemicals were recently identified as potential EDCs and added to the list.

FUTURE RESEARCH DIRECTIONS

It is anticipated that new chemicals will continue to be identified. Future research should focus on the identification of those chemicals that will pose the greatest threat for humans and ecosystems and limit the potential risks. The new scientific targets should then be the identification of new contaminants and their potentially new sources and pathways and the continuous development of the detection techniques and analytical instrumentation down to trace levels. Additionally, drinking water and wastewater treatment processes should further be improved and – if necessary – re-designed in order to effectively remove as many as possible ECs.

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It is reported that compounds such as diazapem, diclofenac, estradiol, fluoxetine and others have not been detected in the effluents from drinking water plants, due to the effective treatment with ozonation, activated carbon filters or membranes, while UV and chlorination were not of the same performance (Snyder, 2008). Advanced water/wastewater treatment processes such as the above mentioned are used to further treat the water effluents, eliminate (as far as possible) the concentration levels reaching surface and groundwater and reduce the related environmental risk. Many technologies have been tested and applied, however there are still many limitations (Kümmerer, 2009). The treatment efficiency of the various methods and technologies varies significantly, given that the treatment depends on the physicochemical characteristics of the compounds (e.g., hydrophobicity), as well as on operation parameters such as temperature, hydraulic retention time and solids retention time. A good example of the complexity in the removal efficiency of ECs is pharmaceutical substances. Most of them are hydrophobic, thus, they tend to cluster and sludge sorption processes may not be very effective. Although most of advanced treatment processes (i.e., oxidation, ozonation, membrane filtration) are very effective in the removal of specific compounds, the main limitation is that none of the available technologies is effective for the removal of mixture of ECs, i.e, most of the technologies are composition/compound-dependent (Schriks, Heringa, van der Kooi, de Voogt, & van Wezel, 2010). Furthermore, it is known whether these technologies will be effective for the future compounds to be identified.

Current fundamental knowledge over the anthropogenic release of ECs to the environment, their possible (bio) transformations and the potential threat they represent to human health and the ecosystems is still incomplete. Although progress in analytical instrumentation allowed for the detection of numerous ECs in surface and groundwater and the identification of the various sources, human and ecotoxicological effects of the emerging environmental contamination remains a challenge. Quantification of exposure levels is difficult due to the insufficient understanding of the natural attenuation processes of ECs once introduced into the environment. Current available data are scarce and do not allow for global conclusions. Effects of long-term exposure and respective impacts of single or even multiple ECs on aquatic life cannot be safely evaluated, while the extrapolation of toxicological data obtained at higher concentrations than the ones occurring in nature does not provide the necessary credentials. In a few words, current knowledge concerning the fate of most of the ECs in the environment does not allow for the prediction of concentrations, exposure levels and effects. Thus, regulation of these compounds is practically difficult since there are not yet recommended limit values. Field studies as well as lab studies are needed in order to deepen our understanding of ECs fate and transformation pathways. Moreover, since the performance of wastewater treatment plants in resistant bacteria removal is still not reliable, further investigations should be carried out to give answer to many uncertainties which still exist, e.g., it is not known which bacteria are subjected to possible mutations and for which antibiotics.

An important parameter which should be further investigated is the potential effects caused by long-term exposure to some compounds. For example, although available risk assessments indicate that trace level concentrations of pharmaceuticals in drinking water do not represent a significant risk for humans, it is not known if this is also valid for long-term exposure even to these low concentrations, as well as the combined impact due to exposure to mixtures of pharmaceuticals. Of course, the necessary prerequisite for all these actions and measures is that there will be extended monitoring programs, which means increased costs for infrastructure and human resources, as well as the development of standardized sampling and analysis protocols which are up to day not available.

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These indicate that there is the need for the development of prediction models for the description of the fate, transport and transformations of ECs in the environment. Further implementation of ecotoxicological studies, toxicity tests and related risk assessment is needed for the development of more reliable databases. Data from these studies are necessary to be listed in databases which will allow the correlation of ECs occurrence in the environment, their concentrations and their effects and the identification of those compounds with the highest risks and the greater threat for the ecosystems. Such data will also assist in the determination of multiple sources. It is also crucial that respective studies will cover larger geographical areas to include regions such as African and South America countries, given that currently most of the available data are derived from Central Europe and North America.

CONCLUSION

Emerging contaminants are widely present and distributed in the aquatic environment. They include different groups of contaminants such as pharmaceuticals, personal care products and fragrances, industrial additives, pesticides, nanomaterials, flame retardants and surfactants, as well as their metabolites and hormones. Many of these compounds are not effectively removed in wastewater treatment plants and residual concentrations are reaching surface and groundwaters. Some ECs are known for their toxic effects and their endocrine disrupting activity. Most commonly ECs detected in Europe are carbamazepine, caffeine, bisphenol A, ibuprofen, triclosan, galaxolide, iopamidol, DEET, phthalates, phenyl ethoxylates, and sulfamethoxazole, among others. There is a variety of point and non-point sources which continuously introduce ECs into the environment.

Current knowledge over the numerous ECs, their environmental fate and their possible effects on human health and the aquatic life is relatively limited and scarce and demands a deeper understanding of their properties and their distribution and transformations in water. Although research conducted during the last 10 years gave a better insight into the risks associated with many ECs such as pharmaceuticals, there are still knowledge gaps concerning the effects of long-term exposure, especially for mixtures of chemical compounds. Future scientific targets should be the identification of new emerging chemicals, the implementation of lab and field studies along with model development to determine their occurrence, fate and behavior in the environment and development of integrated strategies in order to reduce their environmental input. Since there are thousands of ECs present in water, it is practically very difficult, economic infeasible and environmentally unsustainable to implement programs for the detection, risk assessment and removal of all of these substances. The goal is to distinguish the most significant compounds, in terms of related risk for human health and aquatic life, and focus on them, which is the optimal way of using available resources. According to WHO (2011), the key principle in water safety plans is to take into account the whole life cycle approach of the compounds, i.e., their production, consumption/usage and disposal routes.

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KEY TERMS AND DEFINITIONS

Bioaccumulative: Accumulation of a contaminant by an organism at a rate which exceeds the respective extraction rate of the contaminant from the organism.

C-F: Chemical bond of carbon and fluoride.

DDT: Dichlorodiphenyltrichloroethane, a known insecticide.

DEET: N,N-Diethyl-meta-toluamide or diethyltoluamide, common ingredient used in insect repellents.

EDTA: Ethylenediaminetetraacetic acid, used in the industry (e.g., to dissolve limescale) and in medicine and cosmetic industry.

Polarity: Chemical term, which describes the status of electrons sharing between bonding atoms.

Solubility: The property of a liquid (or solid or gaseous) chemical substance (i.e., contaminant) to dissolve in a liquid, solid or gaseous solvent to form a homogeneous solution.

Volatility: The tendency of a substance (i.e., contaminant) to vaporize.

UV: Ultra-violet radiation.

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Section 2

Development and Design Methodologies

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Chapter 9
Integrated Leachate Treatment Technology

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ABSTRACT

In this chapter, the performance of combined treatment of municipal landfill leachate is reviewed. Although individual physico-chemical treatments are suitable for the removal of heavy metals and hydrolyzation of some organic compounds, a combination of two physico-chemical treatments or physico-chemical and biological is required for optimum treatment of stabilized landfill leachate. A combination of two physico-chemical treatments can give optimum results in removal of recalcitrant organic compounds from stabilized leachate, as reflected by a significant decrease of the COD values after treatment. On the other hand, a combination of physico-chemical and biological treatments is required to achieve effective removal of NH3-N and COD with a substantial amount of biodegradable organic matter. In many cases, physico-chemical treatments are suitable for pre-treatment of stabilized leachate. The objective of this paper is to highlight various types of integrated leachate treatments as it has been difficult to get optimum efficiency from single approached treatment.

INTRODUCTION

Over the past 20 years (1983-2005), numerous research studies have been carried out worldwide in the treatment of stabilized leachate using various types of individual and/or combined physico-chemical and/or combined physico-chemical and biological technologies (Kurniawan et al., 2006). Due to the high ratio of COD/BOD, ammonia nitrogen (NH_3-N) and heavy metals in leachate, there are major difficulties presence in treating leachate. Most of the methods used for landfill leachate treatment include coagulation/flocculation, adsorption, membrane filter, sedimentation, air stripping (Marttinen et al., 2002; Bohdziewics et al., 2001; Trebouet et al., 2001). A combination of physical/chemical and biological methods is

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almost necessary for the efficient treatment of heavily polluted leachate (Rautenbach & Mellis, 1994). The selection of the most suitable treatment technique for leachate depends on the characteristics of landfill leachate, technical applicability and constraints, effluent discharge alternatives, cost effectiveness, regulatory requirement and environmental impact (Kurniawan et al., 2006).

Biological techniques can be effective in simultaneous removal of organic carbon and nitrogen for biodegradable (BOD5/COD) ratio > 0.3) landfill leachate. Biological treatment is commonly used for the elimination of the high concentration of BOD and COD due to its simple, reliable and cost effective (Uygur & Kargi, 2004). The application of biological process alone, for example, cannot eliminate the refractory organics and residue. Therefore, additional treatment is often required (Izzet et al., 2003). Biological treatment is mostly the first stage in a combination with additional chemical/physical process. Methods used for biological leachate treatments are mainly aerobic, anaerobic and anoxic processes which are used in combination (Im et al., 2001).The ammonia nitrogen is identified as a major toxicant to microorganisms in the landfill leachate treatment. Therefore, pre-treatment prior to biological treatment is required to reduce high concentrations of NH_3-N (Daekeun et al., 2007). Pressure driven membrane filtration methods have been used along with biological treatment of landfill leachate (Bohdziewics et al., 2001). Prior to biological treatment, ozone pre-treatment should be employed in order to improve COD removal.

The physical/chemical techniques have been used widely for post treatment of biologically pre-treated leachate (Izzet et al., 2003). Physico-chemical treatments can act as a refining step for the stabilized effluent of biologically treated leachate. The use of combined coagulation/flocculation with other processes such as reverse osmosis (Izzet et al., 2003), photo-oxidation process and biological treatment (Kargi & Pamukoglu, 2003a) gave satisfactory results. After an aerobic pre-treatment, ion exchange normally achieves an excellent metal removal from effluents. Prior to ion exchange, appropriate pre-treatment system such as the removal of suspended solids from leachate is required (Kurniawan et al, 2006). Combination of anaerobic-aerobic and rotating biological contactor (RBC) systems in treating leachate improved the removal of organic matter (Park et al., 2001).

PHYSICAL AND CHEMICAL TREATMENTS

Physical and chemical processes include reduction of suspended solids, colloidal particles, floating material, color, and toxic compounds (Renou et al., 2008). Chemical and physical methods, such as chemical oxidation, adsorption, chemical precipitation, coagulation-flocculation, sedimentation/flotation and air stripping were applied successfully for the treatment of landfill leachate (Gandhimathi et al., 2013; Kurniawan et al., 2009; Papastavrou et al., 2009). The combination of the above process reduces the drawbacks of each single process. (Gandhimathi et al., 2013; Zazouli et al., 2012; Papastavrou et al., 2009).

Kilic et al., (2007) conducted a research on leachate treatment collected from Bursa landfill. In this study, the first alternative, pre-treatment with lime + ammonia stripping + neutralization were operated. This alternative achieved 19% COD removal. The second alternative included chemical coagulation + ammonia stripping + granular activated carbon (GAC) adsorption, achieved to produce an effluent COD of 160 mg/L, which complied with the Turkish discharge standard. Consequently, the second alternative was determined to be appropriate according to discharge standard. The following pre-treatment with lime, co-treatment with municipal waste water is appropriate for lower treatment costs.

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A study on the treatment of stabilized leachate was carried out by Zamora et al. (2000) by comparing coagulation – flocculation to the Fenton oxidation ($Fe(II)/H_2O_2$) process in combination with GAC adsorption. In the study, it was found that Fenton oxidation precursory treatment enhanced the adsorption by of GAC for COD removal (443 mg/g of GAC) at pH 4.0, in contrast to application of coagulation-flocculation only (193 mg/g of GAC) at pH 5.7. This may be because of the change of carbon compounds by oxidation to smaller particles than the original compounds, and as a result, the particles were capable of traversing the micropores of GAC. Rivas et al. 2004 also performed a study on the combination of coagulation-flocculation and Fenton oxidation process in treating leachate. The merit of utilizing this combined procedure was to clear the colloidal particles present in the leachate. The result showed that about 90% of COD were removed at an initial concentration of 7400 mg/L and pH 8.5 by using 0.8 g/L of $FeCl_3$.

Gunes et al., (2014), combined coagulation-flocculation and adsorption to treat stabilized landfill leachate. Ferric chloride and aluminium sulphate employed as a coagulant and granular activated carbon (GAC) and waste metal hydroxide (WMH) utilized as an adsorbent. The result indicated that the ideal working pH for the coagulants was at 9.5. The dosage was optimum at 2.4 g/L for both aluminum sulphate and ferric chloride. And of the two coagulants, $FeCI_3$ demonstrated the higher COD removal efficiency (40%) and exhibiting small seasonal variability according to ideal conditions. The adsorption experiment also showed that the ideal dosage for GAC was 18 g/L and WMH was 13 g/L, at the contact time of 12 h. At the optimum conditions of coagulation/flocculation/GAC adsorption and coagulation/flocculation/WMH adsorption, the COD removal efficiencies were 56-63% and 45-48%, respectively. –Besides that, color removal efficiencies were 77-91% and 81-92%, respectively.

Gandhimathi *et al.,* (2013) combined coagulation and adsorption processes for leachate collected from municipal solid waste open dumping site. Coagulation process was examined by using alum and ferric chloride. A low cost adsorbent, fly ash was used for adsorption studies. Coagulation studies were carried out for fresh and stabilized leachate. Adsorption studies have been conducted for alum pre-treated stabilized leachate. The effect of coagulant dose, adsorbent dose, pH and contact time were carried out. The effective optimum coagulant dosages were 0.6 g/L and 0.7 g/L for alum and ferric chloride respectively, for stabilized leachate and incase of fresh leachate 0.8 g/L and 0.6 g/L for alum and ferric chloride, respectively. For the alum pretreated stabilized leachate, the maximum COD removal is 28% using fly ash adsorbent with equilibrium time of 210 min and optimum dose of 6 g/L. Overall COD removal efficiency of 82% was obtained by coagulation using alum and adsorption using fly ash for stabilized leachate. The results obtained showed that combined coagulation and adsorption process can be used effectively for stabilized leachate treatment.

Li et al., (2010) conducted the combined process of coagulation/ flocculation and powder activated carbon (PAC) adsorption treatment method for stabilized landfill leachate. In coagulation/flocculation experiments, coagulants including aluminum sulphate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), polyaluminium chloride (PACl), and polyferric sulphate (PFS) were utilized to study the ideal conditions for the removal of COD, SS and turbidity by jar tests. The ideal working pH for the coagulants was 5.5 to 6.0, which affirmed charge counterbalance as the main method of coagulation/flocculation process. The dosages were determined as 0.6 gAl^{3+}/L for $Al_2(SO_4)_3$ and PACl, 0.6 g Fe^{3+}/L for $FeCl_3$ and 0.3 g Fe^{3+}/L for PFS, respectively. From the result of the coagulants, PFS had shown the highest COD removal efficiency (70%), suspended solids removal efficiency (93%), turbidity removal efficiency (97%), toxicity reduction (74%) and also the least sludge volume (32 mL). The adsorption experiments found that the

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dosage of PAC as 10 g/L and the contact time as 90 min at optimum condition. The removal efficiencies achieved of COD, Pb, Fe and toxicity of the stabilized landfill leachate were 86%, 97.6%, 99.7% and 78%, respectively using the combined coagulation/flocculation and adsorption process.

Motling et al., (2014) combined physico-chemical of coagulation-flocculation and carbon adsorption process an efficient treatment method for MSW landfill leachate. An investigation was taken to examine the phenol and organic load (COD) removal from diluted real life landfill leachate sample using some common coagulants followed by batch adsorption study. Coagulants including aluminum sulphate [$Al_2(SO_4)_3$], ferrous sulphate ($FeSO_4$), and polyaluminium chloride (PAC) were employed for determining their optimum experimental conditions for the removal of COD, SS and phenol along with the interference of pH. The optimum range of pH for the COD removal was found to be 6.0-7.0. The optimum dosages were determined as 1.5 g/L for Al_2 $(SO_4)3$, 2g/L for both PACL and $FeSO_4$. Alum exhibited highest COD removal efficiency (72%) among the all other coagulants tested in the present study. Removal of suspended solids was observed as 92% by using Alum. In the adsorption experiments, the optimum dose was found to be 0.4 g/L by using commercial grade activated carbon and the equilibrium time was observed as 3hr. The combined coagulation-flocculation and adsorption process observed that phenol and COD removal were found to be 97% and 92%,respectively, under optimum condition.

Zamora et al., (2000) compares two pre-treatments by coagulation-flocculation process (CF) and the Fenton oxidation Method (FE) of the activated carbon adsorption process (AC) to optimize the removal of the organic compounds in landfill leachates. The content of organic compounds was measured in terms of three global parameters: colour, chemical oxygen demand (COD) and dissolved organic carbon (DOC). The result obtained in discontinuous reactor conditions showed an increase in colour removal from 1.5 to 2.0 times and a decrease of COD between 0.3 to 0.5 times for the FE-AC treatment, in relation to the CF-AC treatment. On the other hand, the data obtained in continuous reactor conditions (packed columns) showed that the column fed with leachate CF exhibited operation times 1.3 times longer and a better physiochemical quality in the filtrate (COD and colour) than the one fed with the FE leachate. Nevertheless, the adsorption capacities in the colour removal column of COD and DOC were higher for the FE leachate.

Yilmaz *et al.,* (2010) carried out a study using combined system of coagulation-flocculation and air stripping for the treatment of leachate from landfill in the Konya Municipal area. The organic content and color removal were examined by using different chemical coagulants (Alum, $FeCl_3$, $FeSO_4$) and the pH were adjusted with lime, NaOH and H_2SO_4. Ammonia stripping and the efficiency of its removal was investigated. For effluent organic matter content removal, the highest removal efficiency achieved was 44% by using 9 g/L alum at pH 11 adjusted using lime, and efficiency of 45% by using 15 g/L $FeCl_3$ at pH 3. Moreover, color removal in the coagulation experimentations indicated that the highest efficiency of color removal could be obtained when pH was adjusted using lime. The coagulant concentration of 1 g/L yielded similar removal efficiencies as the concentration was increased. The optimum flow rate in ammonia stripping was 1 L/min at an optimum aeration time of 8 hours.

Kurniawan and Lo (2009) carried out a study on the treatment of raw leachate from the NENT landfill (Hong Kong) using hydrogen peroxide (H_2O_2) to investigate the treatment performances of H_2O_2 oxidation alone and its combination with granular activated carbon (GAC) adsorption. From an initial COD concentration of 8000 mg/L and NH_3-N of 2595 mg/L, the integrated treatment process had achieved substantially a higher removal (COD: 82%; NH_3-N: 59%) compared to the use of H_2O_2 oxidation alone (COD: 33%; NH_3-N: 4.9%) and GAC adsorption alone (COD: 58%) under optimized experimental conditions. Further improvement in the removal of refractory compounds was enhanced by the addition of a Fe (II) dose at 1.8 g/L by the integrated treatment from 82% to 89%.

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In another study by Mariam and Nghiem (2010) performed an experimental investigation on a combined electrocoagulation – nanofiltration (EC-NF) for the treatment leachate from Whytes Gully landfill in Wollongong, Australia. It was reported that at the optimum dosage of $Al_2(SO_4)_3$, TOC and turbidity removals by the chemical coagulation process achieved 10% and 65%, respectively. In the combined process TOC and turbidity removals, were approximately 92% and 99%, respectively. The results indicated that an EC – NF hybrid system can be a promising candidate for landfill leachate treatment, particularly for small and decentralized landfills, where simplicity and robustness are required.

The study by Trebouet et al (2001) examined the treatment of stabilized leachate from the Saint- Nazaire landfill (France) using a combination of NF (Nanofiltration) and coagulation. MPT-31 membrane with high negative charge was employed for leachate having COD and NH_3–N initial concentrations of 2150 and 790 mg/L, respectively. The maximum removal was found to be 80 and 21%. However, by employing MPT-20 that has a low negative charge, a lower removal of COD (74%) and NH_3–N (12%) was achieved at the same conditions. The difference of treatment performance between the two membranes might be attributed to the electrostatic effects that affect the repulsion between the negatively charged membrane surface and humic-type compounds. Treatment of landfill leachate using a combination of ozonation and GAC adsorption column was carried out (Fettig et al., 1996). With an initial concentration of 205 mg/L, about 40% COD was removed when 6mg of ozone/mg of dissolved organic carbon (DOC) was applied. Biodegradation inside the activated carbon beds was suggested to be the major mechanism for the removal of organic compounds from ozonated leachate.

Stabilized leachate from the Badazos landfill (Spain) was treated by integrating ozone and GAC adsorption (Oh et al., 2004). Approximate 90% COD removal was accomplished with an initial concentration of 4970 mg/L. Using adsorption after the ozonation step allowed the formation of smaller molecules during ozonation, which are more suitable for adsorption than the big molecules present in the leachate. In addition, adsorption is capable of removing the remaining organic compounds and metal species in the leachate.

The treatment of stabilized leachate from the Berg landfill (Germany) was explored using a combination of NF (nanofiltration) and GAC adsorption/ozonation (Rautenbach and Mellis, 1994). Due to its high rejection rate for organic compounds and high permeate flux, Desal 5K was selected as the NF membrane. An approximate 99% COD removal with an initial concentration of 4000 mg/L was achieved. HCl was used for pH adjustment in order to avoid CaSO4 scaling and for cost reasons. Dong et al., (2014) used filtration techniques in a forward osmosis (FO) membrane system used to post-treat the effluent of a membrane bioreactor (MBR) fed with landfill leachate (LFL). In short-term tests, it was observed that the water flux with the membrane active layer facing the draw solution (AL-DS mode) was lower than that with the membrane active layer facing the feed solution (AL-FS mode) for LFL treatment.

Mathematical models could well simulate the flux evolution of AL-FS mode while the flux of AL-DS deviated from the modeling curve, suggesting that fouling could be rapidly developed within 1 h filtration for AL-DS mode. During long-term filtration, about 98.6% of COD, 96.6% of TP, and 76.9% of ammonium was removed by FO system. A decrease of water flux was also observed with an increase in operation time. Confocal laser scanning microscopy and Fourier transform infrared spectroscopy confirmed the existence of polysaccharides and proteins in the fouling layer. Inorganic fouling was mainly caused by Ca, Na, Mg, K, Si, Fe and Al. It was also found that the effect of cake enhanced concentration polarization played an important role during long-term operation. About 88.9% of the permeate flux was recovered after hydraulic cleaning while it reached 98.9% of the initial flux after chemical cleaning, indicating that chemical cleaning was needed to eliminate irreversible fouling and to recover membrane permeability during long-term operation.

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BIOLOGICAL AND CHEMICAL TREATMENTS

Batarseh (2006) conducted a study on non-biodegradable organic removal of landfill leachate by chemical oxidation combined with biological treatment. In this study, an oxidation removal efficiency of 75% was used. This oxidation removal efficiency was determined from Fenton's reagent optimization experiments performed on matured leachate samples. The recommended oxidation conditions were pH range of 3-5 and a 1.0 g H_2O_2 per gram chemical oxygen demand (COD) dosage with a molar ratio of 0.4 Fe_2 to H_2O_2 and reaction time of 15 minutes. The biological removal efficiency is related to the aerobic biological degradation of treated leachate. The BOD as carbon/dissolved organic carbon (BOD/DOC) was increased from almost zero to 0.15 after oxidation of similar leachate samples, indicating 15% of organic carbon remained after Fenton's reagent is aerobically biodegradable.

Combined treatment of Fenton's oxidation and activated sludge (AS) was performed by Kurniawan et al., (2010). In this study, almost complete removal of COD and NH_3-N was reported for combined reversed osmosis (RO) and UASB with initial COD concentration of 35 000 mg/L and NH_3-N concentration of 16000 mg/L. While integrated Fenton's oxidation and AS (activated sludge) could achieve about 98 and 99% of COD and NH_3-N, respectively, with both initial COD and NH_3-N concentrations of 7000 mg/L. Hybrid treatment of wet oxidation and activated sludge in treating leachate was reported by Avezzu, (1992). In this study, leachate samples were taken from few landfills, namely Brescia, Veneto, Fossalta which located in Italy and Mechernich in Germany. The results showed the removal efficiency of COD were 50, 26, 27, 38%, respectively after undergone those treatments with the initial COD concentration ranging from 3100 – 19 400 mg/L.

Asha and Latha, (2013), conducted a study on mature landfill leachate treatment from Vilappilsala, India. In this study, Fenton process is applied as chemical pre-treatment prior to anaerobic process. After Fenton pre-treatment, the removal of COD, BOD, turbidity, nitrate, sulphate and TSS were 92.1%, 83.5%, 94.2%, 18.8%, 11.0% and 96.6%, respectively. At optimum parameters; pH 3, reaction time of 30 min, H_2O_2/COD ratio 3, H_2O_2/Fe^{2+} ratio 15 and 3 g/L sludge recycling, the biodegradability (BOD5/COD) enhanced from 0.3 to 0.65 while acute toxicity (96 hr LC_{50}) reduced to 6.3%. Fenton's treated leachate after undergone post treatment anaerobically at HRT 13 days, pH 7, COD, BOD, turbidity, nitrate, sulphate and TSS removal was 90.3%, 98.2%, 28.3%, 69.9%, 40% and 78.2%, respectively and toxicity reduced by 22%.

In 2000, Sheng and Chih, reported an investigation of the treatment of an aged landfill leachate by the combination of chemical and biological process. The electro-Fenton method assisted by chemical coagulation was employed for the treatment. The result revealed it to be highly efficient in removing large amounts of refractory organic and inorganic compounds in the leachate. The findings also showed that at an optimum pH 5 yielded better COD and color removal of more than 50%. And at PAC/polymer ratio 100: 1, the amount of PAC required to effect a maximum COD removal was found to increase linearly with the initial leachate COD concentration and a slope of 0.184 mg/L PAC per mg/L of initial leachate COD concentration. It was observed that the electro-Fenton oxidation employed was able to greatly enhance the COD removal of leachate effluent from chemical coagulation. At an optimum pH 4,the oxidation process rendered the leachate effluent totally colorless. It was also observed that at an optimum H2O2 dosage of 750 mg/L yielded a very good COD, color, NH3-N and phosphorus removal in less than 30 minutes.

Research on combined UV/Fenton and sequencing batch biological reactor (SBR) treatment of a semi-aerobic landfill leachate was investigated by Gan et al., 2013. In this study, Fenton pre-treatment of the leachate was optimized by the response surface methodology (RSM). UV/Fenton pre-treatment of

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the leachate was performed under the optimum operating conditions of the Fenton pre-treatment (H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and reaction/irradiation time 1.5 h). The characteristics of the UV/Fenton pre-treated leachate were: COD 390 mg/L, sCOD 330 mg/L, BOD5 136 mg/L, BOD5/COD ratio 0.35, NH_3-N 112 mg/L, TKN 157 mg/L, NO_3--N 6.8 mg/L and colour 99 Pt-Co Unit. SBR treatment of the UV/Fenton pre-treated leachate resulted in COD, BOD_5 and NH_3-N removal of 78%, 81% and 88%, respectively. The final effluent characteristics were: COD 92 mg/L, sCOD 71 mg/L, BOD5 26 mg/L, NH3-N 7 mg/L, NO_3--N 27 mg/L, TKN 13 mg/L and TSS 38 mg/L. The effluent met the Malaysian discharge standard (B) – COD 100 mg/L, BOD_5 50 mg/L and TSS 100 mg/L. Combined UV/Fenton and SBR is an effective treatment for mature leachate from semi-aerobic landfill.

A laboratory scale investigation was conducted by Claudio et al., 2006 aimed at evaluating the effectiveness of mature municipal landfill leachate treatment by a biological stage, carried out in a periodic biofilter with granular biomass (SBBGR), followed by a chemical oxidation step, performed using ozone or Fenton, for further COD removal. The results show that the biological treatment was able to remove roughly 80% of COD in leachate at an organic loading approximately equal to 1.1 kgCOD/m^3/ day). Ammonia removal efficiency was very low (lower than 20%) because of the presence of high salinity and inhibitory compounds. When the leachate was pre-treated in order to reduce considerably the ammonia content, it was found to be possible to reach organic loadings as high as 4.5 kgCOD/m^3/day with a decrease in COD removal of only 10%. The biological treatment was characterised by a negligible sludge production. Ozone and Fenton reagent were used to reduce the remaining COD content presumably made up of recalcitrant compounds. The treatment with ozone was able to remove only 33% of residual COD whereas using Fenton reagent an 85% removal efficiency of COD was achieved.

Rivas et al., (2004) conducted a study on combined sequential coagulation-flocculation and Fenton oxidation processes. The purpose of performing this combined process is to remove the colloidal particles in the leachate. In this study, it was found that about 90% of COD removal was achieved with an initial concentration of 7400 mg/L at pH 8.5 by using 0.8 g/L of $FeCl_3$. The transformation of recalcitrant organic compounds from stabilized leachate using a coagulation – ozonation coupling was investigated by Monje-Raminez et al., 2004. The use of iron (III) sulphate as the coagulant during pre-treatment was found effective. Combined treatment with ozonation was able to reduce 78% COD with an initial concentration of 5000 mg/L.

A pilot-scale study of the application of a combined solar photo –fenton and biological oxidation process for the treatment of landfill leachate was also conducted (Silva et al., 2013; Vilar et al., 2011). They reported that the solar fenton was more efficient as compared to the subsequent biological oxidation process in the leachate treatment. The overall combined treatments were able to remove 86% DOC of which 55% was through solar photo fenton process. The result suggests that the combination of the two treatments improved the efficiency of the treatment as compared to a single process.

PHYSICAL AND BIOLOGICAL TREATMENTS

Biological treatment is the most common practice for leachate treatment. Biological systems can be divided in anaerobic and aerobic treatment processes which include anaerobic filter, anaerobic sludge bed reactor (UASB), aerated lagoons, activated sludge plants, rotating biological contactors (RBC), trickling filter, sequential batch plant and co-treatment with sewage (Stegmann et al.,2005) and well known physical treatment for leachate treatment is air stripping, adsorption and membrane filtrations (Kılıç et

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al., 2007). A combination of two treatments is more efficient and effective than individual treatment due to the fact that a two-step treatment has the ability to synergize the advantages of individual treatments, while overcoming their respective limitations (Kurniawan et al.,2005).

Mojiri (2014) researched on adding a new adsorbent (powdered ZELIAC; PZ) to the SBR technique as another alternative for landfill leachate and domestic wastewater treatment. ZELIAC adsorbent was prepared from zeolite, activated carbon, limestone, rice husk ash, and Portland cement composite. Two reactors were used comprising of Normal SBR and PZ (powdered Zeliac) augmented SBR process. At optimal operating conditions for the SBR reactor was reported at an aeration rate of 4.49 L/min, contact time of 12.05 h and leachate to wastewater ratio 20%, which resulted to about 55.83%, 45.92%, 98.27%, and 33.56% rates of removal for COD, NH3-N, and phenols, respectively. The optimum experimental conditions for the PZ-SBR reactor happened at an aeration rate of 1.6 L/min, contact time of 15.43 h and leachate to wastewater ratio of 20%, which resulted to 82.04%, 71.56%, 98.27%, and 61.98% rates of removal for COD, NH3- N, and phenols, respectively. The results indicated that the PZ-SBR showed higher performance in removing certain pollutants compared with normal SBR.

Other research about SBR treatment showed by Aziz et al., (2011); which in this study, landfill leachate was treated by using two types of the SBR, namely non-powdered activated carbon and powdered activated carbon (PAC-SBR) were used. Throughout this study, removal efficiencies of chemical oxygen demand (COD), colour, ammoniacal nitrogen (NH3-N), total dissolved salts (TDS), and sludge volume index (SVI) were monitored and based on the results, the PAC-SBR displayed superior performance in terms of removal efficiencies when compared to SBR. At the optimum conditions of aeration rate of 1 L/min and contact time of 5.5 h the PAC-SBR achieved 64.1%, 71.2%, 81.4%, and 1.33% removal of COD, colour, NH3-N, and TDS, respectively.The SVI value of PAC-SBR was 122.2 mL/g at optimum conditions.

Lim et al., (2010) also studies on supplemented an adsorbent in SBR treatment using powdered activated carbon (PAC) and also ethylenediamine-modified rice husk (MRH). The objective of this study is to evaluate the performance of MRH compared to PAC as supplemented SBR in the removal of COD and nitrogen from a combined landfill leachate and domestic wastewater. The SBRs were operated with the Fill, React, Settle, Draw and Idle periods in the ratio of 2:12:2:1:7 for a process duration of 24 h. The efficiency of the reactors was assessed by monitoring the effluent quality as well as the adsorption of COD, ammonia nitrogen (AN), nitrite nitrogen and nitrate nitrogen during the Reaction time of an operating cycle at different mixing proportions of the wastewater. The results demonstrated that the equivalent performance of the MRH and PAC augmented SBRs in terms of the performance and degree of COD and ammoniacal nitrogen removal was accomplished at a lower loading rate of MRH in comparison to that of PAC. The better performance of the MRH-supplemented SBR was attributed to be due to the existence of attached-growth biomass which to a smaller extent constrained by toxic components in leachate than suspended-growth biomass. Overall, MRH shows a promising potential for being utilized as an alternative adsorbent to PAC in leachate treatment.

In leachate treatment, because of the high chemical oxygen demand (COD), ammonia nitrogen content and presence of toxic compounds such as heavy metals, direct biological treatment of landfill leachate results in less removal efficiency. Thus, in order to improve the biodegradability of the leachate, coagulation/flocculation and air stripping of ammonia was used as pre-treatment. Kargi and Pamukoglu (2003a); carried out a study on the pre-treated leachate that was treated biologically using an aeration tank operated in fed-batch by adding adsorbent. The experiment was conducted by comparing results of tests in the absence and presence of powdered activated carbon (PAC) respectively as an adsorbent.

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The result showed that PAC addition, improved COD removal significantly, especially at concentrations above 0.5 g/L. However, improvements in COD removals were marginal for PAC concentrations above 2 g/L. And about 86% COD removal was achieved with 2 g/L PAC added with biological treatment, whereas, COD removals by the only biological oxidation process or only PAC adsorption were about 74 and 38%, respectively at the end of 30 h of fed-batch operation. The authors reported that adsorbent concentrations were varied between 0 and 5 g/L. The percentage of COD and ammonium-N removals had increased with increasing adsorbent concentrations. Percentage of COD removals with PAC addition was significantly higher than those obtained when used with the zeolite. However, zeolite was more effective than the PAC in ammonium-N removal from the leachate. Nearly 87% and 77% COD removals were accomplished with PAC and zeolite concentrations of 2 g/L, respectively. Ammonium-N removals were 30% and 40% with PAC and zeolite concentrations of 5 g/L, respectively at the end of 30 h of fed-batch process.

In another study, Tsilogeorgis et al.,(2008) carried out an alternative leachate treatment process by using bench-scale membrane sequencing batch reactor (MSBR) on a stabilized landfill leachate which was obtained from the solid waste landfill of Thessaloniki (North Greece). The MSBR was set up with a hollow fiber ultrafiltration membrane with a working volume of 5L at a non-steady state flow. The mean concentration of the influent leachate was 2456 mg/L COD, 375 mg/L total nitrogen (TN) and 8.2 mg/L PO_4-P. The hydraulic retention time (HRT) was set at a constant state for 10 days for a majority of the assays, in contrast the solids retention time (SRT) was basically limitless. Low COD removal was observed (40% to 60%). The low MSBR efficiency of COD removal was associated to the high SRT. However, the ammonia nitrogen concentration was negligible, moreover, TN removal performance was considerable during the various stages of the MSBR operation, attaining up to a peak value of 88%. Finally, it was observed that MSBR was economically a cost effective process of landfill leachate treatment producing effluent of desirable properties.

Horan et al., (1997) investigated the performance of the Envirex granular activated carbon biological fluidized bed (GAC-BFB) process to treat landfill leachate containing organic material with typical COD values in the range 800 to 2700 mg/l with high concentrations of ammonia in the range 220 to 800 mg/L. Prior to the treatment, lime was added to the leachate to raise the pH to 9.0 and also to reduce any heavy metal impurities. Two identical pilot plants GAC-BFB's were used in series in order to achieve the removal of both organic and ammoniacal nitrogen within the same process.The pH within the reactors were maintained between 6.5 to 7.5. During the early stages of operation, loading rate of 1.56 kg ammonia-N/m3 d was employed. The reactors were able to remove 70% of the ammonia. 60% of COD and achieved a complete removal of BOD. After achieving optimal reactor operating system, it proved to be possible to achieve greater than 90% removal of ammonia at a loading rate of 0.71 kg N/m d; however the COD efficiency remained constant. In order to compare the ammonia removal efficiency of the GAC-BFB system. Two conventional activated sludge reactors were operated in parallel at hydraulic retention times of 24 and 36 hours (equivalent to ammonia loadings of 0.72 and 0.48 kg ammonia-N/m^3 d) and with a sludge age of 20 days. These reactors were not able to nitrify and although a BOD removal of 90% was achieved the COD removal efficiency was very low at 20%. Thus, the GAC-BFB system offers a highly effective option for the biological removal of ammonia from high ammonia leachates with the additional advantage of a good fraction of COD removal.

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PHYSICAL, CHEMICAL, AND BIOLOGICAL TREATMENTS

Mavros et al., (2008) mineralize a leachate from Olive Pomace sequential alum coagulation, activated-carbon adsorption and electrochemical oxidation process are used. The effect of coagulant and adsorbent concentration on treatment efficiency was assessed in the range 0.1–50mM Al^{3+} and 2.5–50 g/L activated-carbon and optimal conditions were established. Coagulation at 7.5mM Al^{3+} resulted in substantial solids and color removal (i.e. 80% and 93%, respectively). This was accompanied by only 30% chemical oxygen demand (COD) reduction (initial COD was about 3500 mg/L). The latter increased to 80% though when coagulation was coupled with adsorption at 25 g/L activated carbon. Electrochemical oxidation of the original effluent for 360 min led to 63% and 82% COD reduction at 10 and 20A current intensity, respectively. When this process was tested as a polishing stage following coagulation and adsorption, overall COD removal reached values of 92% and 97%, respectively. The final effluent was also colorless and solids free. However, the treated effluent still exhibited ecotoxicity possibly due to the formation of ecotoxic oxidation products.

The treatment efficiency of stabilized leachate from the Gramacho landfill (Brazil) by combining coagulation-flocculation and ozonation followed by ammonium stripping for 96 h was evaluated (Silva et al., 2004). This combination was found to be effective for complete removal of NH_3–N with an initial concentration of 800 mg/L. When 3 mg/L of ozone was employed, ozonation was able to achieve 48% COD removal with an initial concentration of 3460 mg/L. Marttinen et al., 2002 suggested nanofiltration and air stripping process for the treatment of low strength municipal landfill leachates to remove of organic matter, ammonia, and toxicity from low strength leachates (NH_4-N 74–220 mg/l, chemical oxygen demand (COD) 190– 920 mg O_2/l, EC50 ¼ 2–17% for Raphidocelis subcapitata. Ozonation was studied as well, but with the emphasis on enhancing biodegradability of leachates. Nanofiltration at 25° C was capable to remove 52–66% of COD and 27–50% of ammonia, the latter indicating that ammonia may in part have been present as ammonium salt complexes. Air stripping (24 h at pH 11) resulted in 89% and 64% ammonia removal at 20ºC and 6ºC, respectively, the stripping rate remaining below 10 mg N/l h. COD removals of 4–21% were obtained in stripping. Ozonation at 20ºC increased the concentration of rapidly biodegradable COD (RBCOD).

A combination of two physical and biological treatments is also efficient as reported by Wang, G., et al.(2014). In this study, anoxic/aerobic granular active carbon is used to assist membrane bioreactors (A/O-GAC-MBR) integrated with nanofiltration (NF)–reverse osmosis (RO) in leachate treatment of the Taizhou Municipal Landfill plant. The result showed excellent and stable removal efficiency with an average above 80% of chemical oxygen demand (COD) and ammonia-nitrogen (NH_3-N). It was noticed that the amount of high-valence metal ions were removed more than low-valence ones. The addition of GAC not only improved the removal of hazardous organic pollutants and heavy metals, but also enhanced the bioflocculation and particle size of flocs, which greatly alleviated membrane fouling. NF and RO membranes were then used for advanced treatment of MBR effluents. NF membrane exhibited excellent color removal rate of 93.75% compared to 41.82% of A/O-MBR. With the advantage of NF pretreatment, RO membrane held a steady and higher flux as well as salt rejection than other cases reported. The final permeate from RO was proved to exceed related qualification for reutilization and can easily be recycled in the industry.

Zhang et al., (2013) studied treatment of stabilized leachate from Zhoushan, Zhejiang (China) using Fenton - submerged membrane bioreactor- reverse osmosis system. In the process, the Fenton oxidation was designed to deliver more samples for the aerobic SMBR treatment under an ideal condition.

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The fenton reactor was loaded with 15 L of leachate sample, and the treated leachate were utilized as influent for the Aerobic submerged membrane bioreactor (SMBR) to increase the removal of organic matters and ammonium. SMBR with a working volume of 40 L were utilized for treatment. A self-made polyvinylidene fluoride (PVDF) hollow fiber module was immersed in the bioreactor. Fenton effluent was stored in the tank and constantly pumped into the bioreactors. The air was supplied consistently to bio- reactor at the steady rate (0.1-0.15 m^3/h) to provide dissolved oxygen and decrease membrane fouling. The MBR effluent was pumped into the Reverse osmosis (RO) modules. The filtration unit comprised of three stacks of plate-frame membrane modules, which was set in the serial arrangement with effective filtrating zone of 66 cm^2. The concentrate was then combined with secondary effluent and returned back to the feed tank. The specimens from the effluent and the concentrate were both collected simultaneously as operation continuous. The result produced high quality effluent with COD less than 15 mg/L and Ammonia-nitrogen less than 8 mg/L and membrane fouling was reduced.

In a study carried out by Wu et al., (2011) on the treatment of landfill leachate using a combination system that comprise of sequence batch reactor (SBR), coagulation, fenton oxidation and biological aerated filtration (BAF) in series. The leachate was treated by a combined plant utilizing a consecutive batch reactor (SBR) as the initial stage, poly-ferric sulfate (PFS) coagulation and a Fenton system as secondary treatment and biological aerated filter (BAF) as the tertiary treatment (Li et al., 2009; Hasar et al., 2009; Wang et al., 2009; Renou et al., 2008). Biological treatment in SBR reactor was operated at normal atmospheric temperature. The supernatant from the SBR was collected and combined together with coagulant PFS without pH alteration in a flocculation basin where coagulation and sedimentation were performed. At that stage, the PFS-treated leachate was further treated by the Fenton system through four stages: oxidation, balance, flocculation, and sedimentation. Supernatant from the Fenton treatment was collected and pumped into the BAF for last treatment. The air was introduced into the reactors from the base.The system was found to achieve removal of COD (98%), BOD (99.1%), NH_4-N (99.3%), TP (99.3%), SS (91.8%), Turbidity (99.2%) and Color (99.6%).

Another study of the treatment of stabilized leachate was conducted by Chemlal et al., (2014), applying a combination of advanced oxidation using photocatalytic reactor with UV- lamp for continuous irradiation of a coated adsorbent media to treat stabilised leachate of Oued smar landfill in Algeria. The photocatalysis analyses were carried out in batch. The photocatalytic reactor comprises of a 3 L capacity tank steel chasis menu, a slanted glass plate is coated with the photocatalytic media (TiO2, silica and zeolite) on which runs a thin layer of leachate to be treated with a cover under which are added three UV-C lamps which ensures constant irradiation of the media. The irradiated leachate obtained was then treated with aerated bioreactor. The leachate even distribution over the catalyst entire surface is provided by a distribution valves. The sample agitation is made with a helical stirrer and the leachate is aerated through by a vacuum apparatus. The biological treatment comprised of the establishment of three bioreactors inoculated with different inoculums ; raw leachate, soil extract from the Oued Smar landfill and lastly the activated sludge. The treatment had reduced the initial BOD5 value by 90% and the initial COD by 87%.

A combination of nanofiltration and microfiltration-PAC hybrid process application after treatment with a Jet-loop membrane bioreactor for the treatment of landfill leachate was explored by Ince et al., (2010) in Turkey. It was found that the nanofiltration (NF) unit alone put after the Jet loop membrane bioreactor to further treat the effluent was not adequate to reduce the COD concentration to desired levels (700 mg COD/L), but the combination of hybrid (MF-PAC) to treat the effluent was able to reduce the COD from the Jet loop membrane to desired levels. The hybrid treatment with application of 8g PAC/L

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was efficient in COD removal yielding lower values than the allowed discharge limit (700mg COD/L). It was also observed that an increase in PAC, the amount of pollutants adsorbed increased yielding an efficiency of 0.169g COD/g PAC. Moreover, it was suggested that the reason for this increased yielding an efficiency was because the Jet-loop effluent does not contain suspended solids. This result suggests that the hybrid treatment process is more effective than a single process.

In the Changshengqiao landfill (China), the treatment of leachate from the stabilized landfill using a combination of air stripping, Fenton, SBR and coagulation process was investigated by Guo et al.,(2010). In the combined successive treatment test run, the landfill leachate was initially applied to the air stripping for pretreatment to withdraw ammonia. The effluent from that unit was then oxidized in the Fenton reactor to remove bio-refractory compounds. At that point, the effluent from the Fenton treatment was combined with sewage wastewater at a ratio of 1:3 and transfered to the SBR unit to improve the removal of organic matter. Eventually, the effluent was transfered to the chemical coagulation reaction to remove suspended solids. The intergrated treatment was run under the ideal conditions for all the processes. COD, BOD5, and NH_3-N of the effluents were measured toward the end of each one process. The general effectiveness of the intergrated treatment was analyzed. It was reported that the integrated system achieved an outstanding performance in the overall removal of COD (93.3%) and NH_3-N (98.3%).

The treatment of leachate from the Herbin landfill (China) was explored by Bu et al., (2010) using a combination of sequence batch reactor (SBR)+aeration corrosive cell-fenton (ACF)+ granular activated carbon (GAC) adsorption in series. With a volume of 10 L, the SBR reactor was operated one cycle every day at room temperature. considering the resistance of aerobic micro-organism inside SBR, tap water was diluted with the leachate 9 times. The SBR was run persistently after acclimation of 1.5 months. The effluent of the SBR was pumped into the ACF reactor. The columnar Plexiglas ACF reactor had a volume of 0.6 L. To accomplish corrosive cell response, the ACF section was loaded with a mixture of iron scraps (350 g) and GAC (100 g) based on the ideal dosage test, bringing about a mass ratio of iron scraps and GAC of 3.5:1. Initially, the iron scraps were activated with 1% hydrochloric acid (V/V) to clear the iron rust thereafter cleansed with distilled water. The SBR effluent was pumped into the ACF reactor with an upflow rate of 6.7ml/min. The effluent of ACF would be pumped into the GAC segment. The columnar Plexiglas GAC adsorption reactor had a powerful volume of 0.28 L. Commercial GAC of 1 mm x 3 mm was filled into the reactor at a dose of 0.9 g/L as the adsorbent. The ACF effluent was pumped into the GAC section at an upflow rate of 9.3 ml/min. It was reported that the removal efficiencies of COD, BOD_5 and DOC were 97.2%, 99.1% and 98.7%, respectively. And also in the final effluent Fulvic-like compounds were effectively removed.

The treatment of stabilized leachate from the Chang shankou landfill (China) using a combination of agitation,coagulation, SBR and filtration was evaluated by Abood *et al*., (2014). Work was carried out by observing a combined successive treatment test run. The landfill leachate was initially fed to an agitation process to deplete ammonia. The effluent from that unit was treated by the coagulation–flocculation process applying PFS as a coagulant to reduce the concentration of organic matter and to alter the BOD /COD ratio. At that point, the effluent was combined with the sewage wastewater at a varying proportion and supplied to the SBR unit to improve the removal of organic matter. Eventually, filtration using a layer of carbon and sand as a viable medium was utilized as a refining procedure to meet effluent release standard. The combined treatment was run under the ideal conditions for each single process. COD, BOD_5, SS, TOC and NH_3 -N of the effluents were measured at the end of each process. The final effluent concentration of COD, BOD_5,SS, NH_3-N and TOC at the end were 72.4mg/L, 22.8mg/L,

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24.2mg/L, 18.4mg/L and 50.8mg/L, respectively, which were below the permissible discharge standard (COD ≤100mg/L, BOD_5 ≤ 30mg/L, SS ≤ 30mg/L and NH_3-N ≤ 25mg/L). This was reported as an outstanding treatment performance with an overall removal of COD (97.4%) and NH_3-N (99.2%).

CONCLUSION

As a conclusion, a combination treatment proves to be more efficient and effective than individual treatment. This could be due to the fact that two or three-step treatment has the ability to achieve the advantages of individual treatments as well as subduing their unit process limitations. A combined treatment is indeed capable of improving the effluent quality and minimizing the residue at a lower treatment cost than an individual treatment.

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Chapter 10
Structure Development for Effective Medical Waste and Hazardous Waste Management System

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ABSTRACT

Management of medical and hazardous wastes is a serious problem especially for developing countries. People are not aware of possible threats and/or they are afraid of the cost of application. Rapid population growth leads municipalities towards proper solid waste management applications. In this study, data were collected from the Turkish Statistical Institute and a general framework was drawn for medical and hazardous waste amounts and disposal methods. Starting from this point of view, the authors analyzed both the Regulation on Control of Hazardous Waste and the Regulation on Control of Medical Waste applied in Turkey. Taking into account all of these factors, this chapter is intended to develop the medical and hazardous waste management system economically and environmentally including waste generation, collection, transportation, disposal and treatment activities. Additionally, it investigates the reasons for lack of proper application of the regulations in light of the statistical data.

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INTRODUCTION

Handling of medical and hazardous waste has been a serious problem for countries all over the world. Economically developing countries are facing the waste management issue more than developed countries. An effective waste management system necessitates special operations, which have to be subjected to wastes in order to prevent damages for both environment and human health. National policy, training of employee and increased public awareness are the fundamentals of medical and hazardous waste management system.

Unless the collection and disposal of medical waste are applied separately, transmission of diseases will be unavoidable. Additionally this situation causes some problems including economic and environmental issues. Therefore, to increase the quality of life, medical waste management system should be applied and shed light on the service manner in terms of technical, social, economic and environmental areas.

Likewise, both hazardous wastes; which affect environment, human health and other living organisms negatively in physical, chemical and/or biological ways; and hazardous waste management system are very important matters for developing societies to deal with. As a result, for the protection of the environment and sustainable development, integrated medical and hazardous waste management system should be developed and applied depending upon related regulations.

As a part of this study, related regulations, application requirements, sources of medical and hazardous waste, classification of waste, responsibilities of waste generators, municipalities and ministries are subjected. Moreover, all stages will be examined separately, starting from the generation to the disposal of waste. Within this context, the following topics will be referred: collection of medical and hazardous waste in a separate way, processes to reduce the amount of waste, temporary storage, transport and methods for disposal.

BACKGROUND

Definition of Medical Waste

The medical waste definition covers the waste that is produced by medical facilities, research units and laboratories. In addition, there are small and distributed sources of medical waste, for example household medical waste which can be expressed as dialysis waste, insulin syringe or hypodermic needles etc. (Tchobanoglous et al, 1993).

According to WHO (2011) around 75% to 80% of waste produced by medical activities are considered as nonhazardous wastes. These are called as “general medical waste” which is produced by administrative activities of medical facilities, and must be processed as household wastes.

Classification of Medical Waste Generated from Healthcare Organizations

Medical waste producers are classified related to the size of the waste that they produce; as small, medium and large. Some examples for these producers can be found in the following table: (Regulation on Control of Medical Waste, 2005) (see Table 1).

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Table 1. Examples of medical waste producers

Size of Waste	Healthcare Organization
Large amount of waste producers	• University Hospitals • Hospitals (for general purposes) • Maternity Hospitals • Military Hospitals
Medium amount of waste producers	• Dispensary, medical centers • Outpatient care centers • Morgue, autopsy centers • Search and experiment centers which are working with animals • Nursing homes • Medical and biomedical laboratories • Animal Hospitals • Blood banks and transfer centers • Emergency rooms • Dialysis centers • Rehabilitation centers • Biotechnology laboratories and institutes • Medical research centers
Small amount of waste producers	• Consulting rooms • Dental health clinics • Veterinaries • Acupuncture centers • Tattoo and piercing activities • Physiotherapy centers • Medical treatment and nursing done at home • Pharmacies • Zoo • Ambulances

Infected Waste

Contagious waste may contain pathogens such as bacteria, viruses, parasite and fungus; and this situation may cause some diseases. This contains the following classes;

- Infectious samples and cultures that are formed in laboratories,
- The materials and equipment that are used for pestiferous patients,
- The waste of quarantined patients (urine, excrement, perspiration, clothes of contagious patients etc.),
- The waste of patients who use kidney machine and have infectious disease (dialysis equipment, tubes, filters single use stuff, laboratory clothes etc.),
- Animals which have infectious diseases in laboratories,
- All stuff that are contaminated with patients who have infectious diseases (both human and animal) (Veeken, 2000).

Pathogenic Waste

Pathogenic waste consists of tissue, organ, parts of human body, fetus, carcass, blood and secretion. Moreover, both human and animal body parts are called anatomic waste and existed in this class. However, this category includes healthy body parts, which may be accepted as sub class of infectious wastes.

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Sharp Objects

This group consists of materials that can cause several injuries. Syringe needles, hypodermic needles, lancet and razor blade, knifes, vaccine sets, saws, broken glasses and nails are the most common examples for sharp objects produced in healthcare organizations.

Pharmaceutical Waste

This group consists of medicines that are expired, spilled and contaminated in some ways. In addition, discarded materials such as bottles, boxes, gloves, masks, connection tubes, hoses, pharmaceutical vials are accepted in this group.

Genotoxic Waste

Genotoxic wastes are high degree toxic materials and may contain teratogenic, mutagenic or carcinogenic characteristics. These materials can cause serious security problems in hospitals and they need to be handled very carefully. Genotoxic wastes may contain cytotoxic medicines, chemicals such as benzene and radioactive materials. Cytostatic medicines and materials have the characteristic of killing and/or stopping the production of significant cells, for this reason they are used to kill cancer cells. Most common genotoxic materials are shown in Table 2 (Veeken, 2000).

Chemical Waste

The chemical wastes are produced during medical operations may be both hazardous or not. The wastes can be classified as hazardous if they have the following properties:

- Toxic
- Corrosive (for ex: acids with pH < 2 or bases with pOH > 12)
- Flammable
- Reactive (explosive, sensitive to any impact)
- Gene poisonous (cytostatic medicines)

Formaldehyde, photographic chemicals, solvent containing wastes, heavy metal containing wastes are highly toxic and sub classes of hazardous waste (Veeken, 2000).

Table 2. Genotoxic materials

Class	Genotoxic Materials
Carcinogenic	• Chemicals: benzene • Cytotoxic and other kinds of medicine: Azathioprine, chiorambucil, chiornaphazine, ciciosporin, cyclophosphamide, melphalan, semustine, tamoxifen, thiotepa, treosuifan • Radioactive materials
Possible carcinogenic	• Cytotoxic and other medicines: Azacitidine, bleomycin, carmustine, chioramphenicol, chiorozotocin, cisplatin, dacarbazine, daunorubicin, dihydroxymethyifuratrizine (for example Panfuran S is not allowed to use any more), doxorubicine, lomustine, methyithiouracil, metronidazoie, mito – mycin, nafenopin, niridazoie, oxazepam, phenacetin, phenobarbital, phenitoin, procarbazin hydrochioride, progesterone, sarcolysin, streptozocin, trichlormethine

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High Pressure Containers

These containers are inert and not potentially dangerous, but if they contact with fire or punctured, they may explode. This class should be treated very carefully to avoid inconvenient circumstances.

Radioactive Waste

Radioactive wastes are contaminated by radionucleotides that include solid, liquid and gas materials. Radioactive wastes can be classified as following (Veeken, 2000):

- Radionucleotides which are out of usage,
- Wastes that are contaminated after treatment (for ex: towels, glass materials, syringes, tubes etc.),
- Wastes which are produced during transportation,
- Wastes contaminated by radioactive materials,
- Wastes that are produced during treatment with radionucleotides,
- Liquid wastes, for ex: remaining liquids from cleaning the medical devices,
- The gases are released during treatments.

Responsibilities Related to Medical Waste

In Turkey, Regulation on Control of Medical Waste (2005) regulates how to collect waste separately, to store temporarily, to transport and to dispose the waste. This regulation gives the responsibilities to municipalities and/or authorized institutions for application of required steps.

According to this directive, the responsibilities and duties of waste generators, municipalities and ministries are given below:

Waste Generators

Health institutions are obliged to prepare and implement the waste management plan, which includes collection, transport and temporary storage of wastes. In addition, the plan must include actions to be taken in case of accident. Additionally they are obliged to:

- Reduce the waste at source,
- Separate and collect medical, household and packaging wastes at their source,
- Use proper bags and containers (as defined by related regulations) for sharp materials,
- Transport wastes by licensed vehicles,
- Build up a place as temporary storage or provide containers,
- Teach and train personnel about waste management periodically,
- Collect data of produced waste and report the data to governorship annually, to archive the documents.

Municipalities

Municipalities are obliged to:

- Make plans and directives to collect and dispose the medical waste,

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- Train people about the directives,
- Collect and transport the medical waste to disposal areas,
- Get related licenses and build/operate sterilization facilities,
- Get license for transporting vehicles,
- Give license for temporary waste collection areas,
- Teach personnel about medical waste management periodically,
- Provide appropriate clothes for personnel who is working in medical waste management,
- Collect data of produced waste and report the data to governorship annually and archive the documents.

Ministries

Ministries are obliged to:

- Coordinate and operate the regulative sanctions in the scope of management system,
- Control and audit the processes from production to disposal, periodically,
- Ensure the coordination with national and international corporations about application of updated technological approaches, as part of management system,
- Give license to medical waste disposal and sterilization plants.

Definition of Hazardous Waste

In US legislation, hazardous waste is described as ''Leftover products that contain corrosive, toxic, ignitable, or reactive ingredients'' (USEPA, 2005). In Europe this term is defined as "such wastes that could potentially increase the hazardous properties of municipal solid waste when landfilled, incinerated or composted" (Inglezakis et al., 2014). Lastly, UK National Household Hazardous Waste Forum provided an explanation for hazardous waste as "any discarded material, which is difficult to dispose of, or which puts human health or the environment at risk because of its chemical or biological nature" (NHHWF, 2008).

In Turkey, there are serious problems related to separation, disposal and recycling activities of hazardous wastes. According to official records come from industrial facilities, around 938.498 tons of hazardous waste is produced. However, the estimated waste production is about 1.3 million tons per year (Ministry of Environment and Urbanization, 2014). Examples for hazardous wastes can be as following (Dogru, 2012):

- Packages that are contaminated by hazardous materials (paint, chemical, oil tins and barrels) and marked with warning symbols,
- Waste oil (oil and grease, emulsion and solutions),
- Oily machine tools,
- Hazardous material leaped clothes and gloves,
- Expired batteries, organic solvents,
- Fluorescent lambs, ink and toner cartridge,
- Pesticides,
- Asbestos containing materials,

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- Filter dusts,
- Cyanide containing hardeners,
- Oil contaminated cables.

There are additional regulations in European Union, which are related to hazardous wastes and its management system. The directive covers the methods reducing the hazardous waste, recycling and disposal activities. In Turkey, our legislation (Regulation on Control of Hazardous Waste, 2005) is compatible with European Union related directives, which are:

- Waste Framework Directive (75/442/EEC)
- Hazardous Waste Directive (91/689/EC)
- Revised European Waste Catalogue (EWC/2002)
- Landfill Directive (1999/31/EC)
- Waste Incineration Directive (2000/76/EC)

However, there were some differences between Regulation on Control of Hazardous Waste and EU directives related to the coding systems. In 2008, Regulation on Control of Hazardous Waste revised and became fully compatible with EU Waste Catalog (2000/532/EC Directive).

Classification of Hazardous Waste

Defining hazardous waste is very complex application, since there are many factors that contribute to waste's nature; it depends on the individuals view (Wentz, 1989). The waste that generated mainly from the economic and industrial activities and harmful for human health (toxic, carcinogen, flammable, explosive and infectious) are accepted as hazardous waste. For instance, batteries, paints, lubricants and some chemicals are in this group.

Classification of hazardous waste is expressed in Regulation on Control of Hazardous Waste as following:

Q1: Production and consumption waste that is not defined below.
Q2: Nonstandard products.
Q3: Expired products.
Q4: Modulated, spilled and/or contaminated materials because of misusage.
Q5: Contaminated materials (e.g. cleaning activities, packaging waste, containers etc.).
Q6: Obsolete materials (e.g. dead batteries, catalyzers etc.).
Q7: Materials that show bad performance (e.g. contaminated acid, contaminated solvent, dead surface salts etc.).
Q8: Industrial waste (e.g. slag, clinker, sediments etc.).
Q9: Cleaning and filtering waste (e.g. cleaning muds, filter dusts, used filters etc.).
Q10: Machine/surface treatment waste (e.g. turning machine waste, milling waste etc.).
Q11: Waste produced from raw material production and cultivation (e.g. petroleum and mineral mining etc.).
Q12: Defiled materials (e.g. PCB contaminated oil).
Q13: Prohibited materials and products.

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Q14: Obsolete products by producers (e.g. agricultural, household, office, commerce and marketing activity waste).
Q15: Waste produced from land improvement and reclamation activities.
Q16: Materials that are not expressed above.

Properties of Hazardous Waste

Hazardous waste is the material that has harmful effects on human health and their environment. Hazardous materials' properties, which can be found in Regulation on Control of Hazardous Waste, are given below:

H1 – Explosive: Materials those are flammable; more sensitive to shocks and friction than dinitrobenzene; reacting and releasing gas under certain conditions.
H2 – Oxidizing: Materials that exhibit highly exothermic reactions when in contact with other substances, particularly flammable ones.
H3 A – Highly Flammable:

- Liquid substances those having a flash point below 21°C (including extremely flammable liquids),
- Substances which may become hot and catch fire in contact with air at ambient temperature without any application of energy,
- Solid substances which may readily catch fire after brief contact with a source of ignition and which continue to burn or be consumed after removal of the source of ignition,
- Gaseous substances which are flammable in air at normal pressure,
- Substances, which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.

H3 B – Flammable: Liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C.
H4 – Irritant: Non-corrosive materials, which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.
H5 – Harmful: Substances which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.
H6 – Toxic: Materials which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.
H7 – Carcinogenic: Substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.
H8 – Corrosive: Materials that may destroy living tissue on contact.
H9 – Infectious: Materials containing viable microorganisms or their toxins that are known to cause disease in living organisms.
H10 – Teratogenic: Materials which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence.
H11 – Mutagenic: Substances which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.
H12: Substances and preparations that release toxic or very toxic gases in contact with water, air or an acid.
H13: Waste capable by any means, after disposal, of yielding another substance.

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H14 – Ecotoxic: Waste which presents or may present immediate or delayed risks for one or more sectors of the environment.

Responsibilities Related to Hazardous Waste

In Turkey, Regulation on Control of Hazardous Waste regulates how to collect waste separately, to store temporarily, to transport and to dispose the waste. This regulation gives the responsibilities to municipalities and/or authorized institutions for application of required steps.

According to this directive, the responsibilities and duties of waste generators and ministries are given below:

Waste Generators

Waste generators are obliged to:

- Take precautions to reduce the amount of waste,
- Make appropriate waste management plan to reduce the harmful effects of the waste to environment and living organisms. In addition, they are obliged to get permission from governorship for temporary storage,
- Record the waste and package/label them as indicated in international standards,
- Manage documentations including waste declarations for prior year and send them to governorship,
- Apply procedures for disposal and storage and fill the international forms if these applications take place out of the plant,
- Monitor international standards for transportation,
- Contribute to expenses for setting up disposal facilities,
- Preserve hazardous waste in durable, impermeable and safe containers, which are in accordance with international standards and located far from production area but in that facility,
- Label that containers with international hazardous waste symbol, amount of waste inside and the storage date,
- Locate waste to ensure safe storage and prevent occurring chemical reactions,
- Take precautions for health and safety issues of the personnel,
- Document accident reports to governorship and contribute to expenses for rearrangement of that area in a month at the latest,
- Leave a personnel in charge for temporary storage and give him/her personal information to governorship (this situation is just for facilities that are producing one tone of hazardous waste in a month),
- Prove that waste disposal completed successfully.

Ministries

Ministries are obliged to:

- Indicate programs and policies to apply waste management system efficiently,
- Coordinate/audit application of regulations and report them to governorship,
- Prepare waste management plan and inform people,

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- Carry out international works on transportation of the waste,
- Audit the disposal facilities and apply necessary sanctions,
- Control and audit closed disposal facilities for 20 years,
- Indicate principles of emergency plans for facilities,
- Coordinate the usage of environmentally friendly technologies and waste management systems.

WASTE MANAGEMENT

Medical Waste Management

The total amount of waste generated by health-care activities, about 80% is general waste comparable to domestic waste. The remaining 20% is considered hazardous material that may be infectious, toxic or radioactive. Lack of awareness, inadequate training, absence of waste management and disposal systems, insufficient financial and human resources and the low priority given to the topic are the most common problems connected with medical waste. Still, many countries do not have appropriate regulations; if they have, they do not enforce them effectively (Prus et al., 1999; WHO, 2011).

Integrated medical waste management is a system in which reduction, minimization, collection by degradation, temporary storage, transportation and disposal mechanisms are examined separately for household, medical and hazardous wastes. In this system, following up the control periods for these wastes are implemented with the light of the legal obligations. Typical flowchart of medical waste management is shown in Figure 1 (Esmen et al., 2013).

To minimize the risks posed by medical wastes to the environment, medical wastes must be treated with the most appropriate technologies. Medical waste handling methods, e.g. packaging, depend largely upon the disposal method or location of the disposal facility, and the existence of state and local regulations.

Separation of Medical Wastes

Firstly, medical wastes are separated whether they are hazardous or not. Then the second separation is carried out for recoverable medical wastes; which are glass, paper, plastic etc.; and these wastes contribute to economy by recovery. On the other hand, thermometers, manometers, mercury containing wastes, dental polyclinic wastes containing metallic mercury and silver (which is used while printing x-ray films) can be recovered. Except those, recovery is not a preferable option for medical wastes.

Clinical wastes including infectious waste, pathological waste, syringe, needle etc. should be collected separately to prevent contamination. This situation results greater gain on medical waste management system. Moreover, expired medicines are directed to pharmaceutical warehouses, waste chemical solvents are separated if they are hazardous or not. Nonhazardous wastes must be separated from hazardous wastes immediately, after that hazardous ones are directed to authorized companies to disposal (Veeken, 2000).

Reduction in the Quantity of Waste

In the light of "polluter pays" principle, waste generators should pay money related to their wastes' amount and type. This approach emphasizes the concept of reduction. To reduce the amount of waste following policies could be applied: lowering the amount of waste produced, using materials repeat-

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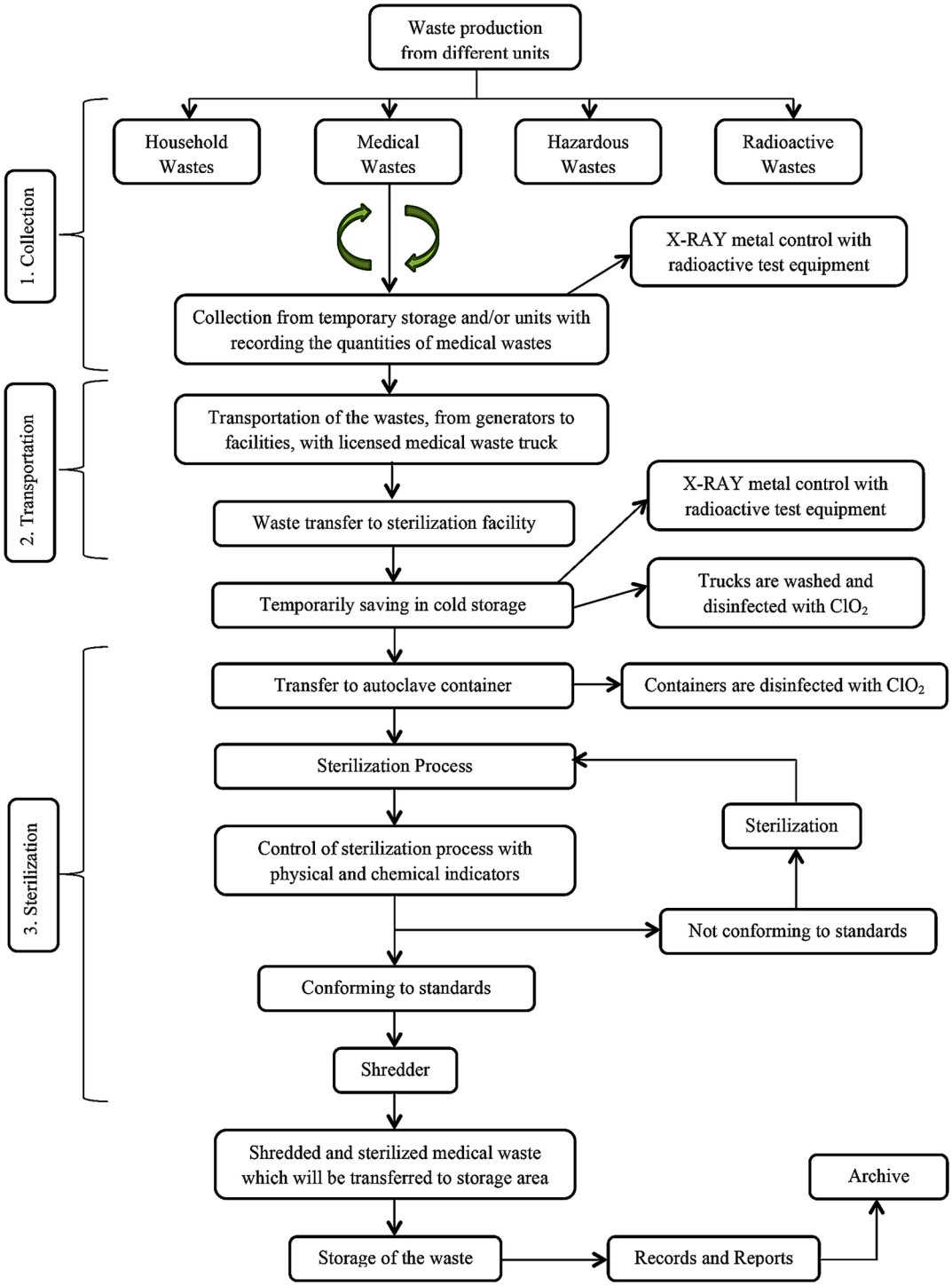
Figure 1. Typical flowchart of medical waste management
(Esmen et al., 2003).



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edly, applying an adequate management and control, separating the wastes, implementing management and control measurements and storing of pharmaceuticals and chemicals. Making changes in the raw materials during production phase, both disposal costs and risks are reduced. These changes can be like using less hazardous chemicals, applying integrated reduction technologies, preferring electronic devices instead of mercurial instruments etc. (Tutar, 2004).

"Polluter pays" principle supports the idea for reduction of waste. This causes decrease both in the cost for disposal and in the amount of waste. In this concept, to implement all of these steps, education of the personnel is required for each workplace.

Collection of Medical Wastes

Wastes from health-care activities are collected separately depending upon their types (such as packaging materials, medical, hazardous or radioactive waste). Although there is an important point, which indicates that these wastes should not be contaminated before separation. Regulation requires generators to segregate sharps, and fluids, from other regulated medical waste to the extent practicable if the waste is intended for off-site transport and disposal. For instance; in Medical Waste Control Regulation, it is mentioned that there are four types of bags, which are special for medical wastes:

- For household medical wastes, black plastic bags are used,
- For packaging wastes, blue plastic bags are used,
- For infectious wastes, red plastic bags (which has to have an universal symbol showing that waste is biohazard /infectious waste) are used,
- For sharp objects, yellow plastic containers are used.

Figure 2. Universal logo for clinical waste
(Regulation on Control of Medical Waste, 2005).

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Regulation requires generators to label packages containing untreated regulated medical waste with the words "infectious waste" or "medical waste" or with the universal biohazard symbol (see Figure 2). Each layer of packaging or container used to meet the packaging requirements must be labeled.

The outer surface of all regulated medical waste containers that are used to meet the packaging requirements must be marked to identify the generator, if the waste is transported off-site. The outermost surface of the container must also identify the transporter and the date of shipment. The markings must be water resistant and required to help identify those persons responsible when waste that has been mismanaged or improperly disposed is found.

The packaging requirements are designed to protect people from exposure to regulated medical waste. Prior to off-site transport, medical waste must be packaged in rigid and leak-resistant containers that are impervious to moisture, sufficiently strong to prevent tearing or bursting under normal handling, and sealed to prevent leakage during shipment. Reusable containers are permissible; in many cases, containers that can be loaded on pallets and mechanically moved can be used, as long as the containers are not subjected to undue stress or compaction during transport, loading and unloading (EPA, 1991).

Temporary Storage

Medical waste that is transported off-site for disposal may be stored in indoor or outdoor storage areas. The location and capacity of a storage area depends on the quantity of medical waste generated, the frequency of pick-ups, urban/rural location, and whether on site or off-site disposal will occur.

Before transporting to disposal area, wastes can be stored in those places or containers for up to 72 hours between October-April and up to 48 hours between May-September. If there is a cooling system and the temperature is between 3 – 8^{o}C, storage time can be extended up to one week.

Properties of temporary storage area, which are explained in Regulation on Control of Medical Waste, are given below:

- It must be closed, and access must be restricted to authorized persons only,
- It must have two divisions, one is for medical wastes, the other one is for household wastes,
- It must be separate from any food store,
- It must be covered and sheltered from the sun,
- The flooring must be impermeable with good drainage,
- It must be easy to clean,
- It must be protected from rodents, birds and other animals,
- There must be easy access for on-site and off-site means of transport,
- It must be well aired and well lit,
- It must be compartmented (so that the various types of waste can be sorted),
- There must be wash basins nearby,
- The entrance must be marked with a sign,
- The doors must be clean and have universal logo for biohazard /infectious waste.

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Transport to Disposal Area

Trucks are the most common type of vehicle used to pick up and transport medical waste. Small vehicles similar to vans are used to pick up small quantities of medical waste from individual practitioners. Dump trucks are sometimes used in rural areas. Flatbed trucks are also used when the waste is stored in large containers, which can be removed from the facility for transport to a disposal facility.

Methods for Disposal

Most medical waste that is not incinerated, and ash from incineration, is disposed in landfills. While infectious medical waste is often treated prior to landfilling, depending on state and local regulations, several types of generators dispose of small quantities of untreated medical waste directly in landfills. Generally, disposal methods are chemical disinfection, sterilization, microwave, landfilling, microwave radiation and incineration (Prus et al., 1999). In this chapter sterilization and incineration, most common methods used in Turkey, will be explained briefly.

Sterilization

This method is also known as autoclaving, which ensures elimination (around 99,99%) or killing all forms of microbial life, including transmissible agents; by physical, chemical, mechanical methods or irradiation (Regulation on Control of Medical Waste, 2005). Sterilization system consists of the following units: feeding system, sterilization unit, fractionation unit, boiler and software system to integrate all units. The sterilization steps can be explained respectively:

1. Transportation of medical waste from cold storage room to autoclave container,
2. Transportation of autoclave container to autoclave system,
3. Autoclaving, in which vacuum pumping and sterilization occur,
4. Boiling,
5. Electronic control system, in which all the data are followed and saved,
6. Transportation of treated waste to grinder,
7. Shredding, where wastes' volume is decreased,
8. Transportation of treated waste to the last container for waiting,
9. Loading treated waste for transportation to storage area
10. Handling

Some advantages and disadvantages of sterilization and factors affecting the effectiveness of this process are discussed as follows (U.S. EPA, 1991):

- **Advantages:** The equipment used in this method is simple to operate, has automatic processes and needs low cost. Additionally, it is safe and because of being closed system contamination does not occur. The method is capable of decontaminating most medical waste classes, reduces the volume and reproduces some plastics. Moreover, this method is easy to test and environmentally friendly.

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- **Disadvantages:** This process does not reduce the mass of material that must be disposed, produces odor, release VOCs and toxic emissions to air. In addition, a potential safety hazard exists because of the hot surfaces in the autoclave.
- **Factors Affecting Effectiveness:** Three important factors in sterilization processes are temperature, pressure, and exposure time. Together with these parameters, the size and material of the load, autoclave bag, and waste's configuration also affect the efficiency.

Incineration

Incineration is a process in which wastes are burned under controlled conditions to oxidize the carbon and hydrogen present in the waste. This method can be used to treat many types of waste; materials which cannot be incinerated remain as residue. In Turkey, because of being the most secure method, incineration is used generally. However, this method is expensive that's why sterilization is used an alternative disposal technology. As discussed below, incineration has some disadvantages as it releases air emissions containing several pollutants. In Turkey, there is a regulation to control the stack gas emissions, and incineration plant has to have the special certificate to operate the plant. Incineration is conducted by İSTAÇ in Istanbul and it consists of the following units: waste receiving unit, vibrating conveyor system, rotary kiln, secondary combustion chamber, filtration system and activated carbon dosing system (İSTAÇ, 2014).

In 2004 (the latest data available on Turkish Statistical Institute), 61502 tons/year medical waste was generated and 8224 tons/year was incinerated. The rest of the waste was buried, discharged to lakes/sea, landfilled and/or transferred to other municipalities' dumps. In addition, a data was collected in 2010, indicating the amount of incinerated medical waste as 17287 tons/year.

Some advantages and disadvantages of incineration and factors affecting the effectiveness of this process are discussed as follows (U.S. EPA, 1991):

- **Advantages:** This method can destroy any material containing organic carbon, also pathogens that found in medical waste. Additionally, reduces the volume and mass of material that must be disposed of by 80-90%. The heat from incineration can be recovered and used to generate stream, which can be used directly or can be used to generate electricity. This helps to reduce the operating cost and makes the process environmentally friendly.
- **Disadvantages:** Main disadvantage of this process is air emissions, which contain several pollutants. It produces ash that contains leached metals, dioxins and furans. Moreover, incinerators are complex, difficult to test, and require experienced personnel. In the same manner, medical waste incinerator's waste is considered as hazardous waste.
- **Factors Affecting Effectiveness:** Firstly, incineration temperature affects the effectiveness, for instance high temperatures increase the destruction of organics. Secondly, the residence time of the solid materials in the incineration is important; the longer time the more complete destruction. Thirdly, the mixing of the waste with the combustion of high temperature air is another parameter. Additionally, the characteristics of the waste can influence incinerator temperature and residence time. As an example; waste material, which contains plastics and paper, has high heat content and will burn quickly and produce high temperatures.

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Table 3. Disposal methods and amounts of medical waste (TurkStat)

Disposal Method	Amount (Tons/Year)		Data Year
	Hazardous Medical Waste	Non-Hazardous Medical Waste	
Landfilling	32.471	13.883	2010
Incineration	17.287	-	
Composting	13	-	
Landfilling	37.195	2.688	2008
Incineration	14.801	-	
Composting	15	-	
Landfilling	5.989	20.559	2006
Incineration	6.474	-	
Composting	17	-	
Landfilling	13.497	-	2005
Incineration	10.408	-	
Composting	-	-	
Landfilling	12.557		2004
Incineration	8.224		
Landfilling	14.042		2003
Incineration	8.541		
Landfilling	14.468		2002
Incineration	7.045		
Landfilling	12.948		2001
Incineration	7.410		

Following table describes the general frame for medical waste and their disposal method statistics in Turkey (see Table 3).

From the graphed data, it is obvious that the most preferred option for disposal of medical wastes is landfilling in Turkey. After landfilling, incineration and composting comes, respectively (see Figure 3).

Hazardous Waste Management

Hazardous waste is considered as dangerous or potentially harmful to human health and/or the environment. They consist of liquids, solids, gases, or sludge and can be disposed of commercial products, like cleaning fluids or pesticides, or the by-products of manufacturing processes.

Resource Conservation and Recovery Act (RCRA) legislation in the United States has been defined hazardous waste as a combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may cause an increase in mortality and/or (ir)reversible illness or pose a potential hazard to human health or the environment when improperly managed (Wentz, 1989).

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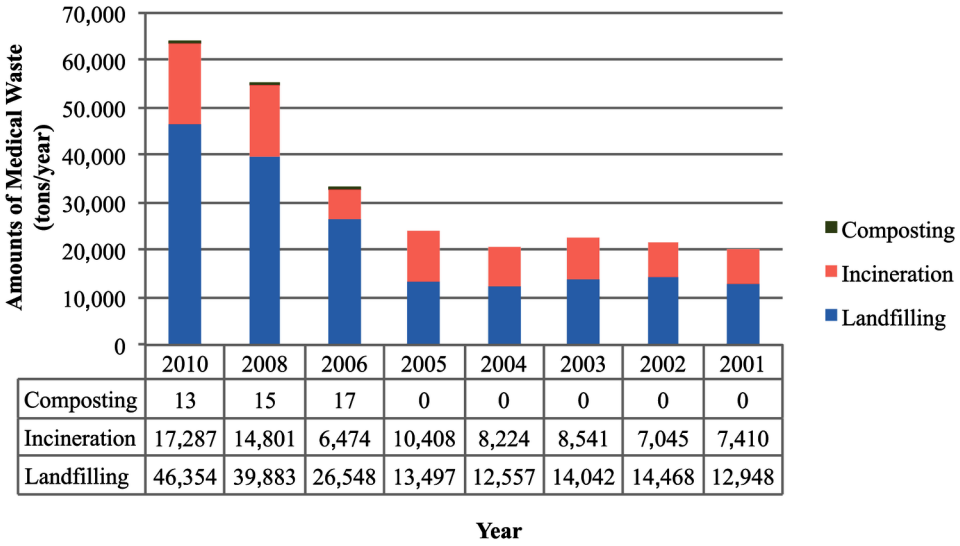
Figure 3. Disposal methods and amounts of medical waste



	2010	2008	2006	2005	2004	2003	2002	2001
Composting	13	15	17	0	0	0	0	0
Incineration	17,287	14,801	6,474	10,408	8,224	8,541	7,045	7,410
Landfilling	46,354	39,883	26,548	13,497	12,557	14,042	14,468	12,948

Integrated hazardous waste management is a system in which reduction, minimization, collection, declaration, packaging and labelling, temporary storage, recovery, transportation and disposal mechanisms are examined separately hazardous wastes. In this system, following up the control periods for these wastes are implemented with the light of regulations.

Separation of Hazardous Wastes

The characteristics must be identified by physical, chemical and biological properties of the waste and the properties should be measured by standardized testing methods. Hazardous waste generated from industries has to be collected and stored separately in accordance with special waste codes (characteristics), which are specified in Regulation on Control of Hazardous Waste (2005). Defining hazardous waste is a difficult process; there are many factors that contribute to the nature of the waste. For instance, the unsafe handling and transportation of waste can result in their becoming hazardous, toxic, flammable or reactive. But if the hazards and characterization of the waste have been determined and they have been collected separately, the risks go away (Charles et al., 1989).

Reduction in the Quantity of Waste

The best approach to avoid the waste is source reduction, which is considered the most preferred option in waste management hierarchy. The EPA waste minimization program offered a hierarchy for approaches to hazardous waste reduction or minimization. These are: waste reduction, waste separation and concentration, waste exchange, energy/material recovery, incineration/treatment and secure land disposal, respectively (Blackman, 2001). Waste reduction, which can both save money and protect environment, should be applied. This includes techniques to separate toxic, hazardous and recoverable wastes from the total waste stream. These are used to increase recoverability, reduce the volume and costs and increase management options. The companies, those have implemented this approach effectively, see it

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as a way to improve their profits and competitions among others. In this case, hazardous waste requires special precautions for transportation, recovery and disposal activities. This situation increases the cost and makes generators to budget for these applications. Source reduction makes these costs decrease and helps elimination of the potential threats (Dogru, B., 2012).

Packaging and Labelling

As mentioned in the Regulation on Control of Hazardous Waste, waste generators should apply packaging and labeling of hazardous waste. Each waste has its own storage tank, for instance for liquid waste it should be carried with impermeable barrels; for solid/dust waste it should be impermeable bag (size depends on the volume of the waste) etc. After packaging, the bags or barrels should be labeled. These labels must include the waste name, waste code, physical characteristic and hazardousness of the waste. Additionally, there are DOT labels for hazardous materials packages that are used to warn people about the effects of the hazardous waste (US. Department of Transportation).

Temporary Storage

Temporary storage indicates the process, which is implemented before interim storage, recovery, recycle or disposal applications. This process is applied by the waste generator and takes place in the facility or any appropriate area out of the facility. The most important point is that, the area whether in or out of the facility, has to be safely protected (Wang et al., 2007).

The accumulation or storage area of hazardous waste must meet some conditions, which are indicated in each country's related regulation. In Turkey, as indicated in the Regulation on Control of Hazardous Waste, these conditions are:

- Facility can store its waste without permission, if the waste amount is 6000 kg for six months, (1000 kg/month each),
- Personnel should be trained and governorship must be informed about his/her communication details,
- The area must be closed, and access must be restricted to authorized persons only,
- The area must be steady, impermeable, safe and convenient to international standards for storage,
- There should be absorbent materials to ensure the protection; drainage channel to collect the leakage, if any,
- Safety precautions must be taken for all emergency cases, such as fire,
- Waste must be labelled, all necessary information should be written on the labels, put in the containers and closed.

Subjects (updates/differences) related to the design of the storage area are determined by an advice issued by the Ministry (Regulation on Control of Hazardous Waste, 2005).

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Transport to Disposal Area

All hazardous waste must be transported in special containers that are labeled with the information about the name of the waste, type of hazard, generator's name and address and "hazardous waste" expression. Licensed transporters' and treatment, storage and disposal facilities' information can be found in municipalities.

Vehicles must have special license for transportation of hazardous waste, and must contain some documents (types: A, B, C, D and E, each for different purposes) to record the process. For example; domestic and international transportation papers should be filled and kept by transporter, also sent to the municipality (Regulation on Control of Hazardous Waste, 2005).

To investigate the waste stream effectively; to prevent the inappropriate waste handling, recovery and disposal; to detect inadequate waste declaration of producers and deficient reporting applications and to interfere the emergency situations, there is a system called MoTAT (Mobil Tehlikeli Atik Takip Sistemi) in Turkey, which is established by the Ministry of Environment and Urbanization in 2012. This is an online system that helps to record all necessary information for hazardous waste generators and transporters.

Recovery

Through various physical and/or chemical treatments, waste is converted into a secondary raw material for different processes. Recovering wastes can contribute a cost effective management alternative. This approach helps to eliminate waste disposal costs, reduce raw material costs and provide income from marketing of the waste. Recovery of wastes is an expansive practice in many processes, for example; in chemical manufacturing the technique is using spent electrolyte from one division as raw material to another; or in printed circuit boards the technique is recovering copper and tin or lead from process wastewater using an electrolytic recovery system (Librizzi; 1999).

Recovery activities that are applied in Turkey, are mentioned in the Regulation on Control of Hazardous Waste as follows (see Table 4).

Table 4. Recovery activities of hazardous waste (Regulation on Control of Hazardous Waste, 2005)

R1	Use as a fuel
R2	Solvent recovery
R3	Organic substance recovery
R4	Metal recovery
R5	Inorganic substance recovery
R6	Acid – base reproduction
R7	Recovery of used parts to reduce pollution
R8	Catalyzer recovery
R9	Oil recovery
R10	Land spreading
R11	Reuse for wastes produced between steps R1 and R10
R12	Recovery for wastes produced between steps R1 and R11
R13	Stocking wastes until processing

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These activities can be done both on-site and off-site. In most cases, the most appropriate place for recovering process is the facility, where waste is generated. Although, they may be recovered at an off-site facility when the equipment is not available on-site, generated waste amount is less or the recovered material cannot be reused (Wang, 2007).

Physical and Chemical Pretreatment

Wastes are processed to some physical and chemical pretreatment applications (i.e. material handling, physical-chemical fining, liquid separation, solidification/sterilization, refuse-derived fuel and sludge drying) to ensure recycling, landfilling or reducing the harmful effect on the environment (Saltabas et al., 2012). After the pretreatment processes, if the wastes become inert and free of hazard, then they can be stored at regular storage areas. This application should be documented by authority and should be applied within the scope of related regulations (Regulation on Control of Hazardous Waste, 2005).

Methods for Disposal

Characterizing a waste to determine the proper cost-effective treatment requires both a description of the waste composition and a definition of hazardous or nonhazardous streams. The selection of the process mainly depends on the chemical composition of the waste.

When disposed improperly, hazardous wastes can contaminate air, soil and groundwater and also increase the risk of human disease and environmental contamination. A large quantity of any hazardous waste can only be properly transported or disposed of by certified environmental professionals. Small quantity of hazardous waste can be handled by generator. Most common methods for disposal are deep well injection, incineration and landfilling, which are mentioned in this chapter as follows.

Deep Well Injection

Deep well injection is a technique, which is applied by pumping liquid hazardous waste through steel pipes into wells, clearances or evaporites. High pressures are applied to force the liquid into the pores, where it will be permanently stored. Applicants should prepare a feasibility study and present it to ministry before using deep well injection. There are some concerns about this method, which are mainly groundwater and aquifer contamination and geological damage. Criteria for deep well injection are determined by ministry and take part in related regulations (Regulation on Control of Hazardous Waste, 2005).

Incineration

Generally, hazardous wastes consist of carbon, hydrogen and oxygen; also they may contain halogens, sulfur, nitrogen and heavy metals in small quantities. If the waste molecules can be reduced to carbon dioxide, water and some additional inorganic substances, this means they can become non-hazardous materials. Because of this reason, incineration is the most preferred option in hazardous waste management. This technology reduced the need for landfills, and related problems like landfill leakage, releasing hazardous materials into environment (Wentz, 1989).

Incineration is the controlled high temperature oxidation of organic compounds to produce carbon dioxide and water. This method requires control of the kinetics of chemical reactions, and represents a combustion process applied to destruct hazardous substances. In Turkey, incineration facilities are

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designed according to related regulations. For this case, in addition to the Regulation on Control of Hazardous Waste, there is one more regulation called Regulation on Control of Industrial Air Pollution. In which, extreme values are mentioned for gas outlet.

Some advantages and disadvantages of incineration are discussed as follows (Wentz, 1989):

- **Advantages:** This method is an advantageous technology for management of hazardous wastes that have high heat-release potential. Waste can be either liquid or solid, the bulkier the materials to be incinerated, the grater the reduction in volume of wastes. Incineration ensures reduction of harmful effects like carcinogen, mutagen and teratogen; additionally prevents disease transmission and adverse effects on other processes. Further, it reduces leachable wastes from landfills and eliminates long term odors caused from landfills. Another advantage of this method is the potential energy recovery of the heat released and recovery of valuable products by recycling, reusing or marketing.
- **Disadvantages:** Main disadvantage is its investment costs; not only initial investment, but also operating costs are higher than many other technologies. In addition, it requires highly trained operators, because the control of this technology is a complex application and the equipment requires high maintenance. In order to provide compliance, qualified supervisory is needed. This method has various impacts on human health and the environment. The emission of odors, particulate matter, and some gaseous substances should be controlled within the scope of regulations. Wastewater and runoff storm water can be affected by the formation of air pollutants, such as hydrogen chloride, sulfur dioxide, carbon monoxide, heavy metals and other ash particulate matters. Both waters must be effectively managed to ensure safety.

Landfilling

Landfills are sites where non-liquid hazardous waste is deposited and covered. This method is designed to minimize the releasing of hazardous waste into environment. If the precautions are enough to protect environment and characterization of the waste is suitable for landfilling, this method can be applied. If limit values are not feasible, physical, chemical and biological treatment must be applied before operation. The limit values are mentioned in related regulations, for this case in the Regulation on Control of Hazardous Waste.

Following table describes the general frame for hazardous waste and their disposal method statistics in Turkey (see Table 5).

From the graphed data, it is obvious that the most preferred option for disposal of hazardous wastes is landfilling in Turkey (see Figure 4).

SOLUTIONS AND RECOMMENDATIONS

The waste management strategies applied by developed countries cannot be translated directly to developing countries. Reasons behind this are lack of resources, legislation, personnel and lower public awareness (Curi, 1993). In most developing countries, medical and hazardous wastes are not considered as an important concept, and because of the absence of proper applications, problems become more serious.

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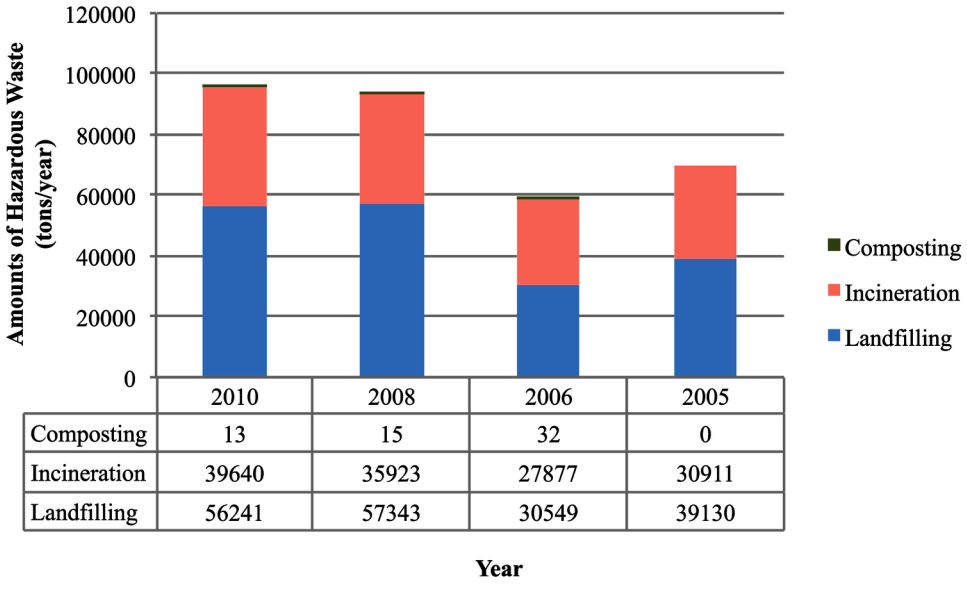
Table 5. Disposal methods and amounts of hazardous waste (TurkStat)

Disposal Method	Amount (Tons/Year)	Data Year
Landfilling	56.241	2010
Incineration	39.640	
Composting	13	
Landfilling	57.343	2008
Incineration	35.923	
Composting	15	
Landfilling	30.549	2006
Incineration	27.877	
Composting	32	
Landfilling	39.130	2005
Incineration	30.911	
Composting	-	

Figure 4. Disposal methods and amounts of hazardous waste



In Turkey, there are insufficiencies while applying regulations. Application ratio of legislations is low, also collection of data is not implemented regularly; as a consequence, environmental related problems are extensive. Tables 6 and 7 show the reasons for the lack of application of related regulations.

It is obvious that the most dominant factor behind the lack of application is economic issues. Other reasons are lack of personnel, technical issues, lack of instruments and lack of information, respectively. Municipalities are responsible for this situation; they have to budget for environmental issues, train personnel and apply all stages mentioned in regulations. Awareness programs on handling of wastes and management of personnel can prevent adverse effects.

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Table 6. Survey results to examine the lack of application of related regulations (TurkStat)

Year	Number of Municipalities	Reasons for Lack of Application					
		Lack of Information	Economic Issues	Lack of Personnel	Technical Issues	Lack of Instruments	Other
2008	3225	223	1.565	1.059	871	818	40
2006	3225	198	1.689	1.081	964	862	2
2004	3213	642	1.701	1.173	951	1.023	224
2003	3215	734	1.837	1.230	998	1.233	184
2002	3215	1.005	1.640	990	717	930	114
2001	3215	942	1.768	1.081	757	970	25

Table 7. Survey results to examine the lack of application of related regulations (TurkStat)

Year	Number of Municipalities	Reasons for Lack of Application					
		Lack of Information	Economic Issues	Lack of Personnel	Technical Issues	Lack of Instruments	Other
2008	3225	341	1.520	996	898	674	97
2006	3225	341	1.507	917	860	598	102

Education of the general population should be increased about waste sorting, recycling, disposing and composting of the waste. For sustainable development and protection of both environment and public health, there should be a system that is applied effectively.

CONCLUSION

There is a growing demand on safe and clean environment. On the other hand, increasing demand on industrial capacity causes increase in waste amounts. Minimization and prevention of wastes is more effective and long-term approaches than to operate treatment plants. Additionally they have short-term benefits such as relief of some disposal problems. For instance, in manufacturing and production of goods, usage of hazardous materials should be lessened. This will ensure prevention of waste and have positive effect in dealing with it. Although, waste minimization, prevention and recycling are not well practiced in Turkey, which results in large amounts of medical waste that is disposed in different ways. If medical and hazardous waste are not handled and disposed separate from domestic wastes, transmission of diseases may occur and this situation has adverse effects on both public health and environment. Efforts have to be made for improving both hazardous and medical waste management technologies. In addition, there are many methods for disposal of medical and hazardous wastes. In Turkey, incineration is the most applied method for both waste groups, which ensures destruction of toxic organic substances and avoidance of risks resulting from improper disposal.

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KEY TERMS AND DEFINITIONS

Public Health: A science and practice for protecting the health of a community. Possible applications can be mentioned as health education, control of diseases and monitoring environmental related problems.

Refuse-Derived Fuel: A fuel produced by dehydration of solid wastes with special technologies. Combustible materials are preferable (i.e. plastics or biodegradable wastes) to ensure high quality refuse-derived fuels.

Risk Assessment: Managers need to think about the factors that might cause harm to people and need to take some special steps to prevent them. This concept is risk assessment and to ensure health and safety of the business, risk assessment should be applied.

Solid Waste Management Hierarchy: A concept developed by United States Environmental Production Agency, which ensures ranking of all methods applied to the solid waste. The hierarchy consists of five steps, they can be sorted from most preferred to less as follows: source reduction and reuse, recycling or composting, energy recovery and treatment and disposal.

Waste Management: An approach that consists of all stages to process waste such as generation, prevention, characterization, transport, storage, treatment, handling, reuse etc.

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Chapter 11
Design and Operation of Semi-Aerobic Landfill

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ABSTRACT

Landfilling is broadly recognized as a proper waste disposal method. Although ranked at the bottom of sustainable waste management hierarchy, final waste disposal technologies like sanitary landfill remain crucial for development country due to increasing waste generation. Since landfill is a permanent disposal site that could cause serious environmental pollution, a proper planning and development of landfill are important in avoiding problems in the future. In this chapter the general principles of landfill design and operation is given at the beginning. Then the following discussions were focusing on the design and operation of semi-aerobic landfill. The revision for design and operation of semi-aerobic landfill working phase were reported separately. Finally the summary of the discussion were given at the end of this chapter.

INTRODUCTION

Solid waste management is a systematic practice of waste generation storage, collection, transport, treatment and disposal (Agamuthu, 2010). Sanitary landfill is one of the important methods for solid waste disposal in waste management system. Even though there are more advance disposal methods have been developed, the sanitary landfill remains as an ideal method for developing country (Idris & Hassan, 2004). The sanitary landfill is a final disposal method that treats and restores the organic portions of the waste to the nature which emphasizing the technical aspects like siting, design, operation and long-term environmental addeddment (Hans & Ramke 2001).

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Table 1. Landfill classification system based on decomposition process employed

Landfill Type	Characteristics
Anaerobic landfill	Solid wastes are filled in dug area of plane field or valley. Waste is commingled with water in anaerobic condition.
Anaerobic sanitary landfill covered daily	Solid waste is covered in a sandwich shape. Condition in solid waste is same as anaerobic landfill.
Improved anaerobic sanitary landfill	Leachate collection system is installed at the bottom of the landfill site. Others are the same as anaerobic sanitary landfill. The conditions are still anaerobic but the moisture content is much less than anaerobic sanitary landfill.
Semi-aerobic landfill with natural ventilation and leachate collection facilities	Leachate collection duct is bigger than the one of improved sanitary landfill. The opening of the duct is surrounded by air and the duct is covered with small crushed stones. Moisture content in solid waste is low. Oxygen is supplied to the solid waste from leachate collection duct.
Aerobic landfill with forced aeration	The leachate collection pipe and air supply pipes are attached. Air is forced to enter the solid waste causing it becomes more aerobic than semi-aerobic landfill.

Unlike open dumpsite, the sanitary landfill is designed to deal with leachate, landfill gas and odor management. The collected wastes are handled at a disposal facility that is designed and operated at a constraint of public health and environment protection. The primary purpose of landfill site is to implement final disposal of the waste with minimum environmental impact. Besides, the sanitary landfill system can be classified based on decomposition process employed. Table 1 describes the characteristics of the landfill types.

Among others sanitary landfill syste,m the semi-aerobic landfill is the most desirable landfill design (MHLG, 2004). It is also referred to as "passive aeration" by the United Nations (UN) and was approved as a new Clean Development Mechanism (CDM) (Tashiro, 2011). Initiated by Prof. Masataka Hanashima of Fukuoka University, pilot semi-aerobic landfill was first tested in 1975 at Shin-Kamata Landfill in Fukuoka, Japan (Chong & Hassan, 2005). Interestingly, the semi aerobic landfill is largely implemented in the eastern part of Asia (Zhang et al., 2013; Sangjae et al., 2014). This is most probably due to the leachate and waste stabilization via passive aeration without using any type of mechanical equipment (Toshishiko et al., 2015). Figure 1 shows the schematic diagram of semi aerobic landfill. In semi-aerobic landfill system, oxygen flows into the waste mass through the leachate collection pipes by passive ventilation to accelerate an aerobic microbial decomposition in the waste body. It hastens waste stabilization and improves leachate water quality (Theng & Mohd, 2005).

Meanwhile, leachate and gas are continuously discharged using leachate collection and gas venting system. Semi-aerobic landfill is claimed to be a simple environmentally and economically sound technology. The advantages of semi-aerobic landfill are listed down as follows:

A. It purifies leachate significantly by increasing waste decomposition rate.
B. It contributes towards global warming mitigation by reducing methane gas emission substantially.
C. The risk of gas explosion and fire hazard is reduced by releasing the gas from ventilation pipes.
D. It converts open dumps into sanitary landfills in an easier way.
E. Earlier landfill rehabilitation is expected through enhanced stabilization.
F. It is cost-effective due to the high degree of freedom in construction material selection and utilization of less intensive leachate treatment system.

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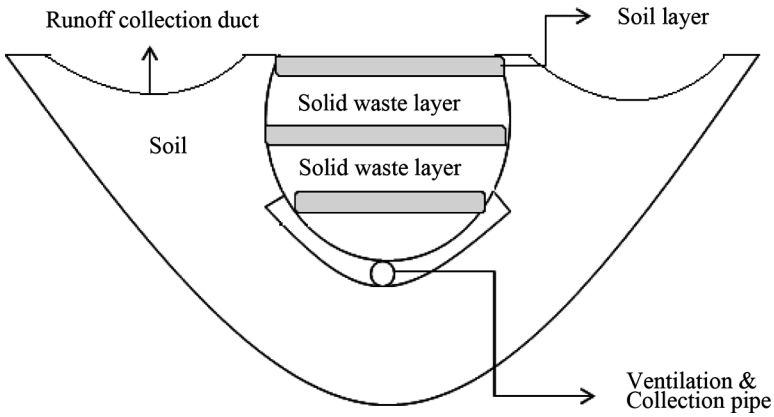
Figure 1. The schematic diagram of semi aerobic landfill



G. It is easy to construct, operate and maintain. Self-purifying capacity is used to stabilize waste body and only requires commonly used machinery and equipment.

The effectiveness of the sanitary landfill site is based on disposal performance in fulfilling the actual need of the region (Peter et al., 2000). In planning the sanitary landfill, it is necessary to determine and establish the master design and operational plan for landfill. Landfilling process includes a series of activity which begin from delivery of solid waste into the landfill site until the maintenance and control of the landfill. Semi-aerobic landfill design requires particular planning by considering the actual site conditions like precipitation rate, ambient temperature, soil foundation and rainwater flow area (Matsufuji, 2007). Therefore, in this chapter, the revision for the design and operation of semi-aerobic landfill working phase are reported.

LANDFILL DESIGN

The design process is an important phase in the development of sanitary landfill.The design of sanitary landfill generally refers to the lifetime and the capacity of desired landfill. Besides, the requirement and the standards of the landfill design are dependent on the landfill classifications. In this section the main principles of design process description and explanation for semi-aerobic are discussed.

DESIGN CONSIDERATION

Design Objective

Generally, landfills are constructed on a phased basis. The initial step of landfill development is landfill design process. The main objective of landfill design is to provide effective control measures to prevent and minimize the negative effects on the environment (Peter et al., 2000). The pollution of surface water, groundwater, soil and air, as well as the resulting risks to human health were among the potential

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negative effect of landfilling waste (MHLG, 2004). The engineering criteria and design concept of sanitary landfill are depending on the ground conditions, the geology and hydrogeology of the site, the potential environmental impacts and the location of the landfill (Peter et al., 2000). Therefore, ground investigations for a landfill planning should provide sufficient information to enable the formulation of a site specific design.

Besides that, the function of landfill design is to provide safety and storing capability of the waste within its environment boundary (MHLG, 2004). The minimal standard function of landfill design should provide retaining function, waste control function and treatment function (MHLG, 2004). Each of the landfill design planning should be kept in workable conditions throughout the operational period, closure and post closure use period. Other than that, the landfill design is used to evaluate the suitability of selected landfill location. Ideally, at the closed landfill site, the continuous monitoring must be carried out before any redevelopment being proposed. The design of monitoring continuity provides future environmental effects and their conditions. Thus, it is necessary to design landfill system which fulfilling the design objective.

Design Requirement

The design requirement for landfill site is necessary to ensure a systematic and consistent approach. The designer should follow the actual practice of design aspects in planning a landfill site. The design requirements are listed as follows:

A. **Waste Characteristic and Lifetime:** Waste characteristic will dictate the control measure needed for the landfill lifetime. The nature and quantities of waste will change the landfill facility conditions and considerations (Menard et al., 2004). The failure of waste type consideration may result in the reduction of disposal capacity and environmental problems. This corresponds to the policy of implementing adequate solid waste treatment from the landfill lifetime (Peter et al., 2000).
B. **Water Measure:** The water control measure is required for the reduction of leachate generation (Peter et al., 2000). It will minimize the amount of water entering to landfill through precipitation, surface water and groundwater. In addition, the water control design is important for the water collection and treatment process before allowing it to be discharged.
C. **Soil and Water Protection System:** The protection system for the landfill soil and water will prevent hazardous chemicals from contaminating groundwater and surface water. A liner system must be designed based on the waste material. Clay and composite liner are applicable for organic waste while other type of waste must meet the prescribed permeability and thickness requirements of the liner (Michael & Tanya, 2002). Thus, the designer must be able to model the effects of any hazardous matter migration through the liner and into the groundwater.
D. **Leachate Management:** The landfill leachate management must be consisted with the collection, storage and treatment systems. These system facilities are to ensure efficiency of the system to keep the accumulation of the leachate at the minimal level (MHLG, 2004). This system must be designed based on the specific waste to be disposed, climate and the volume of leachate to be collected.
E. **Gas Control:** The landfill designer should provide the collection system for the accumulated and migrated landfill gas either for utilization or disposal. The common types of collection system to control the migration of landfill gas are flaring and venting systems.

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F. **Environment Nuisance:** Environmental nuisance such as noise, odors, dust, litter, birds, vermin and fires may arise during the construction, operation, or closure of the landfill. The landfill designer should provide a control system to minimise the environmental nuisance (Peter et al., 2000).

G. **Landfill Stability:** The landfill stability covers the conditions of the landfill slope, the systems components (liner, cover material, leachate collection system and etc.), the waste mass and the capping system (Peter et al., 2000). The landfill designer should provide the landfill stability system to avoid land sliding or any stability failure (MHLG, 2004). In addition, the retaining facilities design is necessary for the landfill stability.

H. **Site Development:** The landfill design must consist with the site development and site infrastructural requirements. Site accommodation, weighbridge, waste inspection area, wheel wash, site services and security facilities are necessary during landfill operation and restoration (Peter et al., 2000; MHLG, 2004).

I. **Landfill Monitoring:** The landfill monitoring process is the collection and comparison of information to the permit and determining compliance (Peter et al., 2000). Permit and engineering drawings, field measurements, sampling requirements for surface water and groundwater monitoring, gas testing, and waste volume data are the data categories that needed in the landfill design (Michael & Tanya, 2002).

J. **Facility Cost:** The landfill design should include the facility cost planning. Predevelopment cost, site preparation and construction cost, operating cost, site closure cost, post closure and maintenance care cost are the cost categories that needed in the landfill design (Michael & Tanya, 2002). The budget estimation for the facility at the design stage is necessary in order to ensure sufficient funds for the landfill development.

K. **Post Closure Care:** The landfill closure steps must accomplish the final certification of landfill report (MHLG, 2004). The post closure care design of landfill is used to monitor the physical layout and the material component of the landfill surrounding. The corrective action for redevelopment plan of the landfill will be taken based on the monitoring report.

L. **Risk Assessment:** The risk assessment design is used to develop control methods and procedures that minimize the harm to employees, the public and the environmental surrounding (Peter et al., 2000). This risk assessment is designed based on the proposed development plan of the landfill.

LANDFILL DESIGN STANDARD

The design of landfill is bonded with a standard compliance regulated by environmental authorized bodies (Michael & Tanya, 2002). The standard provides the outline of technical requirement and approval process for each category of landfill. The design approval must be followed by submission of the application with engineering drawing for each performance specifications (e.g. leachate control system). In fulfilling each requirement, the specific guidelines are provided on different aspect of the landfill design. The guidelines manual is used to assist the general process of landfill design and to provide the updated relevant information. It is necessary for every landfill design to keep the records of the process systematically. The quality control procedures of the landfill design should be used to ensure the design and development process is carried out satisfactorily (Peter et al., 2000).

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SEMI-AEROBIC LANDFILL DESIGNCONSIDERATIONS.

The main consideration of semi-aerobic landfill design is given to the facility specification. The considerations includes the construction cost, maintenance control, leachate discharge pipe opening, leachate collection discharge capacity and material, cross section of leachate collection discharge capacity, protection and perforated areas in leachate collection discharge pipe, protection and installation of gas venting pipe and feasibility of leachate circulation. The detail explanations for each design consideration are given as follow:

A. **Construction Cost and Maintenance Control Capability:** The design of semi aerobic landfill is aiming to reduce the construction cost as low as possible (Matsufuji, 2007). This cost effective landfill constructions are performed using various materials that can be obtained easily. Bamboo, tires and waste barrel are among accessible materials which can be used as facility component for leachate collection pipe, discharge pipe and gas venting pipes protection material (Matsufuji, 2007). Even though, the constructions are using such types of materials, the importance of maintaining health hygiene is not left behind. The construction cost design must be ensured to provide suitable final disposal site with cost effective results. Besides that, the availability of local competent person must be provided prior to the landfill construction. These competent personnel are required to provide maintenance control during the configuration of landfill construction.

B. **Leachate Discharge Pipe Opening:** The design consideration for leachate removal prefers a simple system of maintenance control. The discharge pipe opening is used to supply air into landfill layer and remove the excess of water quickly from the landfill. This discharge pipe opening must always be opened to the atmosphere to maintain the aerobic state of the landfill (Matsufuji, 2007). Figure 2 shows the comparison of leachate discharge pipe opening flow. The natural flow is a cost effective construction method and more efficient compared to the out site and in site pit pump method which increases the operation expenses.

C. **Cross Section of Leachate Collection Discharge Pipe:** The cross section design for leachate collection discharge pipe must be able to supply smooth air flow into the landfill area. Depending on the topography of the landfill area, the cross section design of the discharge pipe can be arranged into different line patterns (e.g. ladder pattern, herring bone pattern). However, the pipe diameter of the main leachate collection discharge pipe is recommended to be small at least 450 mm with spacing range from 20 to 30 m (MHLG, 2004; Matsufuji, 2007).

D. **Leachate Collection Discharge Pipe and Covering Material:** The design of covering material for leachate collection discharge pipe is necessary to avoid the leachate retaining in the landfill (Kim et al., 2009). In order to prevent clogging of the discharge pipe, the thickness of the cover material should be more than 50 cm from the ground level. The width of the cover material must be 3 times more than the diameter of the pipe; this is to ensure the functionality of the collection discharge pipe. Therefore an improved structure of the covering material should be designed in ensuring the air streaming in leachate collection discharge pipes is open for allowing aerobic decomposition.

E. **Protection and Perforated Areas in Leachate Collection Discharge Pipe:** The protection and perforated areas in leachate collection discharge pipe are implemented by using protective layer of buffer blanket, sand and soil cover. This is to ensure a proper streaming of leachate collection and air flow through the landfill. In order to ensure the discharge pipe streaming are smooth, the base should be fixed and built up by packing material around the pipe.

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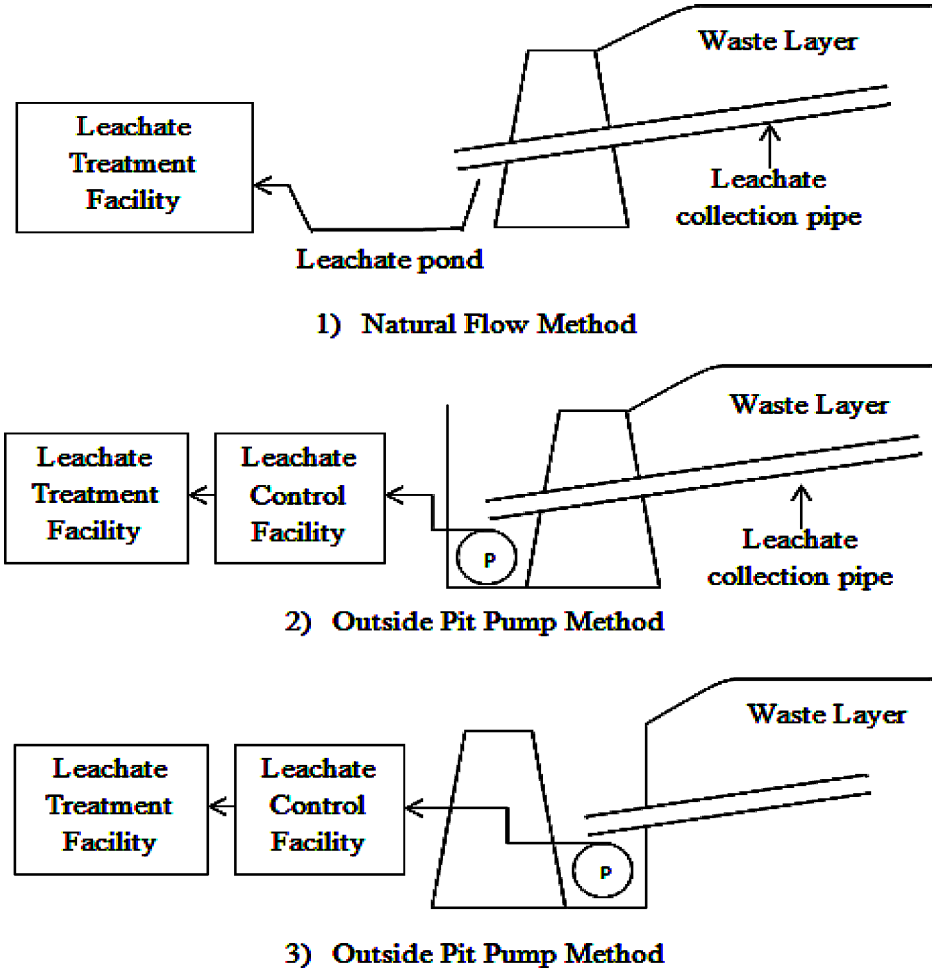
F. **Installation and Protection of Gas Venting Pipe:** The function of the gas venting system is mainly to remove the gas generated within the landfill layers into the atmosphere. The proper design of gas venting facility would support the management of landfill site upon the completion. Therefore, the overall structure, position, size etc. should be considered. The installation design of gas venting system must be equipped with the protection of the venting facility. In the flat landfill site, the spacing for each venting pipe is 20 m to 40 m (MHLG, 2004). However, for landfill with high waste level, the installation of horizontal pipe at every 15 m of waste layer is recommended (Matsufuji, 2007).

Figure 2. The comparison of schematic diagram of leachate discharge pipe opening flow



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LANDFILL OPERATION

The landfill operation is a continuous process after designing and constructing the sanitary landfill plan. The landfill operation describes the operation and maintenance facilities of the specific design elements. In this section, the consideration of semi aerobic landfill operation is discussed.

Landfill Operation Consideration

The landfill operation consideration is important to ensure that the related design and constructed facilities are activated. The operations of the landfill should follow the considered aspects in operating the landfill site. The details of the operation consideration are listed as follows:

A. **Landfilling Process and Waste Handling:** The process of landfilling begins with solid waste delivery into the landfill site. The process followed by spreading, mixing, and covering the waste using final soil (Hans & Ramke, 2001). In this process, the suitable method must be selected based on the specification of the landfill site as well as the volume of waste generated daily. Among the available methods were area method, trench method and depression method. However, there are also other appropriate methods for each series of landfilling activities. Cell construction, dumping, spreading and compaction of the waste landfilling process has each specified method (Hans & Ramke, 2001). Therefore, consideration should be taken in handling the landfilling process. Besides that, the type of waste admitted and landfill equipment used for disposal must be classified into different categories (MHLG, 2004). Although the waste is generally commercial waste, there is also hazardous waste that formed by industrial sector. Thus, the list of waste admitted for disposal must be included as an operational manual of the landfilling process.

B. **Safety Measures:** The landfill operation is involved with many kinds of potential risks. The heavy equipment of processing, transportation hazards, foreign materials in the raw material, noise, dust and fire are among the potential risks that might be occurred in landfill operation (Michael & Tanya, 2002; MHLG, 2004). The accidents cases during the landfill operation could give negative effect to the workers morale and productivity. Therefore, the operational safety system shall be considered in minimizing and preventing the potential risk. The descriptions of the safety measures, security and working activity at the landfill site are necessary for the landfill operational safety. Besides that, permit approval should be provided for every working process in the landfill operation. This permit is used as an identification system for the landfill operation. Furthermore, every work conducted in the landfill must be registered based on the category of facilities, personal involved, processing and type of management.

C. **Monitoring and Maintenance:** The monitoring and maintenance system of the landfill operation are necessary in prolong the lifetime of the landfill. This operational consideration comprises of meteorological data, leachate, gas emissions, ground water and surface water monitoring (MHLG, 2004). The monitoring of the meteorological data is used for the water balance of the landfill site. This monitoring calculation is based on humidity and temperature condition. Besides that, the monitoring of leachate collection is used for the quality and quantity measures. The quality and quantity of the leachate provides the indication of the necessary treatment method (Kashif et al., 2012). Other than that, the gas emissions analysis calculates the potential of gas utilization. The gas emissions monitoring is important to avoid potential of explosion or fire. Plus, the surface and

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the ground water monitoring provide the analysis of the contaminants in the water. This monitoring presents the influence of waste disposal to the ground water. However, the monitoring work must represent all of the landfill area involved.

D. **Supplemental Operation Facilities:** The supplemental facilities can be used to improve the landfill operation efficiency. This supplemental facility is mainly used to enhance the control and management system of the landfill site. However, the addition of the facilities is basically depending on the size and the condition of the landfill. The related supplemental facilities are listed as follows (MHLG, 2004):
   1. Proper access road for transportation
   2. Littering preventer facilities
   3. Fire station facilities
   4. Bunds and retaining walls
   5. Temporary water ponds facilities to prevent overflow of rain water and flood.

OPERATION OF SEMI-AEROBIC LANDFILL

The operation of semi aerobic landfill is mainly concerned on maintaining the aerobic conditions of the landfill. Therefore, the focus of landfill operation is to maintain the collection discharge pipe of leachate and gas venting system. The details for other semi aerobic landfill operation basic items and specifications are listed in Table 2.

Table 2. Basic items and specifications of semi aerobic landfill operation. (Theng et al., 2005)

No.	Item	Specifications
1	Leachate collection and re-circulation facilities Gravels	Estimation of 2063 m3 (2800 tonnes) for both main pipes and branch pipes
2	Leachate collection pipes (Main)	400 m length · 1 pipe (600 mm diameter)
3	Leachate collection pipes (Branch)	150 m length · 30 pipes (450 mm diameter)
4	Leachate circulation pipes and pump	Estimation of whole re-circulation system
5	Collection pond (excavation work)	3 ponds of 15,400 m^3
6	Surface water interception drainage	Drains: 0.6 m deep
7	Drainage installation (with piping system)	Standard concrete drainage with 0.6 m depth, 1600 m length
8	Gas venting pipes	Concrete pipes of 375 mm in diameter · 45 pipes · 16 m length
9	Leachate treatment Facility Aerators	3 units at each primary and secondary pond
10	Monitoring wells Boreholes and wells constructions	2 at upstream, 2 in the middle and 3 at the downstream
11	Primary retention ditch	3 m depth and 2 m width for about 1600 m length
12	Secondary retention ditch	3 m depth and 2 m width for about 1700 m length

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A. **Maintaining Leachate Collection and Discharge Pipes:** The maintenance of the leachate collection discharge pipes is important for keeping aerobic disposal condition in the landfill operation. This maintenance work is to ensure smooth air flow circulation through discharge pipe. The malfunction of the discharge pipe is mainly due to the small size and non-soluble waste material that clogged inside the pipe. Besides that,the small layer of landfill thickness promotes the damage of discharge pipe by the movement of vehicles in the site. Therefore, the application of filter and easily flow waste material must replace the bulky and rough waste material along the discharge pipe leachate collection area. Besides that, the first layer of landfill thickness should be protected with steel plate (thickness> 20 mm) at least 1 m from the discharge pipe to disperse the load stress from the transport vehicle (Matsufuji, 2007). Furthermore, the leachate water level should be controlled to ensure the discharge pipe is open to the atmosphere all the time.

B. **Maintaining Gas Venting Facility:** In semi aerobic landfill operation, the gas venting system is installed vertically within 20 m distance from each other. This vertical gas venting pipe diameter must be 10 cm and covered with 1 m of filter diameter. In order to maintain the aerobic disposal condition, the rising of gas venting facility must be in meandering manner. Figure 3 shows the rising of gas venting pipe in a meandering manner. This configuration enables sufficient time for air and rainwater flow to promote oxygen supply. Practically, the thickness of each waste layer must be 3 m apart from each layer. As shown in Figure 3, the gas venting pipe rising configuration must be installed inclined with the stone filling in each of the waste layer. The connection of the gas venting pipe must be arranged in the center within the waste and stone layer. The direction of the gas venting pipe must different from the previous direction. This step should be repeated up to the specified height of the waste layer. This configuration is used to introduce the air to the waste layer. The air could accelerate the stabilization of landfill sites, improve leachate quality and avoid the anaerobic decomposition (Ishigaki et al., 2011). Nevertheless, the maintenance and prevention step must be taken to avoid the gas venting pipe from broken or collapse due to the load of transport vehicle and landfill material during the operation. The gas venting pipe must be protected with independent construction type which is 50 cm higher than the waste layer (Matsufuji, 2007). Other than that, the installation of temporary steel frame around the pipe could prevent the damage of gas venting pipe during the operation. Furthermore, the steel frame installation enables efficient rising operation of the gas venting pipe in the future.

C. **Maintaining the Aerobic Area and Waste Layer:** The selection of covering soil for waste layer is important during the landfill operation. The less permeability of covering layer can stop the air transmission within the waste layer. Besides that, the leachate that is generated through waste decomposition may retain within the waste layer and form a barrier. In order to avoid this condition, the high permeability covering soil such as gravel and sandy soil are desirable (Brogaard et al., 2013). Other than that, the installation of additional leachate collection discharge pipe may remove the retaining leachate within the waste layer. Therefore, for the mountain area of disposal site (20 m of landfill high), the reliable installation of leachate collection and gas venting system is highly desirable. The width of each waste layer is necessary to be at least 1 m directly above the leachate collection discharge pipe. The vertical layer of gas venting pipe must be filled with crushed rock layer which is on the bottom up through the final layer. This configuration enables more collection of leachate as well as promotes good transmission of air within the waste layer.

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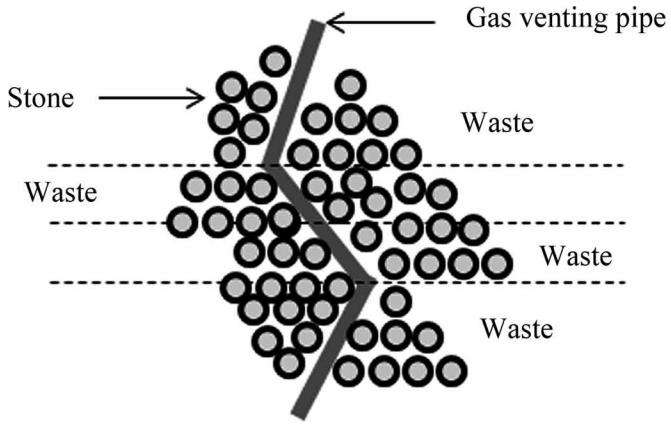
D. **Environmental Monitoring:** In order to ensure the development of aerobic area within the waste layer, the monitoring of leachate and gas generation is necessary (Qi et al., 2013). In semi aerobic landfill, the organic waste is decomposed by aerobic microorganism through solubilization and gasifaction process. Through the decomposition process, solubilize organic substances is converted to solubilize gas of carbon dioxide (CO_2) (Matsufuji, 2007). This process reduced the biological oxygen demand (BOD) value and increased the pH of the leachate. Besides that, the nitrate and sulfate ions are generated through the decomposition process (Matsufuji, 2007). In contrary, the decomposition of anaerobic process produced the accumulation of methane (CH_4), ammonia (NH_3) and hydrogen (H_2 sulfate (SO_4) gases. In fact, the CH_4/ CO_2 ratio for anaerobic landfills and semi-aerobic landfills were reported to be 1.9 and 0.8 (Yang et al., 2012). Therefore, the monitoring of the leachate and gas effluent enables the evaluation of aerobic landfill condition. Other than that, it is used to ensure the quality of the discharged effluent is complied with the environmental standard.

CONCLUSION

The sanitary landfill is an important disposal method in the solid waste management. The development of sanitary landfill enables the utilization of filled land for othernew development. However, the landfill-requires proper planning, design and operation of the sanitary landfill. In this subchapter, the design and operation of the semi aerobic landfill has been discussed. The important factors of design and operation for semi aerobic landfill were elaborated. The main consideration of semi-aerobic landfill design and operation must be given to the facility specification.

In conclusion, the effectiveness of semi aerobic strategy could only be achieved through maintaining the aerobic disposal condition. This condition is mainly depending on the leachate collection system and the gas venting system. The leachate collection discharge pipe and gas venting pipe is specifically used to allow proper air circulation in the landfill. Thus, the design and the operational of semi aerobic landfill are to ensure the acceleration of aerobic microbial decomposition in the waste body. Although

Figure 3. The rising of gas venting pipe in a meandering manner



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the semi aerobic landfill is a convenient, cost effective and reliable implemented system, it requires a full attention of monitoring and maintenance work to be applicable. As a result, the proper design and operation strategy could efficiently promote the practice of the sustainable environment.

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Chapter 12
Items of Consideration in the Design of a Malaysian Landfill

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ABSTRACT

The rate of waste generation in Malaysia continues to rise and this trend has created a pressure on landfills to perform in terms of capacity and quality. This scenario is not unique to the country alone but probably shared by many in the developing world. On one hand newly designed projects are initiated while on the other the old ones are still operating as open dumps. As in most cases with municipalities, a new site is not readily available for the new initiative, thus the existing facility has to accommodate both the newly designed landfill and the existing dump. In most cases also, due to lack of space and economical reasons, the two facilities have to eventually connect with each other and form a single facility. Thus this chapter is not only about designing a new provision but also about amalgamating the new one with the old one. In the design, the new one would require items such as leachate collection and treatment facilities while the old one would necessitate proper cover and drainage.

INTRODUCTION

Solid Waste in Malaysia

Municipal solid waste (MSW) has been defined as to include garbage, refuse, and any unwanted solid material arising from human activities. Disposal of MSW continues to be a major environmental challenge in developing countries including Malaysia.

The rate of waste generation in this country continues to rise each year mainly because of the general and domestic development. The increase has been in line with population and economic growth. In 1998, the yearly waste generated was 6 million tons (0.5-0.8 kg per capita per day). In 2005 however,

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it has increased to 7.43 million tons (Agamuthu, 2006). By the year 2020, the quantity of solid waste generation per year is expected to top 30 million tons (Manaf et al., 2009). Such a tremendous increase is primarily due to the rapid urbanization, increase in population, improvement of per capita income, and changes in consumption patterns (Umar 2009).

Food waste, categorized as organic waste is an important constituent of the solid waste for its unique degradation properties. It represents 32% of the waste composition in Malaysia (Ridhuan, 1995). Typically, an MSW sent to landfill is comprised of food, garden refuse, paper products, plastics, rubber, textiles, woods, and ashes.

Use of Landfills

A landfill allows disposal of large quantities of MSW at an economical cost. Thus MSW disposal by land-filling continues to be the most commonly used method worldwide. In Malaysia, MSW has been disposed off in landfills though some of these facilities have not been properly presented and were simply of open dump category.

The continued used of landfill disposal method is commonly due to convenience. For as long as the adverse environmental effects is tolerated, or mitigated, the use of landfills will eventually transform all waste into relatively inert and stabilized materials (Robinson & Maris, 1983; Williams, 2005). Basically, there are no combinations of waste management practices that do not require landfills. Even in incineration process, there will be waste eventually to be disposed off in a landfill.

The foremost challenge in running a landfill is in ensuring that all operating facilities are designed properly and are monitored not only during operation but also after closure.

Landfill Closure

Designing a sufficient final cover is crucial in ensuring a proper landfill closure (Bagchi, 2004). The final cover is as significant as the liner system that is placed at the base of a landfill early in the preparation. However, the final cover becomes even more important when a liner system has not been used for the base which is common for many of the open dumps that are currently operating in the country. In the Malaysian practice, an open dump is normally closed by having simply about 1 m thick of laterite soil laid over the entire dump area.

Principally, a final cover is applied when a landfill reaches maximum volume capacity in order to minimize rainfall infiltration, reduce leachate generation, and avoid possible environmental contamination. Elshorbagy and Mohamed (2000) define that the covering system of a landfill should involve partial or complete isolation of waste materials from the surrounding environment. Many would agree that the main aim of having a landfill final cover is to decrease or eliminate transport of liquids through the waste. In general, a good landfill final cover should effectively eliminate the generation of landfill leachate as typical landfill leachate contains a large amount of poisonous pollutants that can cause a severe hazard to the surrounding ecosystem (Aziz et al., 2010 (a&b); Bashir et al., 2010).

Generally, the criteria for a sound landfill closure focus on the establishment of a low cost maintenance cover system and on the minimization of infiltration from precipitation. Some of the technical issues that must be addressed by a landfill designer are the changes that will take place with the surface cover barriers such as settlement and damage. A landfill cover simply must be durable in the long term (Murphy & Garwell, 1998). The final cover system should have at least 450 mm of suitable soil for protection

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against infiltration and another at least 150 mm, also of suitable soil, for protection against erosion. The infiltrating protecting layer must have a hydraulic conductivity of less than or equal to any bottom liner or natural sub-soils in order to avoid the 'bathtub' effect. This protection layer against infiltration may have a hydraulic conductivity not greater than $1x10^{-7}$ m/s regardless of the permeability of underlying liners or natural subsoil – with the earlier stated condition applies. If a synthetic membrane is used for the bottom liner, there must also be a synthetic membrane in the top cover. In other words, the top final cover must be designed to have a permeability less than or equal to the permeability of the bottom liner, which both must fulfil the requirement of having a permeability of not greater than $1x10^{-7}$ m/s.

The Geosynthetic Clay Liner (GCL) and the HDPE Geomembrane have often been quoted for use in landfills. The GCL normally has the bentonite layer sandwiched by a reinforcement fabric-mesh on the bottom side and a non-woven fabric-filter on the upper side. The main asset of a GCL is the self-sealing capability in case of puncture or rupture due to the expansive nature of bentonite, provided there is moisture in the vicinity. The HDPE geomembrane is often quoted to have a thickness of 25 mil (0.65 mm) or 40 mil (1.0 mm). HDPE membrane provide an absolute non-penetrable barrier but only when puncture-free or tear-free.

Leachate Management

Leachate management is another important aspect to be considered in designing and running a landfill. Two options or rather, concepts, need to be considered for landfill leachate management i.e., either entombment or recirculation. Entombing is a total infiltration protection method in the design, construction, and maintenance. The entombed solid waste will eventually remain in a state of mummification unless the cover system is breached and moisture enters. Leachate from an entombed landfill may still be pumped out through wells or escape through the base. The latter process may cause pollution to the surrounding water body and therefore undesired.

The recirculation concept, on the other hand, may result in the rapid physical, chemical, and biological stabilization of the waste. In a recirculation system, leachate collected from the waste is reintroduced by spreading over the temporary or daily cover of the landfill. A moisture balance within the landfill accelerates the stabilization process of the waste. Recirculation needs a sound leachate collection system and an efficient leachate injection or spreading system. This approach has the advantage that after stabilization, the facility may be provided with a final cover and thus does not require further maintenance. A more important advantage is that the decomposed and stabilized waste may be removed and used like compost, the plastics and metals recycled, and the site used again (Daniel et al., 1991).

The strategy in Leachate management should take into consideration the age of the landfill. A young landfill, say up to 5 years old, would have higher carbonaceous pollutant concentrations than those of an older landfill, say between 10 and 15 years old (Lee et al., 2010). The BOD, COD, and DOC of the new landfill would have readings in the thousands of mg/l while the same readings of the old landfill would be in the hundreds. The young landfill would also have the metal contaminants higher in concentration in comparison to those of the older landfill.

Landfill Failures

The literature has reported many landfill failures after closures that are attributed to insufficient surface barriers. Even in arid regions, over time, buried waste is vulnerable to transport via rainwater percola-

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tion, gas diffusion, erosion, and intrusion by plant roots, burrowing animals, and humans (Daniel, 1994). The popular design practices have erroneously assumed that surface barrier technology is always well developed and will work as expected, without proper protective or safety measures.

Landfill settlement is one of several ways a cover may fail by. A large post-closure settlement can occur after waste disposal in a landfill. Landfill settlement is generally due to both mechanical compression and biological decomposition of solid waste (Liu et al., 2006). The settlement generally extends over a long period of time which may prolong a landfill lifespan but may also lead to surface retention or stagnation, development of cracks, and failure of the cover system including the tearing of cover geomembrane (Ling et al., 1998).

Understanding the long term settlement pattern is essential in the work of landfill design and rehabilitation. The damage to landfill facilities such as with pipes for facilitating landfill gas escape and drainage of leachate can be avoided if settlement is better predicted. For these reasons, data on compressibility of different types of fresh wastes have been collected and analyzed through a number of researches carried out at Universiti Sains Malaysia. Certain consolidation characteristics have been described and became part of a new knowledge in predicting landfill settlement. Eventually, the settlement will also affect efficiency in leachate collection and recirculation.

Need for Proper Landfills and Management

The running and management of a solid waste disposal facility in the form of a proper sanitary landfill is clearly needed not only during operation but also after closure. A proper planning and design in the early stages will help in having a good operation during the many years a landfill receives waste.

Consequently, a properly run landfill will be easier to close whenever the time comes. A good closure will then facilitate an easier monitoring. All of these processes, when taken together, are part and parcel of an appropriate design of a sustainable landfill facility without which the country where such provision is located cannot be qualified as modern or advanced. In trying to achieve the Vision 2020, Malaysia cannot afford to have a solid waste disposal facility that isn't sanitary or sustainable. Thus the development of proper sanitary landfills throughout the country is a basic necessity. The proper design of a landfill would consider every possible avenue leading to a successful facility. The designers must not only content with local codes for reference but should also refer to international sources. Guidelines have been continually updated throughout the world even from as recent as 2014 and 2015 (EPA Victoria, 2014, NSW EPA, 2015).

Submission of Plans

The Malaysian Department of Solid Wate Mangement (Jabatan Pengurusan Sisa Pepejal Negara or JPSPN) evaluates submitted plans and provides suggestions and comments for the appointed consultants to proceed with design works. Meetings between teams of designers or consultants and officers of the department normally take place in department headquarters in Putrajaya, Malaysia on agreed dates. Many countries around the world have similar departments overseeing activities related with landfill facilities.

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Arrangement of this Chapter

This chapter provides a quick picture to landfill designers particularly those practicing in the Malaysian scenario about aspects that are relevant in their work. A landfill planned for a municipality in the country would be most likely located in an already operating facility although of a lesser quality or presentation. This situation is not only happening here but probably in many other countries especially the developing ones. Section 2 describes some common aspects of a landfill that requires address in a planning, Section 3 discusses design, Section 4 elaborates the liner system, Section 5 deals with leachate collection, Section 6 with gas venting, Section 7 with cover material, and Section 8 with infrastructure. Section 9 closes the chapter by covering various miscellaneous aspects. The examples quoted in this chapter have not all come from a specific site, but from various places in the country and also from abroad. Nevertheless, special attention has been paid to the practices prevailing in the Northern Region of Peninsular Malaysia.

ASPECTS OF A PROJECT

The following aspects of a project are normally considered in the design of a landfill in Malaysia. In most circumstances, a site would have an area run in an open dump manner while another area is being considered for a more proper procedure.

Location

The description of a landfill location normally includes distances to the nearest town, major highway, and JKR roadway. The distance of the access road leading to the site is described to the nearest metre. Maps and figures are almost necessity.

Site Description

Site description normally includes lot number, mukim name, town, and state. The current ownership would be identified. Most likely, an existing open dump would belong to the municipality however an additional area could be an existing private property. The approximate location of the site is normally identified over a Google Maps.

Within the facility, the existing activity and the areas affected are normally described in detail. The areas of each sector are identified including their status – gazetted or not. Certain sector probably has been in operation for some time and it is important to mention this.

The general terrain is normally described as either undulating or flat, and the presence of any stream and depression is also included. Main streams are named and the presence of any bridge crossing is identified. In the case of an existing open dump, the pollution level of the streams is described and colour photos of the water are provided. Polluted streams are normally compared to the unpolluted ones of the same area. Figure 1 shows a presentation of an unpolluted stream while Figure 2 shows a presentation of a polluted one.

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Figure 1. A view of an unpolluted stream

Figure 2. A view of a polluted stream

An Account of the Existing Open Dump

The same site could have an operating open dump in one of its sectors while another is being considered for an upgraded facility. The site of a future landfill cell may just be within metres to an existing open dump. Such is at least the normal case with Malaysian scenario. Thus the circumstances of the open dump are normally described when discussing aspects of the new project. In such case, the existing dumping activities are described in detail. The account would include areas covered and every significant structures of the vicinity, such as transmission lines and telecommunication towers.

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A waste received by a facility is normally identified by the municipality it originates from. The types of waste are most likely domestic, but could be industrial or inert (such as construction waste). The amounts coming from various localities are normally described in ton per day. But a visit to the receiving office at the site could reveal figures that are more real though only estimates, such as:

1. The number of incoming trucks per day from specific collecting municipality or contractor and the tonnage and volume of each.
2. There are also trucks belonging to small enterprises and these could be identified by their number of trips per day and their tonnage and volumes.
3. The final amount of disposal per day for each entity would then be determined tonnage and volume.

Charge per trip could also be recorded for trucks of various categories. For example, the current charge per trip for a 6 ton truck coming into a Malaysian landfill is about RM30 while for a 3 ton truck about RM15. Finally, the daily collection could be determined. This amount can be verified by enquiring the personnel manning the site. A discrepancy could simply be due to inconsistency in calculation or accounting but can be confusing. In such case, an explanation may become necessary. The following Table 1 is an example of presenting waste amounts entering a facility. The tonnage per day can be converted to volume per day by dividing tonnage by density. The density of compacted waste is about 0.5 to 0.6 ton per cubic meter depending on the effort given. A simple experiment can be carried out in the field to determine the actual densities for a particular facility.

The condition of access road leading to the facility requires description and probably a photo too. The number of bulldozers in operation could also be noticed together with the specific type. The front loader bulldozer with chain crawler type seems popular with landfills in many countries. Man-scavengers encamped at landfills are common occurrence in Malaysian facilities – this aspect is normally described by the number of people involved.

A Statement of the Objective

A statement of the objective is the title describing the intention of a project – normally put on letterheads, notice boards, banners, and other significant places. The overall and main objective of a landfill project when an existing dump is involved is normally to design, construct, complete, test, and certify the upgraded overall facility. In Malay, which is the language a statement of the objective is normally put, this is to 'Merekabentuk, membina, menyiapkan, menguji terima, dan mentauliahkan Projek Menaik taraf

Table 1. Table of incoming wastes

	Municipality	Amount of waste (tons/day)
1	Municipality A	300
2	Municipality B	
3	Municipality C	20
4	Municipality D	155
	Total	Approximately 475 tons/day

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Tapak Pelupusan Sisa Pepejal'. The aim of a specific phase of the project however could be to provide a conceptual design, to provide a detail design, or to review a design. A further explanation normally follows a statement of the objective.

A statement of the objective is normally explained or expanded in longer phrases in related documents. The example of an explanation to a statement of the objective is given as follows. 'The existing dumping operation in Sector A of the landfill is at Level 1 category which is as open dump. The intended operation level of the new project is either at Level 3 or Level 4 in accordance with definitions stated in the 'Technical Guideline for Sanitary Landfill, Design and Operation' of the Department of Local Government, Ministry of Housing and Local Government (2006). The consultant is responsible to identify which level of operation is appropriate for the upcoming site or which will finally come into existence in the new facility.'

The explanation could also include some amount of detail estimates such as given in the following phrases. 'The consultant is required to design a sanitary landfill with an operating life of 5 years and with a daily rate of 500 tons. By assuming the waste at site to be normally compacted to 450 kg/m^3, the total volume of the waste in 5 years will be about 900000 tons. The expected height of the new landfill will be about 25 m. Therefore, the area required for the cell will be about 10 ha, including areas for leachate treatment plants and other amenities.'

Solid waste is not homogeneous and also subject to the variation in the compaction, thus the specific weight is usually expressed in a range of values. Typical values are assumed in calculations. Different figures for final volume and final height will change with the assumed density of compacted waste, and vice versa. The typical specific weights are tabulated in the following Table 2.

Consideration for Amenities and Other Aspects

A landfill designer will also be required to decide which of the amenities at site require upgrading or if any of these items to be provided anew. Among the facilities which require consideration are as follows:

1. Paved access roads going into the facility, appropriate for the purpose of operating a sanitary landfill facility.
2. Unpaved roads within the site, appropriate for the operation (gravel roads, concrete slabs, etc.)
3. All signs within the area including for directions and security.
4. Leachate treatment facility which will either be a 'Leachate Treatment Plant', or 'Leachate Recirculation System', or a combination of both, whichever is appropriate for the facility. The selected method must be from the type which can be easily maintained, cost effective, and able to improve the quality of leachate to the standard acceptable for discharge into a common stream.
5. Perimeter drain of concrete type to cater for storm surface runoff and prevent it from entering waste disposal area.

Table 2. Typical specific weight of landfill waste

Type of Waste	Range (kg/m^3)	Typical (kg/m^3)
Normally compacted	362 - 498	450
Well compacted	590 - 742	600

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6. A leachate collection system which may consist of leachate collection pipes and leachate collection ponds.
7. Underlying liner system which will consist of clay or GCL, HDPE or GCL, drainage layer, geotextile, and gravel layer.
8. Gas collection system.
9. Wells for monitoring underground water.
10. Weigh bridge and control booth
11. Site cabin with basic amenities.
12. Power and piped water supplies.
13. Concrete wash basin – for washing outgoing trucks.
14. Perimeter fence – PVC coated chain link type, 1.5 m high, and stainless steel gate.
15. Guard house – cabin type with basic amenities.
16. A facility for recycling at site in the form of a shed or open shade together with a conveyor system (if needed).
17. Cells for construction waste.

The designer is also normally required to provide the following:

1. An assessment of the technical, cost, and environmental aspects of the project.
2. Design proposal for the landfill, the preparation of tender document for construction works/activities, and tender selection.
3. Detail design of landfill including related facilities which are cost effective, appropriate for the site and purpose, and easy to maintain.
4. Approvals from related agencies

Nevertheless, the actual aims of a planning and scope of work of a designer for specific projects are normally defined and they differ from one project to another. In most cases, a specialist is required to provide a conceptual design; an assessment of the existing amenities at site which can be retained, or are required anew; disposal manual; and costs for construction, maintenance, and operation.

CONCEPTUAL DESIGN ASPECTS

A conceptual design consists of objective, literature review, capacity analysis, landfill concept, proposed layout, and note on the existing practice at site which is normally open dumping.

Objective

A conceptual design report could be preliminary, interim, or final, submitted by the designer in fulfilment of the requirements of Terms of References. The main objective of a conceptual report is to illustrate the designer's approach in carrying out the task. The Malaysian Department of Solid Wate Mangement (Jabatan Pengurusan Sisa Pepejal Negara or JPSPN) evaluates submitted plans of various stages in the process prior to the final approval. The topographic survey is almost a mandatory aspect of each submission as it conveys the objective of the design in a single graphical presentation.

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Literature Review

Information on the various types of landfill can be conveniently found in the literature. Basically, they are classified by the decomposition process – anaerobic, aerobic, and semi-aerobic. The difference between these can be sought conveniently in the literature. When fully implemented with facilities and features, a normal landfill for Malaysian scenario would come under the category of semi-aerobic, although with lesser aeration that would otherwise be required for a landfill of such category. An anaerobic landfill is one that does not allow air to circulate within the waste; a semi-aerobic landfill is one that partially allows air circulation; and an aerobic one is one that allows maximum air contact with the waste and leachate.

Landfill Capacity

The designer is normally required to design a sanitary landfill with an operating life of the number of years and with a daily rate of tonnage as required by the owner. The total waste volume will be generated by assuming the waste at site to be normally compacted to about 450 kg/m^3, which is about the average density of a normally compacted waste. However, there are the normally assumed yearly increases of 1.3% for population growth and 2% for industrial growth. A simple calculation would yield the estimated amount of waste for the number of years given. Landfill cells would then be appointed to cater for the figures. The designer must also keep in mind that that at least an area must be reserved for stockpile of cover material, which is normally coming from the excavation of the cells. Otherwise, this material has to be imported from somewhere else. An estimation exercise of a landfill volume based on accumulated mass is given in Table 3. The table also relates area of landfill to final height. In this case, 12 hectares of land will be required to cater for waste disposal for the given number of years, with only one cell appointed.

The same area can also be divided into 3 proposed cells. The three given cells have areas shown in the following Table 4, which together may amount to an area slightly different from the first assumption. The capacities of cells are also given in the table.

Land Filling Options

During operation, certain cells might have been covered while operating the other. Such scenario is given conceptually in Figure 3; however, this is just an example. In this case the landfill consists of three cells namely Advanced Cell 1, Advanced Cell 2, and Final Cell which is positioned over the fully covered Advanced Cell 1 and Advanced Cell 2.

Table 3. An estimation exercise of a landfill volume

	Cell No.	Area (ha)	Mass to cater (ton)	Volume to cater (m^3)	Thickness of waste or final height (m)
1	Just 1 cell	12 ha approx	992,800	2,206,222 waste + 330,933 daily cover + 551,555 liner components = 3,088,710 m^3	25

Note: Assuming unit weight of 450 kg/m^3 (for normally compacted waste)

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Table 4. An estimation exercise of areas of various cells in a landfill

	Cell No.	Area (ha)	Mass to cater (ton)	Volume to cater (m^3)	Thickness of waste (m)
1	1	4.95	398,089	884,643	25
2	2	3.64	292,283	649,518	25
3	3	4.04	324,490	721,089	25
Total		12.63	1,014,862	2,255,250	25

Note: Assumed unit weight is 450 kg/m^3 (normal compaction)

Figure 3. Progress in a landfill consisting of 3 cells

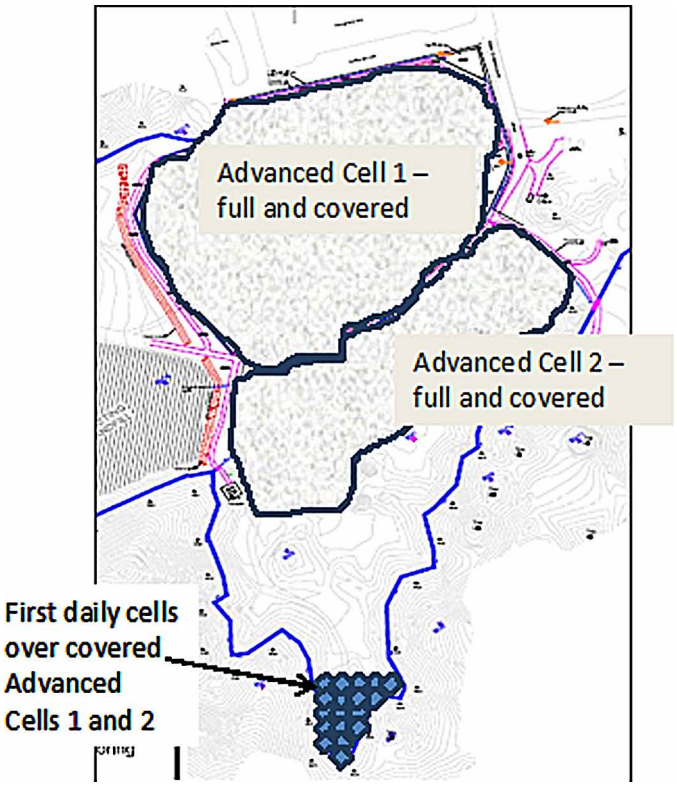

Figure 4 is another representation of a landfill arrangement which indicates presence of 3 cells - Cell 1, Cell 2, and Cell 3. Note that Cell 2 is located over closed Cell 1 and Cell 3. The disposal procedure in this case can be either by Option A or Option B. In Option A, Cell 1 is separated from Cell 3 in order to provide space for stockpiling of cover material. While operating Cell 1 for example, cover soil dug up from developing Cell 1 can be located over Cell 3. The procedure could mean that the two cells would be created not at once but at different times. Option B would be to develop 2 cells – Cell 1 and Cell 3 - at once and as one cell, but in such case, a large flat area elsewhere will be needed for stockpiling the cover material. Depending on space availability, one option may be more preferred than another.

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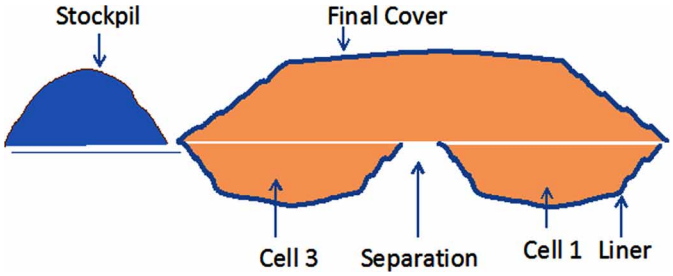
Figure 4. A landfill with 3 cells



Berms and batter faces will define the walls of a landfill. Diversion channels will be constructed to divert storm water out of the landfill area. Leachate channels will lead to leachate holding pond and on to leachate treatment plant. The cells may be 100% lined with impermeable membrane – HDPE membrane or Geosynthetic Clay Liner (GCL). The access road into the landfill will not cut through the lining but over ramps to be built over the lining. Leachate collection system will be featured by an assembly of pipes with mains running along the central depressions on the bed. A landfill can be small and technical, or large and old style.

Most Malaysian facilities, when closed, would fall under the category of anaerobic landfill. The semi-aerobic status is next in the improvement ladder and something that is desirable. Given the specific circumstances, some facilities may qualify for the semi-aerobic type. In a semi-aerobic landfill, leachate is discharged as soon as it is collected to reduce the seepage. Fresh air is brought in through the same pipes that carry the leachate to enhance waste stabilisation, improve leachate quality, and reduce the cost of final treatment of leachate. Gas is released through gas ventilation pipes to reduce gas pressure and the likelihood of gas explosion. This type of landfill is cost effective as the initial investment and the maintenance expenditure is lower than that of the aerobic type. For the Malaysian scenario, the semi-aerobic conditions can probably be achieved by having oversized leachate pipes.

Providing a Proposed Layout of Landfill

Providing a proposed layout of a landfill requires a good comprehensive understanding of the parameters surrounding the facility. The first decision would be with external surrounding perimeter. In case of undulating terrain, the immediate results of having borders would be the slopes which will be designed according to standards of the civil construction industry in the country.

Berms will be about 2 m to 3 m wide and batter faces will have slopes of 1:1.0, 1:1.5, or 1:2.0 depending on other factors but mainly soil properties. Factor of Safety against sliding failure will be checked and it must be at least 1.5. Berm drains will function as either storm drains or leachate drains depending on the stage of operation.

An example of the proposed initial layout of a project together with a final cross section is given in Figure 5. However, this particular one is not Malaysian. In this case an ample space has been provided for leachate treatment plant and other facilities which can be upgraded, downgraded, or modified from the drawing as the process of the design progressing.

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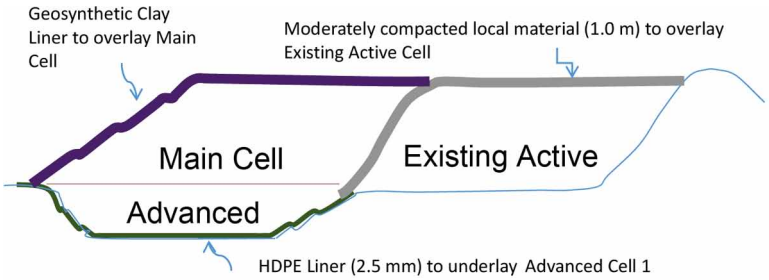
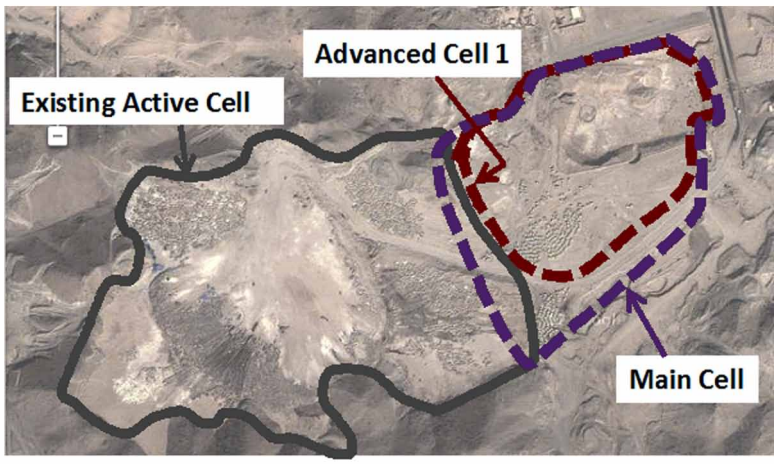
Figure 5. A proposed initial layout of a project (a) Cross Section and (b) An aerial view over a Google Maps



(a)



(b)

Among the features that can be incorporated into the drawing are:
Existing paved access road going into the facility – originating from main road and ending at disposal areas.

1. Guard house which will be located just inside the entrance or just across the second bridge.
2. Power sub-station.
3. Weigh bridge.
4. Wash through.
5. Workshop.
6. Parking space for trucks (lorry).
7. Truck washing facilities.
8. Leachate holding pond.
9. Leachate Treatment Plant (LTP).
10. Proposed landfill cell.
11. Stockpile of daily (intermediate) cover material.

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12. Perimeter storm diversion drain.
13. Retention pond

In this case, the lnadfill consists of 3 cells: Existing Active Cell which is a currently running open dump, Advanced Cell 1, and Main Cell – the latter cells being the ones to be properly designed. Advanced Cell 1 will be generally excavated down to about 12 meter below the existing ground level and will be filled up to 13 m or slightly above the existing ground level. When full, the main cell on top of it will begin operation. Meanwhile, the Existing Active Cell will continue to operate until a certain convenient stage when it will be closed.

Another example is given in Figure 6. In this case, Cell 1 and Cell 3 are prepared together in the beginning with a separation embankment built in between. When the two adjacent cells are full and closed, operation of the overlying cell would commence.

A Description of the Existing Open Dump

The existing open dump in a landfill facility would require a descriptive assessment. If the dump is ready for closing, a closure design can be appointed – an example of such design in simple terms is given in Figure 7.

A covered dumpsite would probably contribute to leachate generation as much as the open dump would. The issues will be addressed in the new design. The basics will however go as the following:

1. As the covered dumpsite of the old open dump does not have proper underlining, the cover will be strengthened in terms of capability to resist infiltration. This cover may involve a layer of compacted laterite soil, 1 m thick, as commonly practiced in the Malaysian scenario. The designer will provide specifications for the closure which will address the issues of surface runoff, leachate production and treatment, and gas control.

Figure 6. An example of conceptual cross section of a landfill

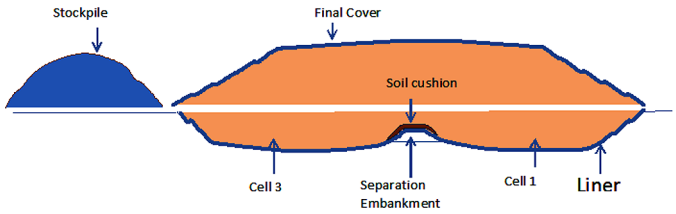
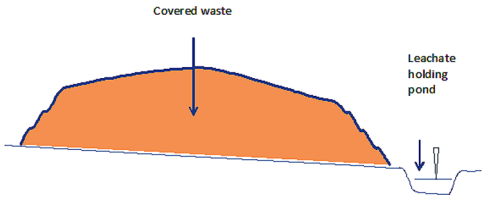


Figure 7. A probable future cross section running through the existing dump



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2. Once the new cells of the landfill are ready to receive waste, dumping will cease at the existing open dumpsite. The open dump site will be tidied and topped up with final cover. Some waste may be transported to the new cell.
3. Leachate originated from the closed dump may be treated together with leachate of the new cell. Leachate from these sites will be arrested via interception drains and wells. In the best possible manner, leachate from the dump will be channelled via drains, pipes, and intermediate collection pond, to the appointed leachate treatment plant. The location of the new leachate treatment plant should be just below the new cell or cells.
4. Perimeter storm diversion drains will be constructed around the closed dump areas.

The Sorting or Recycling Facility

The sorting or recycling facility provides an area where recyclable materials are sorted for recycling. Once waste deposited over the sorting platform, the waste will be lesser in density, at about 300 kg/m cu or about 3 m cu per ton. A truck with 6 ton waste will have a volume of about 18 m cu. when its content is deposited over the sorting platform. Thus the sorting platform should be at least capable of handling about 250 m sq. of waste spread. The content of two trucks will amount to about 0.15 m (about 6 inches) thick if spread evenly over the entire area of the platform. Of course, not all incoming trucks will head to the sorting building upon entering the facility. Some will go directly to the landfill. Thus the sorting building will only cater part of the waste.

LINER SYSTEM

Literature Review

A liner system refers to the whole components of a liner, not just the geomembrane. A landfill liner, or composite landfill liners, is intended to be a low permeable barrier, which is laid down under landfill sites. The liner retards migration of leachate, and its toxic constituents. Landfills generally require a layer of compacted clay with a minimum required thickness and a maximum allowable permeability, overlaid by a high-density polyethylene geomembrane. Chipped or waste tires are also used to support and insulate the liner.

The primary forms of mechanical degradation associated with geomembranes result from insufficient tensile strength, tear resistance, impact resistance, puncture resistance, and susceptibility to environmental stress cracking (ESC). In selecting liner material, these properties are examined for their suitability in the project.

Landfills are designed with cells that are lined to prevent groundwater contamination. Normally, for a municipal facility, the liner consists of a two foot layer of low permeability, re-compacted clay soil. Over this layer, high-density polyethelene (HDPE) secondary plastic liner is installed to cover the entire bottom and sides of the landfill cell. This plastic liner, which is chemical resistant to corrosion and damage, is then welded together and tested to ensure a continuous seal in accordance with regulatory requirement.

A blanket of geotextile fabric, composed of synthetic, felt-like fibers, is laid above the primary liner system, along with a geonet made of mesh-like plastic. Together, these prevent fine clay particles from clogging the leachate collection layer and promote removal of leachate from the liner surface.

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Liner facility is installed to prevent pollution of public water bodies or groundwater by leachate discharge from the landfill site when installed at the base of waste body. When installed on top or side of waste body, it prevents the increase of leachate volume caused by inflow of surrounding ground water into the landfill site.

The structures and types of liner facility used shall conform to the topographical and geological conditions of the landfill site, soil conditions, ground water conditions, as well as the location of leachate collection facility. The thickness of a base liner facility shall be determined in accordance with its classification, quality of materials, construction standard, subterranean condition, joint method, corrosion and durability. The general thickness of liner facility is given in Table 4. The use these various geosynthetics for the project are sometimes kept optional due to cost implication. Simply speaking, the landfill liner may consist of one, two, three, or even more layers of geosynthetics depending of various factors. The decision of using either one out of the many choices will best be made after carrying out a site investigation for the selected site.

The situation with the foundation will affect the cost of geosynthetics. A soft foundation may be subject to settlement and therefore must be treated first. A sound foundation of sandy material should be ready for laying geosynthetics with reduced cost. Obviously, the surface landscape will affect the overall work effort.

A network of leachate collection pipes will be assembled on top of the impermeable base liner. Drainage aggregates will be spread throughout the area and topped with a filtration geotextile where waste will rest upon.

Normally, the provision will be made to install horizontal as well as vertical liners at appropriate locations and appropriate use. Horizontal liners will form the base of landfill cells while vertical liners will be used underneath waste (or leachate) retaining dam and in location where it is intended to protect leachate side migration.

The thicknesses and other specifications of geomembranes are conveniently available in the literature.

LEACHATE COLLECTION AND TREATMENT

Literature Review

Leachate is collected at the base of a landfill via a network of collection pipes to collect leachate generated from the landfill site and channelling it to a pre-determined facility for treatment before discharging it to the environment.

The treatment of leachate can be through one of the followings:

1. A combination of bio-treatment and physio-chemical.
2. A combination of recirculation, bio-treatment, and physio-chemical.
3. A combination of recirculation and natural attenuation.
4. A combination of recirculation, natural attenuation, and physio-chemical treatment.

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Leachate Collection Facility

The collection facility is aimed to collect and channel the leachate generated from the landfilled waste layers to the leachate treatment facility. The leachate volume generated in a landfill should be kept minimized and removed immediately to the leachate treatment facility, so that there will be no trapped leachate in the landfill site. This is to ensure the water pressure acting on the liner facility and waste retaining facility is minimized. This also serves to supply air into the landfilled waste layers through the collection pipes for the semi aerobic sanitary landfill. The general conceptual layout plans for a leachate collection facility are shown in Figure 8.

Components of a Leachate Treatment Facility

Leachate Treatment System

A leachate treatment system may consist of a combination of recirculation, natural attenuation and physio-chemical treatment. When there is ample space available, the wet land treatment will be a good option. The concept of such treatment is shown in Figure 9. A leachate treatment process can be divided into several sub-processes involving various structures such as leachate collection sump, grease grit chamber, aeration lagoon, sedimentation tank and natural filtration before the leachate final discharged.

A relatively new leachate treatment procedure has been recently proposed for the landfill practice in Malaysia, namely the electro-flocculation, which will require a plant to be set up in the area designated for leachate treatment plant. The details of the procedure are partly given in Figure 10.

By this method, the leachate will be first stored in the influent raw water storage tank and then pumped into the treatment water tank for further adjustment. Chemical treatment is carried out in order to adjust the load characteristics at specific feed rate for 24 h/day. Coagulant will be dosed in automatically by mean of dosing pumps to coagulate the unsettleable solids in the leachate. In this process some non-

Figure 8. Conceptual layout plan for a leachate collection facility

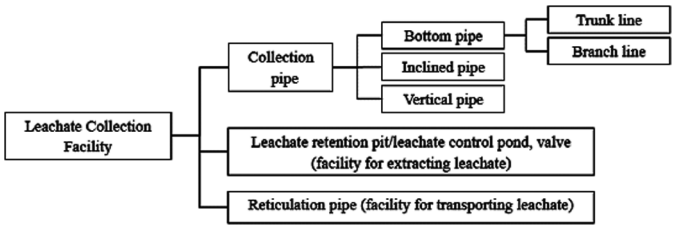

Figure 9. A conceptual leachate treatment facility

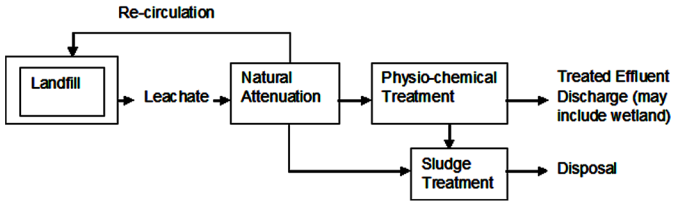

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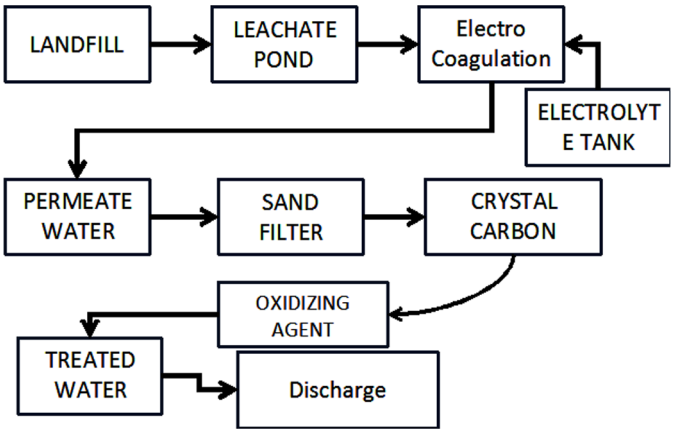
Figure 10. An electro-flocculation process in leachate treatment



biodegradable components that are present in the lechate will also be reduced. Thereafter the solid will be allowed to floc and settled in the tank. After the flocculation process, the flocculated water is fed into a micro filtration system to remove most of the settled solids. The filter media for the filtration system will be about 200 microns. Particles sizes larger than this will be remove this way. The partially clear liquid with lower solid content and smaller particles will be fed into the electro-coagulation processor.

In the electro-coagulation process, the electrical current is introduced into water via parallel plates constructed of metals that are selected to optimize the removal process. The electro-coagulation process moves the electrons through the water between positive and negative plates. Sufficient residence time in the chamber is designed for the system so that the electric current destabilizes, dissolves, and alters the charge on the surface of the suspended matter. The removal of particles by electro-coagulation process is enhanced by the surface reaction, so the surface area of the electrodes within the chamber is designed based on the removal capacity by square cm per litre per minute. The electro-coagulation process does the following:-

- Removes heavy metals as oxides
- Removes suspended and colloidal solids
- Breaks oil emulsions in water.
- Removes fats, oil, and grease
- Removes complex organics
- Destroys and removes bacteria, viruses, and cysts
- Reduces Sludge Volume
- Uses no chemicals
- Addresses contaminant problems
- Processes Waste Streams with up to 5% solids.
- Harvests Proteins, Oils, and Metals

A thick layer of sludge comprising of oils, grease, solids, and other contaminants that was previously present in the leachate will float to the top and form sludge at the surface. These floatable matters will be scraped and removed continuously using a scraper. The collected sludge will be transferred into the

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sludge holding tank. The solids in the holding tank will separated from the filtrate using a plate and frame filter press. The permeated water of the dewatering system will be returned into the water tank for further treatment. The almost dry solid will allow drying of the sludge bed.

The clarified water coming out of the electro-coagulation unit is finally filtered using another filtration system in order to remove particles less than 20 microns. The filtered water then goes into the treatment water tank before being fed into the Activated Carbon Filter. This filter in turn removes more impurities such as total dissolved solids (TDS), turbidity, heavy metals and many dissolved organics. The process will also remove chlorine content. The treated water will be suitable for use as chemical solution, boiler feed, general wash water, and fire hydrant. The treated water may not be good enough for drinking or human consumption unless further treated.

Collection Sump

Landfill leachate in a landfill is normally diverted into a collection sump. Before entering the collection sump, the leachate in normally filtered from solid waste by Mechanical trash screen and fine trash screen. A level sensor may be installed in the sump in order to aid pumping and monitoring operation. Other data such as Temperatures, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and ammonia content can be collected by using suitable sensors. The collection pump is normally equipped with pump of submersible type. The collected leachate can be pumped into grease grit chamber for grease and grit separation.

Grease Grit Chamber

Grease grit chamber functions to separate grease from leachate. Grease trap is normally shall be equipped with sensor to identify trapped grease level. With increasing amount of grease in the trap, additive can be dosed in. Grease free leachate may then be diverted to the aeration lagoon.

Aeration Lagoon

Aerators of floating surface type may be employed. This instrument transfers air into the leachate helping biological oxidation reaction. It also mixes and promotes contacts between air and leachate for the biological reaction to take place. Besides natural air, oxygen can be injected into the aeration lagoon to enhance the reaction. To maintain an optimum pH of the leachate, sodium hydroxide as a chemical catalyst can be dosed in accordingly and the resulting pH monitored. From the aeration lagoon, leachate with lower BOD can be diverted to the sedimentation tank.

Sedimentation Tank

The sedimentation tank may be equipped with air pipe with air transferred in using blowers. Here, polyelectrolytic and flocculant solution can be added in to treat the COD materials producing sludge that sinks at the bottom of the sedimentation tanks. A scrapper can be employed to remove the sludge. The sedimentation tank can be equipped with sensors that detect leachate content. From the sedimentation tank, before the final discharge, the treated effluent can be further treated by natural method.

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Red Bed System

Natural filter of red bed can be employed. Underneath the ground, filtered, treated leachate (clear water) can be collected via culvert before being discharged to the drains. Here, the clear water can be monitored just to ensure it meets the discharge requirements.

GAS VENTING SYSTEM

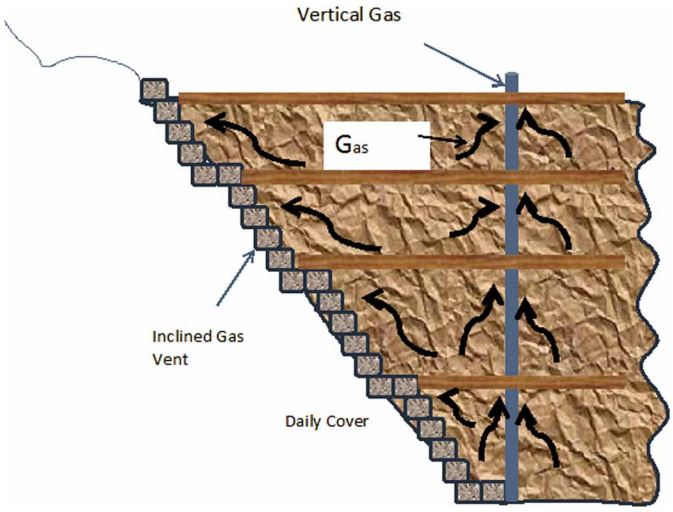
Literature Review

The main function of a gas venting system is to release gases generated from the landfill layers as soon as possible in order to prevent the adverse impacts caused by the gases. The gases are generated by the decomposition of organic materials in the landfill sites, which may cause fire disasters or affect the surrounding environment and human health.

Components of Gas Venting System

Gas venting system may be designed with no impediments to the activities on the landfill site. The main components of a gas vent system are normally not much more than perforated PVC pipes and simple gabions. The gas can be collected and burned, but it can also be released to atmosphere. A cross sectional view of a landfill with gas vents in place is shown in Figure 11. The vertical gas vents normally have intervals of between 30 m and 40 m. The vertical gas vents will be made of perforated PVC pipes while the inclined gas vents will be gabions arranged in place.

Figure 11. Inclined gas vent and vertical gas vent



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COVER MATERIAL

Literature Review

A cover minimizes infiltration from precipitation, and hence minimizes leachate generation. A cover develops a cap that is not more permeable than the bottom liner system. It promotes drainage from the surface with minimal erosion. It accommodates settlements and subsidence. The operation should be with minimum maintenance.

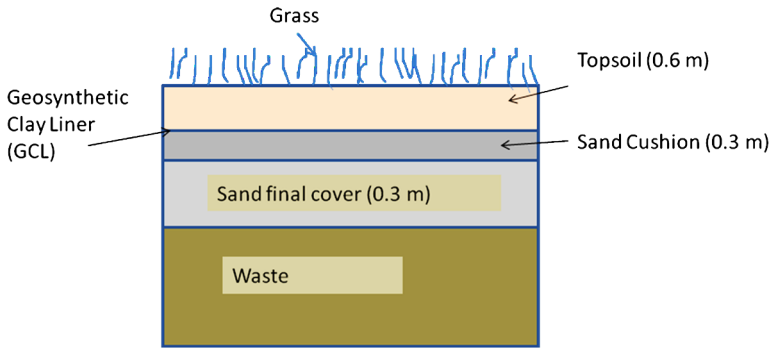
Daily Cover

Daily cover for the Malaysian scenario is normally laterite soils amounting to about 150 mm in thickness. Soils excavated during site preparation can be put aside in stockpiles and be used as daily cover.

Final Cover

Final cover in Malaysia is normally and mainly laterite soils amounting to about 1 m in thickness if used alone. An ideal cover layer however should consist of many more components such as shown in Figure 12. The vegetation cover is needed to minimize erosion and bring about naturalization process. Top slopes between 3% and 5% are recommended to avoid pooling and erosion. A surface drainage system must accommodate runoff to avoid rills and gullies. To avoid clogging, a separation filter is recommended between the drainage layer and the vegetative support layer. The 0.5 mm (minimum thickness) geomembrane (also called liner) must be protected by a bedding of sand free of stone or sharp objects 15 cm above and below the barrier unless the clay below and the drainage layer serves as bedding. The final cover may not have all the components of an ideal landfill.

Figure 12. A proposed final cover profile of a landfill



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INFRASTRUCTURE

Access Road

To ensure proper management and operation of a new sanitary landfill, additional facilities may be established at the site such as access road, site office, and weighbridge, amongst others. These can be new facilities to the existing dump, and are generally related with control and operations of the proposed landfill. The rest of proposed infrastructures have been mentioned in earlier sections.

In case of an existing dump, an access road may already exist connecting the lot to a federal (JKR) road. This access road is normally in good enough condition with existing premix surface and probably bridges. Figure 13 is an example of an access road suiting the above description. The access road probably has own reserve, except here and there where it strays into private lands – this will have to be addressed. The road probably is littered with rubbish. If the existing road is deemed safe and capable of providing nominal flow of traffic for the purpose of running the facility, it may only require minimum improvement. Nevertheless, the aspects must be addressed in the designer's report.

Proposed Roads

New roads for a proposed landfill could come from two categories:

1. Access road i.e., road connecting entrance from a federal carriageway and landfill.
2. Internal service road i.e., roads within landfill site.

Figure 13. An access road leading to a dump site

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Recommendations could involve the followings:

1. Widening or upgrading the access road. A new upgraded road should come with drainage facilities.
2. Stretches that have intruded into private lands should be addressed such as by acquiring the lands or straightened or redesigned in order to correct the situation.
3. Adequate road furniture should be provided.
4. An internal service road shall cross an overhead power lines perpendicularly (at 90 degree) to the ground footprint of the lines.
5. Wash trough will prevent outgoing trucks from dirtying access road.

Weigh Bridge and Control Booth

Weighbridge is a basic requirement of a landfill. It is used as base for recording the quantity of incoming wastes to the landfill. Normally, at least two (2) unit of weighbridges are needed – one for entry and another for the exit. The weighbridge should come with control booth to house the staffs doing the recording and inspection. The weighbridges will be positioned at strategic locations where the vehicles pass through when entering and leaving the landfill site.

Site Cabin with Basic Amenities

A site office is required to facilitate day to day activities such as supervision, inspection, and weighing of the incoming vehicles. The site office will also serve as centre for overall land filling activities such as the management of cover soils; and operation, maintenance, and monitoring of leachate treatment facility. A good site office facility will enable an easier control of the entire landfill operations. The facility shall be equipped with utilities such as water supply and electricity, and complete with communication systems. Other facilities such as worker's rest room, locker room, showers, toilet, weighing room, and store are also required.

Truck Washing Facilities and Wash Trough

A truck washing facility is normally provided for washing trucks after every waste disposing activity. To prevent collection vehicles from carrying dirt onto the public road, the vehicle wash through should be installed at where an unpaved road meets paved one.

Underground Monitoring Station (Well)

The monitoring of groundwater in areas surrounding the landfill site shall be carried out for the following reasons:

- To check the quality of the groundwater to ensure that the liner system of the landfill site are functioning well without any leakage.
- To detect pollution at the earliest possible time so that immediate remediation works can be carried out in order to minimize adverse impacts to the groundwater and the surrounding environment.

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A monitoring well shall be constructed to capture water directly below the subterranean level. In addition, the groundwater monitoring station shall be constructed downstream of the landfill site where a pollutant dispersion is at its fastest rate. This will allow a comparison of groundwater quality between the upstream and the downstream. The monitoring well shall be at least 100mm in diameter. Further aspects of a good monitoring well are widely available in the literature.

Mechanical and Electrical Facilities

The mechanical and electrical facilities may include the followings:

1. Generator
2. Electrical systems
3. Firefighting system
4. Communication system
5. External electrical system/street lighting and compound lighting
6. Security lighting
7. External telephone
8. Aerator and mechanical system for Leachate Treatment Plant
9. Air conditioning and mechanical ventilations
10. Lightning protection system

Other Infrastructures

Other infrastructure may include the followings:

1. Workshop
2. Perimeter fence and drain
3. Guard house
4. Sign boards
5. Ramps over waste dams

MISCELLANEOUS

Bore Holes and Monitoring Wells

The positions for site investigation (SI) may be decided based on site situation but the main aim is these should represent the whole landfill area. A number of SI points should be drilled by wash boring method while additional points can be carried out by piezocone and/or macintosh method. Each cell should at least have one SI point located within. The penetration positions should be evenly distributed throughout the landfill area, more or less.

A borehole drilled for SI may be converted into a functioning monitoring well and if so it should be finished as one. It is preferable to locate a monitoring well either near a river, next to plantation ground, or on low ground in order to capture the out flowing ground water.

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Excavation and Construction of Cells

An excavation is almost always expected in the preparation of a new landfill cell. The depth of excavation will be normally limited to about 1 or 2 m above water table. The bottom of a cell should not breach the ground water table in order to avoid possible contamination.

Excavation on higher ground would result in having slopes bordering the new facility. A cut slope should be finished with batter faces having either 1:1, 1:1.5, or 1:2.0 gradient, which ever that would result in acceptable Factor of Safeties (FOS). These FOS against sliding should all be at least 1.5. Berms should each be about 2 to 3 m width. The vertical distance between two berms should be 5 to 6 m maximum. The final excavation design however could be affected by actual findings from site investigation or laboratory tests on soil samples.

The positioning of cells should allow for space for stockpiling of cover material. Excavated material may be stockpiled in another cell that is already closed or not yet operating. While operating an active cell, the cover soil dug up from developing it can be located over another cell not yet dug or already covered. While operating Cell 1 for example, cover soil dug up from developing Cell 1 may be stockpiled over Cell 2 and Cell 3. In other words, if there were three cells in a landfill, these may be developed not at once but at different times. It is also possible to develop all cells at once, but in such case, a large flat area elsewhere will be needed for storing the cover material.

Cell Bund and Leachate Dam

The higher ground of an area designated for a cell may get excavated more so than the lower ground. The lower ground is more likely to get encircled with bunds to prevent it from inundations. In case of a leachate spill, simple dams may be appointed to confine it before channelling to the collection pond.

Cell for Inert (Construction and Agricultural) Waste

An area of the landfill may be designated for inert waste. This area will not require an underlying protection because the waste will have no contaminating consequence. Inert waste shall not be mixed with municipal waste because the cost of disposal per volume of the latter is more costly than of the former. Also, the volume above an inert cell should not become another cell of municipal waste because leachate will then be produced and the downward migration would contaminate the underlying cell which has no liner. Also, agricultural waste should be separated from construction waste as the latter is more likely used as recycled construction material than the former. An agricultural waste would turn into compost after a certain period of time and can be used in farms and planting grounds.

Disposal Activity near Power Pylon and underneath Power Transmission Line

All activities related with landfill operation shall not breach the 30 m clearance distance from any power pylon. An internal service road inside a landfill shall cross at 90 degree or perpendicular to the ground print of any power transmission line. A vertical clearance of at least 10 m should be allowed between a permanent landfill structure to the power transmission line running above it. On either side of a transmission line, no structure shall be allowed to remain within 25 m distance to it.

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Wash Trough

Wash trough will prevent outgoing trucks from dirtying access road. It normally uses water from a detention pond of surface runoff.

Leachate Treatment Plant (LTP) and Leachate Holding Pond (LHP)

The leachate treatment plant (LTP) will occupy a certain amount of acreage and this can be located economically underneath a power transmission line if such exists in a facility. A leachate holding pond (LHP) too may economically located in an area underneath a power transmission line.

Closure

Multiple cells will merge into one during closure. A cover geomembrane can be designed to embrace the whole landfill area. For the final cover, a sufficient amount of top soil topping and installation of drainage system will ensure a good protection against rain infiltration possibility. A service road too can run over it provided there is a sufficient thickness of embankment to protect the membrane from puncture by passing vehicles.

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Chapter 13
An Approach to Sustainable Watershed Management:
Case Studies on Enhancing Sustainability with Challenges of Water in Western Maharashtra

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ABSTRACT

Western Maharashtra consists of drought prone villages, which around seventy years ago were facing drastic challenges regarding water requirements. People living in such areas started to migrate from these villages in need of food and water. The chapter focuses on few case studies of drought prone areas of Western Maharashtra which made a move towards sustainability and has created an excellent model of watershed projects. Several practices like ban on cutting trees, terrace farming, contour bunding, drip irrigation, sprinkle irrigation, introduction of cooking stoves, rotational grazing, efficient water distribution and change in cultivation of agricultural crops according to the climate were followed which led the village to become a model for Aadarsh Gaon (An Ideal Village). The author has used secondary data from previous research work and critically analyses the case studies on water management in drought prone areas of Western Maharashtra which managed to become a model for sustainable use of water.

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INTRODUCTION

The State of Maharashtra is located in the Western parts of India and is classified into five regions namely, Konkan, Desh (Pune region), Vidharba, Khandesh and Marathwada. Along the Arabian Sea the state has a coastline of 720 km. Maharashtra is home to renowned historical monuments, caves, temples, festivals and a bustling lifestyle. Moreover, it is housed by large number of educational institutions, industries and service sector organizations and 45% of total population in the state lives in urban area. As the second most populous state, Maharashtra is one of the most developed states of India and plays a key role in the overall economic development of country as major educational and financial institutions are located in this state. The current population of Maharashtra is 121 million people accounting for over 9.29% of the total population of India.

With time large population has been shifted towards urban areas, while rural areas have undergone limited shifts in their boundaries. Cities like Thane, Mumbai, Raigarh, Ratnagiri and Sindhudurg are separated by the Western Ghats which receive heavy rains (>1000 mm) whereas the rain-shadow region towards the east of the Western Ghats suffers from low rainfall. Furthermore, far Eastern regions of Maharashtra again receive a good rainfall. Western region comprises of Nashik, Satara, Sangli, Kolhapur, Solapur, Ahmednagar, Aurangabad and Pune which has comparatively low rainfall than other district of Pune since they lie in the rain shadow region of the Western Ghats. The rain shadow regions receive an average rainfall of 500-600 mm. The state has a pleasant climate throughout its season with rainfall exceeding to 6000 mm in Western Ghats to 500 mm in the rain-shadow regions. The state has been surrounded by Krishna, Godavari, Tapi, Narmada and Konkan River providing water for the need. About 50% of the Maharashtra region lies in the drought prone area of Deccan plateau (nidm.gov.in/pdf/dp/Maharashtra.pdf). In the past few years it has been noticed that the Western region of the state is facing severe water scarcity problems. Most of the water supply in this region is happening through water tankers. Water being the life is essential at every step of day-to-day activity and therefore must be sustained for a better living.

This chapter focuses on the key approach towards watershed management, a topic of great concern in present era of climate change. Watershed management is an approach towards life of the earth since excess water flow leads to soil erosion, floods and other natural calamities which ultimately destroy the resources of living and scarcity of water again concludes to drought (Dixon & Easter, 1991). Western Maharashtra consists of drought prone villages which around seventy years ago was facing drastic challenges regarding water requirements. People living in such areas started to migrate from these villages in need of food and water (Foster et al., 2009). Then a commerce student Mr. Popatrao Pawar took an initiative to become Sarpanch (Head) of the Hiware Bazar village and tried to change the history of the village. Several practices like ban on cutting trees, terrace farming, contour bunding, drip irrigation, sprinkle irrigation, introduction of cooking stoves, rotational grazing, efficient water distribution and change in cultivation of agricultural crops according to the climate were followed which led the village to become a model for Aadarsh Gaon (Phand & Arya, 2007). Mr. Anna Hazare thirty years ago also took an initiative to achieve watershed resources by implementation of Programs through public participation in Ralegan Siddhi village of Parner (Sharma, 2006).

The authors in the present chapter have used secondary data from previous research work and critically analyses the case studies on water management in drought prone areas of Western Maharashtra which managed to become a model for sustainable use of water. The objective of the chapter is to focus on case studies in the drought prone areas which managed to survive efficiently with a successful water management and to discuss measures for a sustainable watershed management with reference to Maharashtra.

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GROUNDWATER MANAGEMENT IN WESTERN MAHARASHTRA

Groundwater is defined as the water available in the aquifer below the ground at the zone of saturation which can be dug through machines and water extracted as bore well, tube well or by other means. The groundwater table is abundant in Eastern part of the country than in the Western part. The Western region has limited water leading to depletion of water resources.

NABARD has been utilizing the finance for developing wells in the rural areas. The increasing tariffs on water can make a sustainable use of water for irrigation by the use of diesel and electric wells (Moench & Kumar, 1995). This electricity tariff will lead to increase the efficient utilization of groundwater and use of electricity (Kumar & Singh, 2001). With time due to variation in the climate, the groundwater level has gone down due to less rainfall and the unhealthy use of water.

L.A Bill No. XLII 2009 has been introduced to ensure the sustainable water management in Western Maharashtra and established state groundwater authority and district groundwater authority to protect drinking water resources and managing the groundwater exploitation within the districts of Maharashtra. This has led to forward a law for managing the demand and supply of water for various purposes at different sectors. This act is commonly called as the Maharashtra Groundwater Development and Management enacted in the year 2009. This act focuses on valuable terms required for sustainable management of water as described in Table 1.

It is the responsibility of the state authority to check the polluters in the ground water both in the rural as well as in the urban areas and make it safe for drinking purpose for the population. The State Authority and the State Government ensures the implementation of integrated watershed development and management. It is the responsibility of the State Authority to charge water for the highly water intensive crops grown by the farmers. This practice has been made to ensure the sustainable management of water. Training Programs have been held by the state authority to ensure awareness in the rural areas of Maharashtra regarding integrated water management. The Program discusses on the best practices for the implementation of watershed management. Watershed Water Resource Committee supplies ground

Table 1. Valuable terms used in sustainable management of water

Rainwater harvesting	This is the essential part for water management which cannot be ignored. The rain water must be stored or collected instead of being wasted. This water can be conserved for future purposes.
Aquifer	This refers to a structure for storing saturated water underground.
Area of influence	Refers to the area beneath the ground which is modified for pumping purpose.
Artificial water recharge to groundwater	refers to the water being available due to the natural climatic conditions
Deep well	This is the groundwater dug deep in the soil covering twenty- five strata of the soil and includes bore well, tube well and even sixty meter deep.
District watershed management committee	Enrolled under section18 for the better management of groundwater in the districts.
Drinking water purpose	This was included in the bill for assessing the demand and supply of drinking water for the human population of the state.
Groundwater surveys and development agencies	Under the water supply and sanitation measures the survey is made underground in Maharashtra and the developing agencies manages the water supply in the state.
Integrated watershed development and management	is the key for the sustainable management of water in the state

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water for the highly water intensive crops with terms and conditions. The District Authority shall take the responsibility to preserve the drinking water from the groundwater. At times of water scarcity in the areas, the District Authority regulates the extraction of water from any well and manages to supply water within the area of one kilometer of the public drinking water source. The inspection of wells is carried out and the water is tested in terms of quality and any contamination.

The State Authority has a watershed water review committee who is responsible for water management in the villages of Maharashtra affected by water scarcity. The Watershed Water Resource Committee comprises of a chairman of the Panchayat Samiti, one representative from the water supply and sanitation measure, one from the water use association, elected members of the Panchayat Samiti, block development officer and member of village and water committee. It is mandatory that one-third of the members of the water resource committee must be women. The Watershed Water Resource Committee allocates the water budget of every area and on the basis of availability of water all the year around, the cropping pattern of that particular area is decided. The groundwater and developing agency carry out the hydro-geological study of a particular area for the management of water.

The Maharashtra Groundwater Act 1993 has been enacted to protect the drinking water for the rural population and also to regulate the exploitation of groundwater. The Government of Maharashtra has enacted a new law under Groundwater Act to ensure the sustainable supply of groundwater, protecting drinking water, conservation of groundwater resources and provide beneficiary schemes in rural as well as urban areas to support the ground water protection. The bill also provides the following proposals as mentioned in Table 2.

Table 2. Clauses of the bill proposed in 2009 for enhancing sustainable water management

Clause	Sub-clause	Objectives
1		The state Government has been assigned with the power to bring out the act of watershed resource development.
2		Such authorities must be specified by the state Government which can provide water from the public drinking water resources.
3		The state groundwater authority must exercise the power on discharge of water to different sectors. The state authority must be assisted by the groundwater surveys and development agencies, one expert from the field of groundwater and one women representing the user of groundwater.
4	1	An official gazette must be notified in the area
5		The area where the groundwater has improved must be denotified by the state authority.
6	3,5	The state Government is assigned with the power to restore the groundwater quality with the minimum water standards and it's preservation for drinking purpose.
7		Registration of the owners of the wells in the notified as well as non-notified areas of the state must be ensured by the state authority.
8	1, 3, 5, 4	Permission should be granted to any person by the state authority for digging well in the area for drinking purpose. The use of existing deep wells is ensured and permissions should be obtained by the district authority for the users of groundwater.
9	3,6,7, 8,10	District watershed management committee should look after the efficient implementation of integrated watershed management plan. The state Government shall issue the guidelines for disincentives the use of water for water intensive crops. The State Government must prescribe the efficient manner for rain water harvesting by the top roof method in urban areas. Incentives shall be provided to the water resource committee by the state Government.

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Table 2. Continued

Clause	Sub-clause	Objectives
10	1, 3	The state Government must give directions regarding the cropping plan in a particular area based on its water requirement. In case for the cultivation of water intensive crops, the farmers may approach to the water resource committee for discharge of groundwater.
12		Compulsory registration must be done by the rig owners and other operators in consultation with the groundwater survey and developing agency.
14		The state authority can direct special order to water resource committee or the village groundwater surveys and developing agency for sustainable management of water
16		The state Government can assign responsibility of the state watershed management council to the state water council
18	1, 2, 3	The state Government can constitute a district committee called as district watershed management committee as per need. The members of the district watershed management committee can be appointed by the state Government. The decisions carried out by the district watershed committee shall be then implemented by the district authority.
19		For artificial recharge of water Integrated watershed management plan should be prepared by the district watershed committee.
20		Power has been assigned to the district authority for public drinking water source.
21		The district authority shall see the influence of the area under public drinking water source.
22		The excess discharge of water can be prohibited by the district authority from any well for a particular period of time. The state Government also holds the power to prohibit the discharge of water from a well for a particular period of time.
23		The extraction of groundwater can be regulated by the district authority in the village
25		The district authority shall declare any area as water scarcity area for a specific period of time
26		The district authority can place an order to extract water from any well in case of water scarcity.
27		The state Government looks after the method of payment charged by the district authority.
28	1	The state Government is assigned with the power to look after the manner in which a person sinks a well and the preservation of the soil
29	1, 5, 6	The state Government shall look after the work of the water resource committee as per required. The terms of the official members of the watershed water resource committee are assigned by the state Government
30	1, 4, 5	The state Government has the power to look after the manner in which the watershed water resource committee prepares the groundwater plan, which is notified by the district authority. The cropping pattern will be then decided on the basis of the water budget by the watershed water resource committee with consultation to the state Government.
32	1, 4	The state Government has the power to give permission for the artificial recharge of water.
33		The watershed water resource committee shall promote the participation of people for sustainable and equitable management of water.
34		The watershed water resource committee implements plans in coordination with Panchayat.
35		The watershed water resource committee can regulate or prohibit the mining of sand under the recommendation of district authority.
36	2	The service charge and fees shall be collected by the watershed water resource committee for the use of groundwater
37		It is mandatory for the watershed water resource committee to submit its report to the Gram Sabha
39		The state Government prescribes the time for the water budget to be prepared for the watershed water resource committee.
40		Rules are made for the account statement submitted annually.

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Table 2. Continued

Clause	Sub-clause	Objectives
43		The groundwater surveys and developing agencies shall assist the watershed water resource committee for watershed preparation.
45	1	The state Government shall prescribe the rules for the hydrogeological studies carried out by the groundwater surveys and developing agencies.
46	1	The state Government has the power to look after the manner in which the Panchayat and other local bodies looks after the maintenance of the water bodies and the water budget. The artificial water recharge structure is also taken care of.
47		The state Government shall look after each and every rule and the manner in which it is followed for a sustainable water management.
56	1, 2	An appeal can be made to the state Government with fees for going against the orders of the district authority.
58		Difficulties must be removed in following such rules for the ground watershed management

Source:http://www.slideshare.net/ruralindia/maharashtra-groundwater-development-and-management-act-2009.

CASE STUDIES ON ENHANCING SUSTAINABILITY OF WATER IN WESTERN MAHARASHTRA

Maharashtra occupies a total area of 3,07,713 square kilometers with an average annual rainfall of 1433 mm. Majority of the area of the state lies in the Deccan belts. The rocks of different areas are confined with different characteristics which divides the area into unconsolidated, consolidated and semi-consolidated.

Wadgaon

This is a village which is suffering from water scarcity. Roof top rainwater harvesting was found as the best measure for conserving water in this village. This has been implemented in most of the areas of the village and the measure was also supported by the Panchayat of the village by constructing several water storing structures in the local nullah.

Watershed Warud Taluka in Amravati

Due to water scarcity the groundwater has declined to a very lower level in this village. This led to the construction of three percolation tanks at Manikpur, Benoda and Bhindi and ten cement plugs or nullah bunds at Alora, Benoda, Mamdapur, Malkhed, Temburkhed, Loni, Sendurjanaghat. Five underground water storage tanks were also constructed for conserving water.

Watershed at Yuvraj Taluka in Jalgaon

The Yuvraj taluka has a declining groundwater by one meter every year due to cultivation of banana. For sustaining water in the region a total of three percolation tanks were constructed at Ichkeda, Haripura and Dongaon. Injection well, recharges shift, dug wells and nullah's were constructed in the village to fulfil the water requirement of the village.

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Watershed at Yaval Tehsil of Jalgaon

Percolation tanks and recharge shifts have been constructed at Borkheda, Wadri, Sangvi and Dongarda to allocate water in twenty-eight villages of Jalgaon district. The storage capacities of these tanks were found to be seventy-one to ninety-eight thousand cubic meters and a catchment area of 0.425 to 4.273 sq.km each and a submergence area of 12.35 to 42 thousand sq.m.

Warud at Amravati

Roof top rain water harvesting was initiated as a project in the village by the Panchayat samiti. Roof top area of 500 sq.m was used for rain water harvesting. This water has been used for storage of water in the ground well. The ground water well level showed a substantial increase in its level due to roof top rain water harvesting. The water stored from the rain water harvesting was an essential measure for storing water at times of need and a major portion of the water stored was used to increase the level of groundwater.

RALEGAN SIDDHI

Ralegan Siddhi is a small village of Parner taluka of Ahmednagar District, Maharashtra. The village was once under the hands of poverty followed by the scarcity of water and limited agricultural growth. The village was very badly shattered due to climate change and unsustainable management of water. Agricultural crops were badly ruined and farmers faced few bad days.

Figure 1. Scenario of Ralegan Siddhi village in 1975

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Figure 2. Hind Swaraj Trust run by Mr. Anna Hazare

THE NEW BEGINNING FOR CHANGE IN RALEGAN SIDDHI

It was Mr. Anna Hazare who made the first step to bring out a change in the village some thirty years ago. With consistent and committed efforts of Mr. Anna Hazare, the village came out to be named as the first ideal village of Maharashtra. Mr. Anna Hazare made a successful implementation of sustainable practices in the village.

Prohibition on grazing of agricultural crops, cutting of trees, consumption of alcohol, shramdan and regeneration of water resources were some of the practices for the development of the village. In the present scenario availability of water resources in the village for irrigation in agriculture land has been found to be the luxurious asset for the village. Phand & Arya (2007) made a detailed study on the developing trends of Ralegan Siddhi before and after sustaining practices and came to a conclusion that the village has twelve hundred acres of land out of seventeen hundred which are under irrigation. This has led to increase in the agricultural yield and ultimately this has led to increase the number of livestock animals. In 2007, it was found that dairy sector in the village contributes to Rs. one crore per annum (USD 1,50,212/- pa). Practices of this nature have made the village full-fledged with drinking water, school facilities, roads, medical hospitals and sanitation thereby making it sustainable. Further the model of Ralegan Siddhi village was taken as the Aadarsh Gaon Yojana for other villages. This model focused on practices for making water safe for drinking and was taken as Aadarsh Gram Yojana in about three hundred villages across Maharashtra.

The implementation became famous and was based on five principles namely shramdan, ban on cutting of trees, ban on grazing, ban on consumption of alcohol and introduction of family planning as one of the sustainable practice. With shramdan, forty thousand contour trenches were built for conserving water and increasing the groundwater table. Along with contour trenches several trees were planted around. The trees like neem (*Azadirachta indica*), babul (*Acacia nilotica*), kashid (*Cassia siamea*) and shisam (*Dalbergia sissoo*) were given preference.

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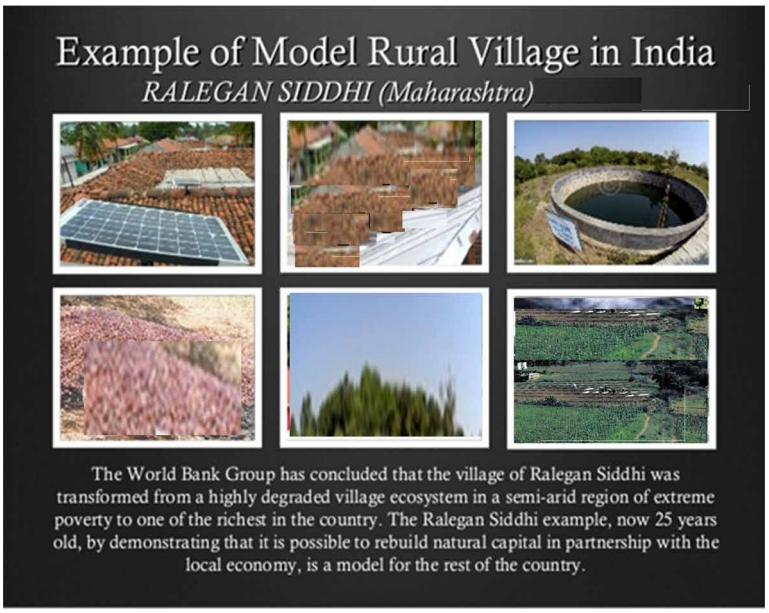
Figure 3. Ralegan Siddhi as an example of Model Rural Village



HIWARE BAZAAR

Hiware Bazaar is one of the village located in Ahmednagar District which has been suffering from drought conditions. During British rule, Hiware Bazaar village was full of joy and peace since it was surrounded by the hills therefore it had a pleasant weather during rainy seasons which resulted into wells and groundwater table to be filled with water all the year around.

This promoted agricultural crops with good yield and the farmers of the village chose agriculture as their main occupation for living and trading their crops in Mumbai. With time the things did not remained

Figure 4. Drought conditions in Hiware Bazaar

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the same and with the growing population trees were cut down for wood and agricultural land were shifted towards construction of houses. With the decrease in the number of trees the soil left barren with excess of erosion and maximum water being wasted into the floods. This resulted into wash down of the fertile soils into rain and the village drowned down to adverse conditions. In 1972, things did not remain the same and the wells were left dry with the groundwater table went significantly down. Shortage of potable water led the people to lead a miserable life. People began shifting away from the village and the farmers' crop lands converted into deserted ones. Losing the means of their life farmers got addicted to alcohol and few committed suicide. By 1973, things got even worse with 80% people being addicted to alcohol and agricultural land turned into desert. With no means of survival Government officers were scared of being posted in the village, therefore only blacklisted candidates were posted there as a punishment. By the year 1988, the village was ruined in terms of economic, social and environmental aspects. The teachers in the school rushed away from the village and the schools were locked in waiting for the good teachers to return. This resulted into adverse education system in the village. Therefore it was found that not only elders but children also suffered from the scarcity of water in the village.

NEW BEGINNING IN THE WESTERN REGION

Hiware Bazaar Village

As discussed in the background it is clear that the village wanted a change for the need of water as their survival. The young generations saw some ray of hope for sustaining the village and requested Mr. Popatrao Pawar for becoming the sarpanch (Head) of the village in the election. By 1990 Popatrao Pawar was elected as the sarpanch on a condition that villagers must not quarrel among themselves. Pawar called out Gram Sabha for hearing the needs of the villagers and found out that the basic needs of the farmers in the village was water for drinking and agricultural purpose which had resulted an adverse impact on their health and environment.

Figure 5. Popatrao Pawar transformed the village from drought to a sustainable one

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The need for water in the village was given prime importance with other needs. To begin with Mr Pawar planted tamarind saplings which were destroyed by the villagers because it was not considered relevant for them. This promoted the sarpanch to educate people as his first step for the betterment of the village and also for sustaining water. The schools were painted with playground and education was started as an initial step in the village. The primary school led to high schools where teaching was made by the youngsters without charging any fee from them. The next step was to generate availability of water in the village. The villagers requested the forest department for initiating afforestation in their village but the overgrazing practice made by the villagers had made the farm barren. Therefore, their request was not taken by the forest department. In 1993, the villagers went to Ralegaon Siddhi and Aadgaon in Kolhapur to understand the water management practices implemented there. This visit taught them measures to fight with scarcity of water in the drought regions. In 1993, with the support of forest department around seventy hectare of village forests was regenerated and sustainable practices were made to conserve water. Contour trenches around the hills were found to be the most important measure for saving water from wastage and also for maintaining the fertility of the soil. Contour trenches in Government land led to plantation of about 45000 trees. Plantation of trees was carried out on hills which helped to conserve water. Pits were dug to store water and grazing was prohibited. The practice of cooking food in chulhas was also banned and a shift towards LPG (Liquified Petroleum Gas) was made in order to save the trees and avoid cutting down of wood. In 1994, a NGO called 'Yashwant Krishi Ram Va Panlot Vikas Sanstha' was established consisting of eleven members who planted local trees and limited the plantation of Eucalyptus and Subabul which consume a lot of water from the soil. In order to review the initial steps taken and continue for further development, the villagers felt that it was necessary to have a social audit body at place in the village. This led to audit in the village and by 1994 the transparency and accountability were regarded as the key for the village development. In 1994, twelve agencies were implemented under employment guarantee scheme for addressing water scarcity problems. Hence then Hiware Bazaar was selected as the Aadarsh Gaon Yojana by the Government of Maharashtra (Sakhuja, 2008). The Aadarsh Gaon Yojana was based on prohibition of grazing, cutting down trees consumption of alcohol and promotion of family planning and labors (Sangameswaran, 2006). Following were the main five principles which made Hiware Bazaar as the Aadarsh (Ideal) village.

1. **Ban on Tree Cutting:** Cutting down of trees for wood as fuel or fodder was strictly prohibited in the village. This led to the promotion of long lasting trees and thereby replacing the conventional chulhas with LPG.
2. **Restrictions on Grazing:** Grazing was also restricted as it resulted into tremendous soil erosion and wastage of water. As a remedy for the farmers having animals rotational grazing was thought to be a better means.
3. **Family Planning:** According to Malthusian Theory of Population it was found to control the growing population to meet the need for food. This practice had a limitation that family planning was not made a part of the health concern.
4. **Ban on Consumption of Alcohol:** The basic purpose of this step was to save the people from the evil effects of alcohol and also to minimize the gap between their debt and consumption. People addicted to alcohol were provided bank loans for purchasing animals in order to run their life.
5. **Shramdam:** This was a common practice which led to promotion of agricultural practices and water conservation measures for the village.

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Several water harvesting structures and wells have been constructed in the village for storing water in times of need. The production of grass also increased from 100 to 6000 tons by the year 2004, which resulted to increase the livestock animals with the farmers and this resulted in increase in the milk supply (Singh, 2010).

Implication of Water Rules in the Village

Water rules were made for the distribution and use of water. The rules for distribution of water were bifurcated into two, one being for people who get access to water and another for the distribution of water. Water is supplied to lands as per the ownership and groundwater is accessed through private wells.

Impact of Watershed Management in the Village

The main effect of watershed management is an increase in the groundwater table and the percentage people being benefitted from the water also increased tremendously. This also led to increase in employment since the practices involved a great number of labours. Drinking water was supplied to every households and this resulted into good health of people. During drought situation water was available both for domestic as well as agriculture purposes.

Phand & Arya (2007) conducted a research study on Hiware Bazaar village of Ahmednagar District to find out the impact of Aadarsh Gaon Yojana in the villages and also the status of the village before and after the implementation of Aadarsh Gaon. The Aadarsh Gaon Yojana was implemented on 15 August, 1994. From the research conducted it had been found that the total village area remained the same before and after. The total area for plantation of trees had increased with good storage structures, nullah bunding, increasing number of wells and contour trenches. The cropping pattern grown in the agricultural land was also found to change as per the availability of water in the area throughout the season. With increase in the number of animals the total production of milk also increased. The areas having no schools were found to be led by two or more schools.

As regards to adaptation of sustainable measures in Hiware Bazaar for sustaining water, the contour bunding was practiced in the area of 414 hectare, cement nullah bunding in an area of 4 hectare and nullah bunding in an area of 51 hectare. The two measures helped in assuring conservation of soil and water for future needs. Afforestation was also considered as an important aspect for enhancing sustainability in the village in an area of 404 hectares. Tree plantation was made along road side covering a length of six kilometers. Storage as well as earthen structures was constructed in an area of 9 sq.km for conservation of water

SUSTAINABLE WATERSHED MANAGEMENT

A sustainable water use is defined as the use of water beneficial for all the users without reducing the need for other users being human beings, animals and also natural resources (Gleick, 1998). The demand for water is not just limited for fulfilling the need of water but also the wants of people for water in future. Variation in the stock and flow of water that changes the availability of water at proper time and space and variations in the demand for water use disturbs the sustainability of watershed management. The disturbance in sustainability of water is mainly caused due to increasing human population and chang-

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ing technologies. The first and foremost task to be done for sustaining water is to control the above two problems. Since the increasing human population requires enough water for meeting their needs and the technologies which is changing every now and then decreases the amount of water required for the social benefit. The sustainability of water can be managed by controlling the disturbances created by the four parameters namely, water requirement for human being, water requirement for environment, maintenance of water quality standards and the renewable water resources maintenance (Gleick, 1998). Maharashtra is the first state in India to take an initiative for sustaining water and prepared a state disaster management plan giving importance to water requirement in the state. It is also the first to regulate water resource authority for regulating water requirements and its availability.

Balawadi and Tandulwadi: These are the drought prone villages which faces problems for water availability for the agro based industries and plantation of sugarcane crops which requires a lot of water. Baliraja Memorial dam was constructed in South-Western Maharashtra which allocated water to the villages for meeting the farmer's irrigation needs as well as the household domestic needs of the villagers. The dam changed the living style of the village and addressed the water issues in the village.

AN APPROACH TO SUSTAINABLE WATERSHED MANAGEMENT

Das (2006) reported in his research different approaches and Programs for sustainable management of water. In the present era with the upcoming challenges of water, the availability of water for the fast growing population of the country is a matter of deep concern. In many parts of the rural areas availability of safe water is a major problem while few areas are facing scarcity of water. With this thought it has become very essential to take some initiatives for sustaining water for different uses. Various centrally sponsored schemes have been working for accelerating water in the rural areas by the implementation of minimum water tax for conserving water. During 1981-91, United Nations International Drinking Water Supply took an initiative step for sustaining water and concluded that drinking water must be paid or charged by the user in order to give it a value. Government also took an initiative step for making water available to the rural areas and came out with Sector Reform Program. The Sector Reform Program Swajaldhara comprised of four basic elements namely, demand for water, accountability, contribution of people and community participation (Das, 2006). The Constitution 73rd and 74th amendments act in the year 1992 focused on drinking water supply, water management and sanitation measures in rural areas from the Panchayats and Nagarpalikas (Corporation). The drinking water supply in rural areas are managed by the Ministry of Rural Development; Ministry of Water Resources at the central level; Public Health Engineering Department at the state level; Zilla Parishad, executive engineer from public health engineering department and district rural development agencies at the district level; and taluka Panchayat, gram Panchayat and village water and sanitation centre at the block level. The five year plan of Indian Govt. has brought different policies and Programs to come over from the issues of water scarcity. The problems of rural water are managed by the respective bodies as mentioned above in the state, central, district and block level. In 1950, constitution of India was set up and first national water supply was started in 1954. Then in the year 1956-1972, public health engineering department was set up at the state level to look after the rural water supply in towns and villages. Rural water schemes were sanctioned by financial terms in 1968 followed by the accelerated rural water supply Program in 1972 for handling the problems of the village related to rural water supply. In 1974, the Programs related to minimum need of water supply were introduced in states. The accelerated rural water supply Program

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identified the problems of the village for supply of drinking water throughout the year with a sustainable management of water in 1977. National Drinking Water Mission was initiated in the year 1986 for the application of conservation measures for sustaining supply of water. Ultimately the National Water Policy evolved in the year 1987 to look after the planning of different water resources and supply of drinking water in India. In 1991, the National Drinking Water Mission was renamed as Rajiv Gandhi National Drinking Water Mission. This Mission put forward standards for the supply of drinking water to the rural population. The year 1996-1999 began with audit of water resources with World Bank and other agencies. All the developments led to Swajaldhara Program in the year 2002 and the national water policy was revised by the National Development Council.

Several Government agencies, World Bank, German Development Bank and other non-Government organizations are indulged in the implementation of an efficient water supply in Maharashtra. The effort started with the dug well era from1960 to 1970, which provided several dug wells with power pumps. The year 1971-1985 led to the bore well era where bore well technologies came into existence leading to several hand pumps and power pumps. Rural piped water supply era arrived from the year 1985 to 1997 which led to increase in the number of piped water supply scheme in the rural areas. Several water projects were handled in this era. The year 1997 to 2000 began with the Master plan era which led to expenses for different water supply schemes. Since the year 2000 the policy reform era was evolved for delivering water in the rural areas and providing several sanitation measures in the rural area (Das, 2006). This made Maharashtra to be the first state known for launching Program for allocating water resources and sanitation services. The Government of Maharashtra has implemented several Programs for conserving groundwater. Shivkalin pani sathawan yojana is one such Program started by the Government of Maharashtra for storing rain water, rainwater harvesting, construction of tanks for water storage and other measures which can sustain water. A large number of Programs and schemes have been developed by Government of Maharashtra for conserving water.

The Government has also implemented two programs namely the Sant Gadge Baba Gram Swachatha Abhiyan and the Total Sanitation Campaign (TSC) based on the sanitation measures. The Government has focused the hygiene and sustainable practices for clean rural area.

CHALLENGES OF WATER IN WESTERN MAHARASHTRA

In rural areas of Maharashtra, water has been suffering with several challenges. The major issue of concern is about the water industry to work efficiently meeting the demand of water. It has been found that the groundwater has been over wasted for the private productive use and must be controlled. The first challenge faced by the Maharashtra sector for the availability of water is the technologies which interfere with the sustainable water management (Das, 2006). In 2002 the state Government of Maharashtra took an initiative to address the water resources in rural areas of thirty three districts of Maharashtra. After testing of water it was found that the water in such districts was contaminated. The districts like Jalgaon, Buldana, Akola, Washim, Wardha, Nagpur, Bhandara, Chandrapur, Yavatmal, Parbhani, Jalna, Nashik, Bid, Latur, Ratnagiri, Sangli, Sindhudurg and Solapur are facing problems regarding groundwater quantity as well as quality. The water table has been found to decline (increase in vadose zone) in the districts of Akola, Beed, Bhandra, Buldana, Chandrapur, Gadchiroli, Gondia, Hingoli, Jalgaon, Jalna, Kolhapur, Latur, Nagpur, Nashik, Nandurbur, Thane, Sindhudurg, Sangli, Solhapur, Satara, Ratnagiri,

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Parbani, Osmanabad, Yavatmal, Wardha and Washim with problems in taluka. The TDS, fluoride and nitrate content in water is high causing severe problems (Scott et al., 2005).

Eastern districts of Maharashtra are facing problem of high presence of iron in water while the ground water in Akola, Amravati and Buldhana are facing problems of salinity. One third of the area under Maharashtra lies in the rain shadow region mainly from the Western part of Maharashtra and Marathwada. The problem arises when such regions lying in the rain shadow regions cultivate high water intensity crops. Most of the rain shadow regions of Maharashtra consist of porous rocks which drains water quickly (Das, 2006). Government has led to Programs for increasing water supply for rural areas. Many wells have been dug to overcome water scarcity problems in Maharashtra. The limitation to such a program is that majority of the wells dug by the Government scheme are left dry in the summers with few of them aquifer polluted due to deposition of debris. Most of the problem arises due to lack of appropriate information about the status of water in the area or there is delay in the implementation of rural water scheme. In most of the rural areas people are resistant to take up the Programs or policies implemented by the Government easily (Das, 2006).

Farmers are very sensitive to water prices. The lowest water use efficiency is that point when farmers continue to apply irrigation till the net marginal productivity becomes equal to zero. The price shifts in the market results in the shifts in the selling price of water. The farmers generally do not go for water markets because the demand and supply do not match among themselves and the returns obtained from the crops are higher than the selling price of water. The farmers have to pay for the water on hourly basis and pay a percentage of their crop yield as a charge for water. The well owners charge water on the basis of the opportunity cost for excess water supply for irrigation. If water is charged on volumetric basis then the farmers would generally shift towards the cropping pattern which gives higher yield return from per unit of water consumed. This results into a limitation that supply of water for agriculture has been found to be limited so water is charged at a higher price for agriculture. The table given below reflects the status of availability of water in different districts of Maharashtra:

INITIATIVES TAKEN BY THE STATE MAHARASHTRA REGARDING MANAGEMENT OF SUSTAINABLE WATER REQUIREMENT

Maharashtra state is the first to carry out an initiative for sustaining water requirement in the state and is the first to prepare a state disaster management plan. The state has undertaken several managing plans regarding a sustainable use of water which are given in the table below (Table 3).

CONCLUSION

The Maharashtra state has several challenges regarding availability of water due to the structural location of the regions since the area has been classified into Eastern and Western Maharashtra. It has been found that there are few regions in the state which are drought prone while few of them are affected by floods, cyclones and earthquakes. Some regions receive adequate rainfall where as in few region rainfall is very limited. Diverse climatic conditions are seen in Maharashtra due to its location thereby affecting the availability of water in few regions. Inspite of the above challenges the state has been able to overcome the challenges of water scarcity by adapting sustainable practices in the state for enhanc-

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Table 3. Status of availability of water in different districts of Maharashtra

Sr.no.	Districts	Status of Water Availability
1	Nashik	Declared as drought by Government of Maharashtra in 2003. Affected by flood in the monsoon season.
2	Yavatmal	Flood prone areas
3	Parbhani	-
4	Raigad	-
5	Pune	Declared as drought by Government of Maharashtra in 2003
6	Ratnagiri	Can be hit by cyclones
7	Satara	Declared as drought by Government of Maharashtra in 2003
8	Sangli	Declared as drought by Government of Maharashtra in 2003
9	Solapur	Declared as drought by Government of Maharashtra in 2003
10	Sindhudurg	-
11	Beed	Declared as drought by Government of Maharashtra in 2003
12	Chandrapur	-
13	Gadchiroli	-
14	Kolhapur	Flood prone areas
15	Nagpur	Affected by earthquake
16	Bhandara	Affected by earthquake
17	Dhule	-
18	Jalna	-
19	Mumbai	Affected by floods, cyclones and earthquake.
20	Nanded	Affected by flood in the monsoon season
21	Ahmednagar	Declared as drought by Government of Maharashtra in 2003
22	Amravati	Flood prone area
23	Akola	Largest flood prone area
24	Thane	Flood in monsoon and drought in summers.
25	Wardha	Flood prone areas
26	Aurangabad	Declared as drought by Government of Maharashtra in 2003
27	Dharashiv	Declared as drought by Government of Maharashtra in 2003
28	Latur	Declared as drought by Government of Maharashtra in 2003

ing availability of water for future needs. In rural areas of Maharashtra, water has been suffering with several challenges. The major issue of concern is about the water industry to work efficiently meeting the demand of water. It has been found that the groundwater has been over wasted for the private productive use and must be controlled. The first challenge faced by the Maharashtra sector for the availability of water is the technologies which interfere with the Sustainable Water Management (Das, 2006). In 2002, the Government of Maharashtra took an initiative to address the water resources in rural areas of thirty three districts of Maharashtra. After testing of water it was found that the water in such districts is contaminated. The districts like Jalgaon, Buldana, Akola, Washim, Wardha, Nagpur, Bhandara, Chan-

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Table 4. Managing plans undertaken by the State of Maharashtra for sustaining water

Sr. No.	Managing Plans	Characteristics
1	State Disaster Managing plan	Maharashtra is the first to prepare a state disaster management plan. The plan addresses the risks due to floods, cyclones, accidents and other disasters in the state. Such issues are undertaken by the state to solve the problem. The water disaster is also undertaken in the plan for the proper management.
2	District Disaster Managing Plan	The districts facing problems of disasters are undertaken in the plan by the Government of Maharashtra. These problems include earthquakes, floods, cyclones, industrial disasters and accidents which must not be ignored.
3	Disaster Management plan	The center for disaster management was set up in the month of august in 1996 with an objective to develop plans for preparing the state from any disaster like earthquakes, floods, cyclones for a sustainable water management.
4	District disaster management plan	The district disaster management plan has been developed to analyze the occurrence of disasters in the district and improve the preparation for overcoming the challenges of the disaster.
5	District Disaster Management committee	The district disaster management committee analyses the occurrence of disasters reviewing the threats in order to improve the fulfilment of the demand for water in the state.
6	Maharashtra state disaster management authority	Under section 14 of the disaster management act 2005 Maharashtra state disaster management authority came into existence in 24th May, 2006 involving chief minister, deputy chief minister, ministers, official members and the chief secretary.
7	State emergency operation center	The emergency operation center tackles the hazardous events which can lead to emergency situation.
8	Maharashtra water resource regulatory authority	It has been evolved with an objective to regulate water resources within the state and analyze the issues regarding use of water.
9	State executive committee	This committee was developed with chief secretary, additional chief secretary, member secretary and other secretary.
10	Hydrological projects	It was developed in the year 1996 in Nashik with an objective to improve hydrological data and assess the availability of water.
11	Dam safety organization	It evolved in 1980 in Nashik for the inspection of large dams.
12	Government department soil conservation	It was organized by Marathwada Sheti Sahayak Mandal in Adgaon at Aurangabad
13	Government department soil conservation and soil forestry	It was organized by local organization under Mr. Anna Hazare at Ralegan Siddhi in Ahmednagar
14	Aadarsh gaon yojna	It was organized by Yashwant agriculture and watershed development at Hiware bazar in Ahmednagar
15	Indo-German watershed Program	This Program was organized at Vijju Bhulgaon in Ahmednagar
16	Indo-German watershed Program	It was organized by SEWA at ambewadi in Beed
17	N.G.O	Organized by Manavlok at Bhavthan in Beed
18	N.G.O	Organized by Afarm at Damoli in Beed
19	Drought prone area Program	Organized by Sarwodaya welfare at nandgaon khadeshwar in Amravati
20	Drought prone area Program	Organized by Sarwodaya welfare at Nandgaon Khadeshwar in Amravati
21	Drought prone area Program	Organized by Chandrapuri maharaj shikshan prasarak at Pimpalgaon in Amravati
22	Drought prone area Program	Organized by Prabhodankar Thakre at Dharani Chikaldhara in Amravati
23	Drought prone area Program	Organized by Mahila Utkashtha at Hirangimangulpur in Wasim
24	Drought prone area Program	Organized by Shriram Sukhshainik at Sanglud in Akola

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Table 4. Continued

Sr. No.	Managing Plans	Characteristics
25	Drought prone area Program	Organized by Gomukh trust at Sangamner in Ahmednagar
26	National watershed development Program in rainfed areas	Organized by Prabodhani at Bariewadi in Ahmednagar
27	National watershed development Program in rainfed areas	Organized by agriculture department at Chale in Pune
28	Agakhan foundation	Organized by Dilasa at Yevat in Yavatmal
29	Shivalin Pani Sathawan Yojana	The system of rain water recharge was launched. Drinking water was stored by different rain water harvesting structures.
30	Artificial recharge of water	This scheme was initiated by the central ground water board at viii plan at Warud
31	Recharge of aquifers	This scheme was initiated by the central ground water board at viii plan at Yuval
32	Maharashtra Artificial Recharge to groundwater	This scheme was initiated by the central ground water board at ix plan at Jalgaon district
33	Maharashtra roof top rain water harvesting	This scheme was initiated by the central ground water board at ix plan at Warud in Amravati district
34	Maharashtra roof top rain water harvesting	This scheme was initiated by the central ground water board at ix plan in KITS campus at Ramtek
35	Artificial Recharge structures	This scheme was initiated by the central ground water board xi plan in Rajbhawan in Nagpur

Source: http://nidm.gov.in/pdf/dp/Maharashtra.pdf

http://www.ctara.iitb.ac.in/water/waterplanning/maharashtra.pdf

Watershed Development in Maharashtra: Present Scenario and Issues for Restructuring the Program. ö Technical Report. Pune: SOPPECOM.

http://cgwb.gov.in/documents/case-studies-rwh-ar-may2011.pdf

drapur, Yavatmal, Parbhani, Jalna, Nashik, Bid, Latur, Ratnagiri, Sangli, Sindhudurg and Solapur are facing problems regarding groundwater quantity as well as quality. Western part of Maharashtra has been affected by several measures of water scarcity. There have been several sustainable measures being adopted by the people of the villages of the Western Maharashtra which has made their living easier by allocating water for irrigation as well as household domestic needs. Not only the people of the villages even the Panchayat samiti and central Government has supported several schemes for sustaining water management in the Western part of the state. There has been a great participation of the central groundwater board regarding the sustainability of water in the eighth, ninth, tenth and eleventh five year plan. With instant application of the sustainable practices it has been found that several villages located in the Western part of the state are doing great work for enhancing water availability through storage of water in earthen structures as well as through rain water harvesting. Several other measures like afforestation, terrace farming, contour bunding, tree plantation along road side and limitations to grazing of animals have led to conservation of water as well as the soil. Villages like Ralegan Sidhdhi, Hiware Bazaar, Wadur, Yaval, Yuvraj and Wadgaon have come up with sustainable practices for allocation of water for future needs. Villages like Ralegan Siddhi and Hiware Bazaar which once had severe water problems are now called as the Aadarsh Gaon (Ideal Village) and are the true symbols for sustainable water management in a drought prone area. The Maharashtra Government has also come up with several schemes which have supported the sustainability of water. Several initiatives have been taken by the

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Maharashtra Government for overcoming the challenges in availability of water in the Western regions of the state. Supportive mechanisms has been followed to encourage agriculture in the Western areas and to control floods by the construction of bunds and dams which otherwise may have destroyed the villages and also will lead to soil erosion making the soil infertile for agriculture. Thus, in the current era of climate change, sustainable water management practices at the local level is the need of the hour to resolve the problems at state and national level.

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Chapter 14
Characteristics of Chitosan Nanoparticles for Water and Wastewater Treatment:
Chitosan for Water Treatment

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ABSTRACT

Chitosan is a naturally occurring biopolymer originating from several microbial species as well as crustacean species, such as shrimp and lobster. Chitosan has excellent physical and chemical properties that allow its use in various environmental applications especially in water treatment. It is a biodegradable polymer, and it is inexpensive providing an environmentally friendly and economic option for water and wastewater treatment. Chitosan offers a myriad of applications through chemical coagulation and flocculation, antimicrobial properties, adsorption capabilities, and nanofiltration and can provide a sustainable route for water and wastewater treatment. This book chapter elaborates the recent developments in chitosan applications in water and wastewater treatment.

INTRODUCTION

Water---an innate right---is somehow squandered even in the 21st century. Approximately 10,000 people die as a result of inadequate water supply and related third-world issues every day (UNwater, 2015). Currently, civilizations are growing at twice the rate of the availability of water resources, and it is projected that up to 1.8 billion people will experience absolute water scarcity by 2025 (UNwater, 2015). The importance of economical, clean water cannot be overstated in a society facing environmental issues such as pollution of water resources, droughts, and increasingly dwindling freshwater availability.

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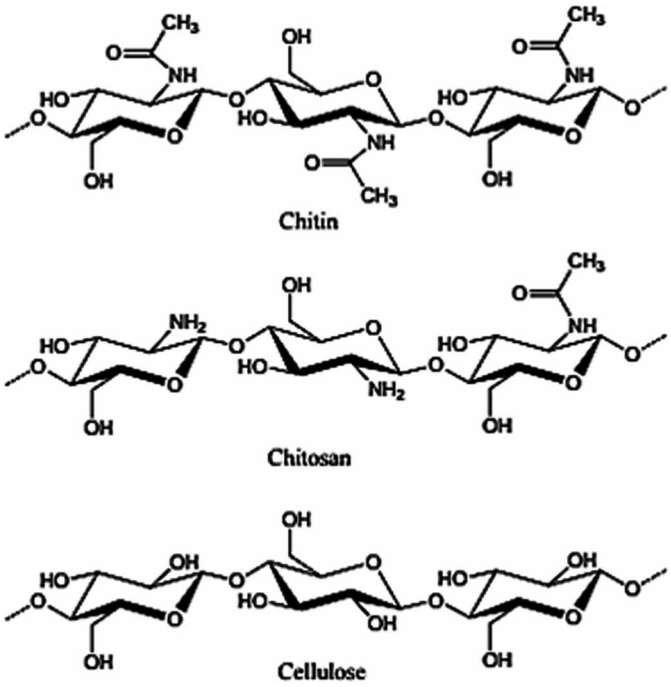
Fortunately, modern day science might have the answer in a naturally occurring polymer: chitosan. Chitosan is simply derived by the deacetylation of shellfish exoskeletons. Chitin can also be found in fungi, cell walls, and yeast. Although small, this nanoparticle continues to substantially impact water treatment through its idealistic properties, diverse applications, and economical potential. These diverse applications of chitosan include coagulation and flocculation for water and wastewater treatment, antimicrobial properties, adsorption capabilities of dyes and heavy metals, and desalination through nanofiltration. Many physical and biological properties of chitosan produce a linear polysaccharide ideal for water and wastewater treatment applications.

CHITOSAN PROPERTIES AND PREPARATION

Chitin, as shown in Figure 1, is the acetylated precursor to chitosan. The removal of these acetyl functional groups allows for higher solubility due to the increase in positive charge. Due to its deacetylation, chitosan is considered a pseudo-natural biopolymer which is predominantly characterized by its degree of deacetylation (DD) and molecular weight (MW). Considering that these two properties are directly proportional, the degree of solubility can be seen as inversely proportionate to the MW and directly proportionate to the DD. The degree of deacetylation is a molar percentage which differentiates chitin from chitosan at precisely 50% mol. This 50% DD allows for solubility in acidic aqueous solutions.

Acetylated Chitosan, or Chitin, is known to exist in two allomorphs, α and β. The more abundant α Chitin is found within traditional yeast, fungi, shrimp, crab, krill, lobster, and crawfish. The less abundant β Chitin is found within the protein in squid pens and is not an industrial source. Beyond knowledge of

Figure 1. Chitin, chitosan, cellulose (Alvarenga, 2011)



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the biopolymer's source, differentiation can be determined through Nuclear Magnetic Resonance (NMR) spectroscopy and infrared in conjunction with X-ray diffraction (Younes & Rinaudo, 2015). Moreover, whereas α Chitin contains two antiparallel molecules per unit cell, β Chitin contains merely one. β Chitin is more reactive; however, both α and β allomorphs remain insoluble.

Chitosan's solubility can also be affected by the distribution of acetyl compounds as well as ionic concentration. Chitosan's cationic property enables it to strongly adsorb negatively charged toxins. This positive charge can be modified by pH, while chitosan acts with inverse efficacy to its pH for coagulation and flocculation. This capability of changing solubility and cationic charge through pH causes both desirable and undesirable aspects considering that the extent of coagulation and flocculation can also be manipulated to repel particles and prevent agglomeration.

Chitosan Preparation

Chitosan can be prepared through both enzymatic and chemical routes. Chemical route is much more common due to production rates and greater economic viability. Preparation begins with extraction from one of its various sources (Figure 2); however, raw chitin is primarily acquired from the cuticles of shellfish. Both chemical and biological extraction suffice with chemical being the predominant methodology. The extraction process begins with grinding and washing of raw materials followed by deproteinization. Deproteinization essentially depolymerizes the biopolymer while removing any protein which is the primary cause of allergic reactions to shellfish. Reagents used for deproteinization include sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), and several others. As shown in Table 1, there are multiple concentrations, temperatures, and durations used for NaOH, the most common deproteinization solvent. These variations include 0.125 M to 2.5 M concentration, 25°C to 100°C, and one half hour to overnight soaking in the solution.

Following deproteinization, demineralization removes calcium carbonate as well as other minerals. Although hydrochloric acid (HCl) solution is generally used, nitric acid (HNO_3), sulfuric acid (H_2SO_4), and others will also achieve demineralization. Similar to deproteinization, demineralization's solvent and extent vary with raw materials. Generally two to three hours will suffice; however, much longer incubation times can be used. As the incubation time increases, the potential for degradation of the polymer increases as well. Additionally, the greater the temperature of the process, the more quickly and effectively the solvent will penetrate the chitin matrix. Moreover, the demineralization process may directly affect the physicochemical properties through "high temperatures, longer incubations, high acid concentrations, and granulometry" resulting in potentially undesirable structural changes (Younes & Rinaudo, 2015).

Following deproteinization and demineralization, the chitin must be extracted and dried with acetone. In order to convert the chitin to chitosan, the material must then be deacetylated. This is one of the most important processes in the preparation of chitosan due to its effect on the biopolymer's properties through acetyl group distribution, MW, and viscosity. These properties can be affected by temperature and incubation period. Although this chemical process is performed either heterogeneously or homogeneously, a hot, heterogeneous NaOH solution is most common. In contrast, a homogeneous reaction process would require 12-24 hours of pre-swollen chitin in an alkali solution. The alkali solutions used for either heterogeneous or homogeneous reactions must penetrate the amorphous region and typically leave some crystalline structures intact. These solutions will yield a maximum DD of 75-85%.

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These methodologies for preparation directly affect the simple physicochemical properties of the chitosan produced. The differential characteristics enable diverse applications through many physical forms such as chitosan powder, dehydrated chitosan flakes, crystalline chitosan, chitosan nanoparticles, and even chitosan as a modification to pre-existing surfaces. Chitosan surface engineering has proven to be an incredibly complex category, ranging from chitosan biosorbents to chitosan acting as an active layer for nanofiltration surfaces. These various physical forms allow for maximum efficacy of the biopolymer for any desired application.

Table 1.Chitosan preparation procedures

	Deproteinization				Demineralization			
Source	**NaOH Concentration**	**Temperature (°C)**	**Number of Baths**	**Duration (h)**	**HCl Concentration**	**Temperature (°C)**	**Duration (h)**	**References**
12 species of crustaceous and cephalopods	0.3 M	80-85	2 to 7 depending on source	1 h each	0.55 M	Room	15 min to 1 hour repeated 20-5 times depending on source	(Tolaimate, Desbrierews, Rhazi& Alagui, 2003)
Shrimp	0.125 M	100	1	0.5	1.25 M	Room	1	(Madhavan & Nair, 1974)
	0.75 M	100	1	-	-	-	-	
Shrimp	1.25 M	100	1	0.5	1.57 M	20-22	1-3	(Moorjani, Achutha & Khasim, 1975)
Crab	0.5 M	5	1	2	1.57 M	Room	5	(Muzzarelli, Tanfani, Emanuelli & Gentile, 1980)
Crab	1 M	80	1	3	1 M	Room	12	(Mima, Miya, Iwamoto & Yoshikawa, 1983)
Crab	1M	100	1	36	2 M	Room	48	(Shimahara, Ohkouchi & Ikeda, 1992)
Crab	1M	100	3	72	1 M	Room	-	(Hackman, 1954)
Crab	1.25 M	85-90	3	24	1.37 M	Room	24	(Broussignac, 1968)
Crab/Lobster	2.5 M	Room	3	72	11 M	20	4	(BeMiller & Whistler, 1963)
Krill	0.875 M	90-95	1	2	0.6 M	Room	2	(Anderson, de Pablo & Romo, 1978)
Lobster	1 M	100	5	12	2M	Room	5	(Hakman & Goldberg, 1974)
Squid	2 M	Room	2	One night	1 M	Room	One night	(Kurita et. al, 1993)
	2 M	100		4				
Lobster	10% w/v	100	1	2.5	10% HCl 90% formic	Room	18	(Horowitz, Roseman & Blumental, 1957)
Krill	3.5% w/v	25	1	2	3.5% w/v	20	1.5	(Brzeski, 1982)

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Table 1. Continued

	Deproteinization				Demineralization			
Source	**NaOH Concentration**	**Temperature (°C)**	**Number of Baths**	**Duration (h)**	**HCl Concentration**	**Temperature (°C)**	**Duration (h)**	**References**
Lobster	5% w/v	80-85	2	0.5	5% w/v	70	4	(Blumberg, Southall, van Rensburg & Volckman, 1951)
Crawfish	3.5% w/v	65	1	2	1 M	Room	0.5	(No, Meyers & Lee, 1989)
Crab	1 M	50	1	6	1 M	20	3	(Brine & Austin, 1981)
Shrimp	1% w/v	65	1	1	0.5 M	Room	-	(Wu & Bough, 1978)
Shrimp	3% w/v	100	1	1	1 M	Room	0.5	(Bough, Salter, Wu & Perkins, 1978)
Shrimp	4% w/v	100	1	1	5% w/v	Room	-	(Sluyanarayana, Yashodha, Mahendrakar & Puttarajappa, 1987)

Note. Reprinted from Younes, I., & Rinaudo, M. (2015). Chitin and chitosan preparation from marine sources. Structure, properties and applications. Marine drugs, 13(3), 1133-1174.

CHITOSAN CHARACTERIZATION

Certain methodologies for characterization of chitosan can ensure a thorough deacetylation and transformation from chitin to chitosan. Determination of the DD is a high priority. Methods such as H-NMR Spectroscopy, Titration, and Infrared spectroscopy are primary means of characterization and determination of DD.

Fourier Transform Infrared Spectroscopy

Infrared Spectroscopy (IR) provided below determines the organic functional groups present within the chitosan produced by Czechowska-Biskup et al. (2012). It should be understood that as the acetyl functional group is removed, the number of IR bands decreases to show the loss of the presence of amides. As shown in Figure 3, bands referencing hydroxyl, carbon, carboxyl, and amide bonds are all present. In order to determine the DD, multiple equations can be utilized. However, due to the inexact numerical nature of an FTIR, the calculations themselves are only estimations. For this particular sample, the DD was determined to be 77.84 $\pm$2.36, 66.11 $\pm$ 2.36, -12.5 $\pm$ 23.30, and 74.60 $\pm$3.60 through the use of FTIR. More importantly, the bands become less pronounced upon increased DD.

Zeta Potential

Zeta potential is a significant characterization of chitosan nanoparticles not only for the calculation of Degree of Deacetylation but also due to properties dependent upon surface charge interactions, i.e. antimicrobial, adsorption, and coagulation. The greater the positive charge of the chitosan nanoparticles,

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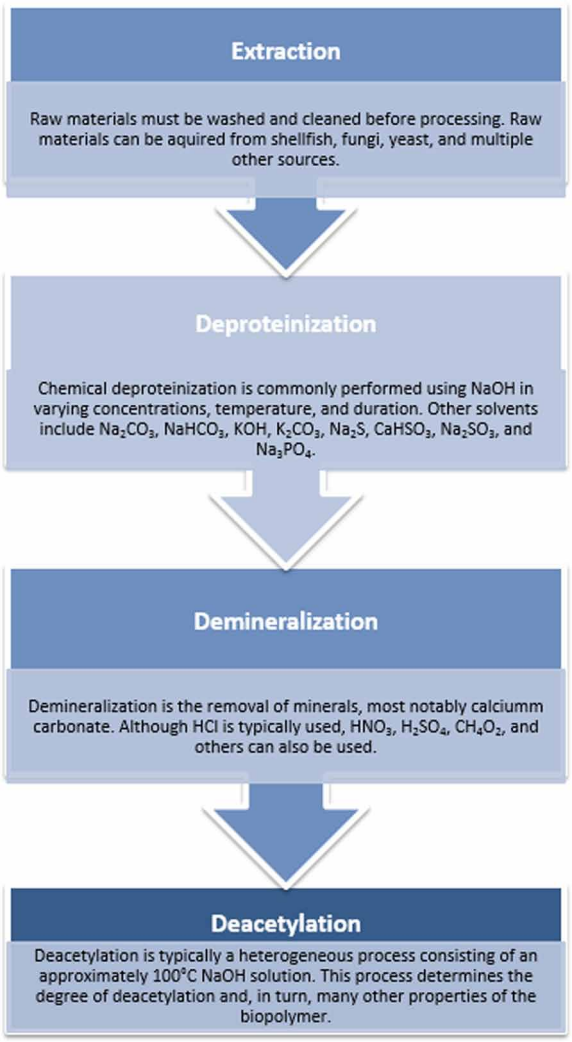
Figure 2. Generalized Chitosan Preparation Process



the greater will be the antimicrobial properties exhibited by modifying the permeability of the cellular membrane. in addition, a higher zeta potential present in the nanoparticle can further attract and coagulate toxins within a solution. Research by Qi et al. (2004) determines a range from 30.8 to 68.9 milliVolts (mV) present in nanoparticles purchased from Chitosan Company of Pan'an. The mean charge is shown to be at 51 mV and the DD was determined to be 85%. The DD directly affects zeta potential by removal of negatively charged acetyl groups while the MW is also important due to the quantity per monomer. In further studies focusing on cationic-anionic ratios, an average zeta potential of 28.0 ±0.6, 28.8 ±0.7, 30.3 ±0.4, 31.4 ±0.5, and 32.4 ± 11.1 mV with increasing particle size was determined, respectively (Abbas, 2010).

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GENERAL APPLICATIONS OF CHITOSAN

Being one of the most abundant biopolymers in the world, chitosan's slew of functionalities and properties only add to the vast applications and uses spanning fields from biomedicine to paper finishing. Within the biomedical field, chitosan is being considered for controlled drug release due to its swelling in acidic medium, antacid properties, and prevention of stomach irritation. In ophthalmology, chitosan is being researched for contact lens use due to several properties including "optical clarity, mechanical stability, sufficient optical correction, gas permeability, particularly towards oxygen, wettability, and immunological compatibility" (Kumar, 2000). Chitosan is an ideal polymer for the use in cosmetics and hair care products. More importantly, it also has a spectrum of uses within water treatment and wastewater treatment systems such as coagulation and flocculation, antimicrobial properties and uses as a biosorbent material to remove dyes, metal ions, and salt. Within the coagulation and flocculation functionality alone, many pollutants and suspended particles have successfully been removed and separated including algae, oil-in-water emulsions, brackish water, and lead and chromium wastewater.

Nontoxic and Allergen Considerations

In addition to desirable physicochemical properties for water and wastewater treatment, chitosan is surprisingly nontoxic to those with shellfish allergies and can be used as an antihistamine. Despite its shellfish origins, it remains non-toxic to those with shellfish allergies when applied externally. In 2011, a study was conducted to consider if HemCon, a chitosan bandage mandated for soldiers which stops bleeding, would cause adverse reactions from patients with shellfish allergies. The study concluded that 100% of the patients with predispositions to shellfish allergies were unaffected by the chitosan powder applied externally to wounds. However, this was contradicted when a very small percentage of the public reported delayed onset contact dermatitis to a chitosan cream. Although for some, shellfish increases allergic responses, chitosan could potentially decrease anaphylaxis responses for those with peanut allergies. Currently being tested on mice, this treatment has a 47% efficacy (Bae et. al., 2013). Its antihistamine properties have also resulted in a patent granted in 2011 for topical application.

WATER TREATMENT APPLICATIONS

Due to the interrelated concepts of water treatment and wastewater treatment, coagulation and flocculation are present for both processes as well as for antimicrobial purposes. The following sections will not only discuss studies in which chitosan is used for chemical coagulation and flocculation or antibacterial purposes, but also the mechanisms through which it achieves the goal.

Coagulation and Flocculation in Water Treatment

Among many other preferential processes, chemical coagulation is widely used due to its efficient removal of toxins. This coagulation is due to a chemical's cationic charge which attracts and conglomerates negatively charged toxins. Traditionally, aluminum sulfate, "alum", is used for this process; however, mass mildly toxic chemical addition and sludge generation is a downfall of this option. Considering this, chitosan is a viable option due to biocompatibility which allows degradation of sludge by microorganisms

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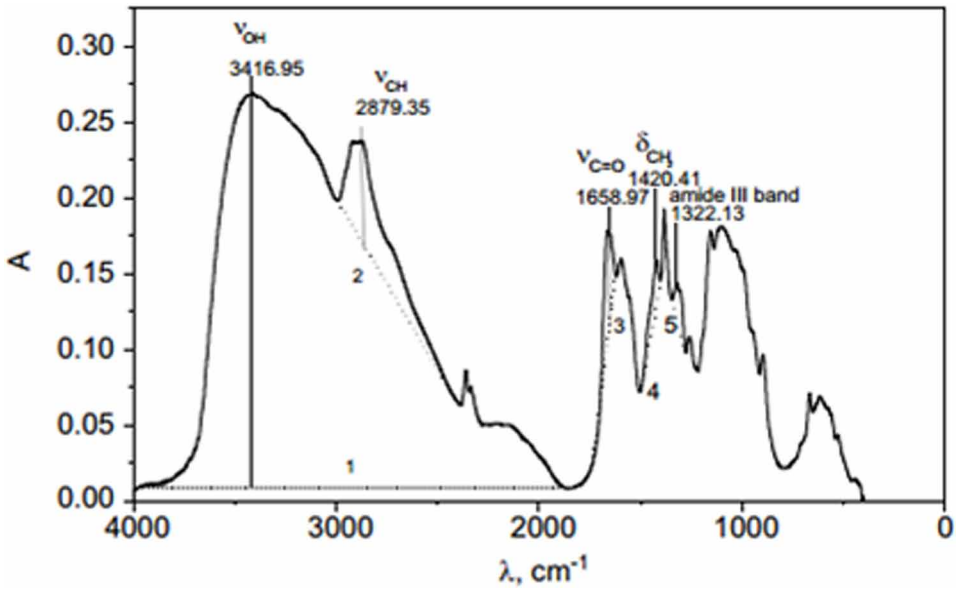
resulting in less landfill usage. As a result, the use of chitosan for many bioeffluents has been explored including food waste, oil-in-water emulsions, effluents containing dyes, lead and chromium wastewater, partially purified sewage, and algal waters. It has been observed that increased MW results in greater coagulation; however, the relationship is nonlinear. Moreover, a greater DD at equivalent MW further optimizes coagulation. This somewhat necessitates a balancing act between MW and DD seeing as an increased DD decreases MW. A greater MW creates greater removal of NTUs and suspended solids (SS) with a reduction in biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Contrastingly, a greater DD which decreases MW results in increased removal of inorganic nutrients and organic compounds. All in all, the DD and MW of chitosan should be tailored to specific applications and purpose. The mechanism of chitosan coagulation-flocculation is shown in Figure 4.

Due to lack of degradation of alum sludge as well as the slight toxicity of alum itself, more biocompatible options such as chitosan must be explored. Recent research has compared traditional alum with high velocity mixing versus proposed chitosan with ultrasound-enhanced flocculation (Fast et al. 2014). Chitosan for coagulation and flocculation creates flocs less vulnerable to shearing although less likely to flocculate again after shearing has occurred while traditional alum is highly vulnerable to shear but can easily agglomerate once more (Fast et. al, 2014). Moreover, the pHs of turbid waters are not a deterrent to alum's treatment efficiency; whereas chitosan only remains soluble in acidic pH solutions. Another significant advantage to the use of chitosan is the much lower dosage necessary to remove turbidity; this, in turn, reduces exposure to consumers compared to alum usage. Ultimately, a 1.5 mL dosage of chitosan using ultrasound was the most effective at removing turbidity (Fast et al. 2014). Further research conducted by Fast & Gude utilized a much wider range of NTU and dosage. Results expressed increased efficiency of chitosan with increased turbidity (2015). Furthermore, the longer the

Figure 3. Chitosan Fourier transform infrared spectroscopy (Czechowska-Biskup, R., Jarosińska, D., Rokita, B., Ulański, P., & Rosiak, J. M., 2012)



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sedimentation time, the lower the final turbidity. In conclusion, optimal conditions were indicated at 40 NTUs and 30 minutes flocculation time which produced an optimal 94% removal efficiency which rivals conventional alum at 99%.

Although fresh surface water resources emphasize the removal of algal blooms, salt water constitutes 96.5% of Earth's water with approximately 1% of the global population reliant upon desalination resources (Desalination, n.d.). Future global outlook by the United Nations foresees a massive increase to 14% by 2025 as stated by Christopher Glausson, publisher of Global Water Intelligence. One of many issues desalination industries face is the quality of received saltwater due to high turbidity. Research on chitosan in alkaline medium was conducted in order to determine efficiency as compared to alum at a dosage range from 0-370 mg/L and pH 2-11(Altaher, 2012). Results showed a 97.5% removal of NTUs using significantly less dosage and in turn less toxicity and exposure than alum. The optimum removal efficiency was found at pH 8.1 and 18 mg/L.

Beyond types of water and wastewater which chitosan effectively coagulates, multiple apparatus for which have been studied due to an increase in household water treatment and on-site water treatment interests. In an attempt to address ceramic water filtrations (CWF) lack of virus removal mechanisms, chitosan was tested for *Escherichia coli* K011 and coliphage MS2 contamination with CWF apparatus (Abebe, Chen, & Sobsey, 2016). CWF traditionally uses silver nanoparticles which produce uncertain results. Chitosan hydrochloride, chitosan acetate, and chitosan lactate were tested with 30 minute coagulation, flocculation, and sedimentation. The resulting waters were filtered by gravity flow and sampled. The mean reductions were 4.7 and 7.5 $\log_{10}$ for *Escherichia coli* and 2.8 to 4.5 $\log_{10}$ for MS2. Resulting turbidity present meets both US EPA standards (<1 NTU) and World Health Organization (WHO) guidance. Furthermore, the treated water met viral and bacterial reduction health targets.

Although chitosan is an effective biocoagulant for many water sources, including pre-treated sea water, various types of monomers can be co-grafted onto chitosan to provide further specific functionalization and utilization. Non-ionic co-polymerizations include acrylamide, N-vinyl formamide, and N,N-dimethyl acrylamide. Cationic monomers include (2-Methacryloyloxyethyl) trimethyl ammonium chloride, 3-(Acrylamide) propyl trimethylammonium bromide, N-binyl-2-pyrrolidone, and diallyl dimethyl ammonium chloride. Lastly, anionic grafts include with methacrylic acid and 2-Acrylamidoglycolic acid. However, the most established and commonly grafted nonionic polymer is acrylamide. Overall, the most common chitosan graft would be positively charged copolymerization due to increased efficacy of charge neutralization during coagulation and flocculation (Yang et. al., 2016).

Antimicrobial Properties

One cornerstone property of chitosan is antimicrobial and antifungal abilities. These abilities within a nanoparticle vastly increase possible functionality. It is considered effective in drug delivery schema such as vaccines, insulin adsorption, and even wound treatment as shown in Figure 5 (Qi et al. 2004).

In another study, chitosan nanoparticles are applied to *E. coli*, *S. choleraesuis*, *S. typhimurium*, and *S. aureus* bacteria to determine antibacterial activity. Considering copper nanoparticles also exhibit antibacterial and antimicrobial abilities, copper-loaded chitosan nanoparticles were prepared through ionic gelation. These samples were then left at 121°C with the bacteria at varying concentrations. Minimum Inhibitory Concentration (MIC), or the lowest concentration which causes absorption of the

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bacteria, was tested as well was Minimum Bactericidal Concentration (MBC). MBC is defined as the lowest concentration of the antibacterial solution which eradicates 99.9% bacteria. The results of this study are shown below.

Although chitosan effectively eradicates 1-$\log_{10}$ bacteria of each strain tested, it is less effective than the copper-loaded chitosan alternative. Due to chitosan's sensitivity to pH, the test was only used in a highly acidic solution of pH 6.5.

Two mechanisms that facilitate antimicrobial properties are exhibited by the biopolymer. The initial mechanism is believed to create an impermeable layer surrounding the cell which prevents necessary transport from the cell. This effect on microbial cells is only present in slightly acidic solutions and has the potential to be reversed in different solvents. Secondly, the chitosan prevents the synthesis of RNA and protein by invading the cell's nucleus. For the latter effect, DD must be increased to increase electrostatic interaction with the negatively charged microbe. For the former, MW must increase in order to permeate the cell membrane.

Table 2. Doxycycline, Chitosan Nanoparticles, and Copper-loaded Chitosan Nanoparticle Bactericidal Comparison (Qi, L., Xu, Z., Jiang, X., Hu, C., & Zou, X, 2004)

Bacteria	Doxycycline		Chitosan Nanoparticle Suspension		Copper-loaded Chitosan Nanoparticle Suspension	
	MIC	MBC	MIC	MBC	MIC	MBC
E. coli K88	1	8	1/8	4	1/16	2
E. coli ATCC 25922	2	16	1/16	2	1/16	2
S. chloeraesuis ATCC 50020	4	32	1/8	4	1/16	2
S. typhimurium ATCC 50013	4	64	1/4	8	1/8	4
S. Aureus ATCC 25923	1/4	8	1/4	8	1/8	4

Figure 4. Coagulation and flocculation of algal turbid water with Chitosan as coagulant

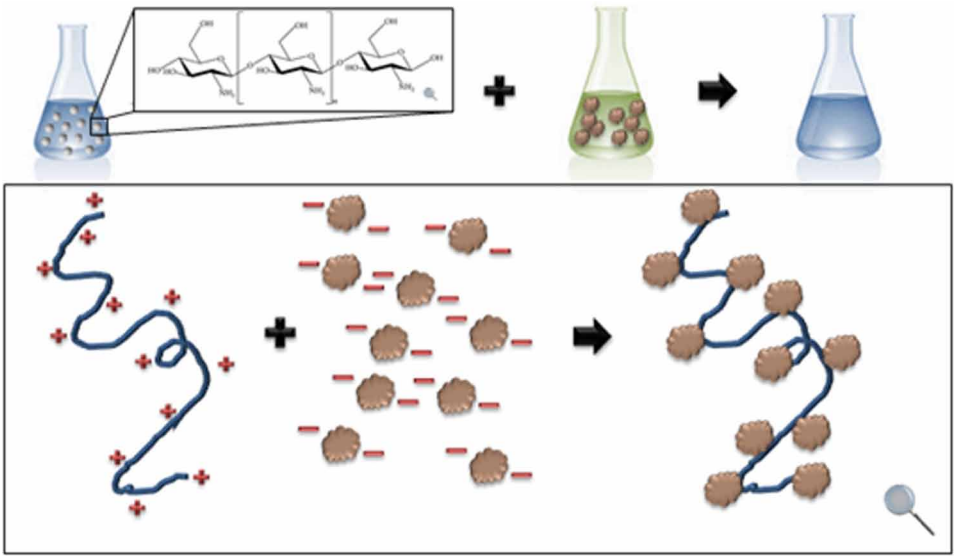

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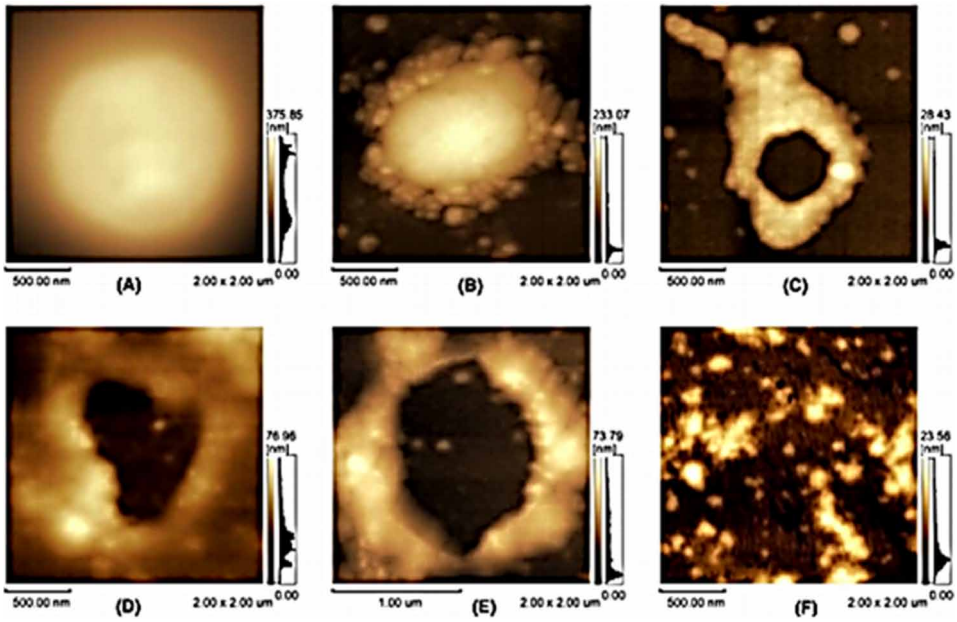
Figure 5.



WASTEWATER TREATMENT

In contrast to water treatment, wastewater treatment generally converts unusable water into an environmentally safe effluent by reducing the BOD (biochemical oxygen demand), COD (chemical oxygen demand), and SS (suspended solids). By reducing the SS, the BOD and COD can be lowered as well. These are extremely important parameters to wastewater considering potential ecological catastrophes caused by high BOD levels. Due to this concept, coagulation and flocculation are two of the most important processes for water treatment as well as wastewater treatment.

Coagulation and Flocculation in Wastewater Treatment

As previously mentioned, the importance of the coagulation and flocculation step in water and wastewater treatment cannot be overemphasized. What makes chitosan a great potential industrial and municipal coagulation and flocculation agent is not merely its effectiveness, but also its nontoxic nature and the plethora of effluents which are successfully treated with a much lower concentration than is necessary with alum. This process is primarily due to multiple flocculation mechanisms including simple charge neutralization, charge patching, bridging, and sweeping. Simple charge neutralization is inherently the neutralization of positive and negative charges present within the cationic biopolymer and anionic toxin or effluent. Charge patching creates flocs of biopolymer and effluent with the overall particle's charge. Bridging allows larger flocs created by adsorption onto the biopolymer and other primary flocs. Lastly, sweeping allows the entrapment of particles within a net-like structure of biopolymer. These flocculation mechanisms have been tested in food waste, seafood and fish processing wastes, brewery wastewater, surimi wash water, bentonite suspension, organic suspensions, kaolinite, bacterial suspensions, particulate and dissolved contaminants, effluents containing humic substances, effluents containing dyes, pulp

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and paper mill wastewater, oily wastewater, oil-in-water emulsions, agriculture wastewater, effluents containing metal ions, effluents containing phenol derivatives, partially purified sewage, brackish water, lead and chromium wastewater, poultry waste, coal mine wastewater, algal waters, egg industry effluent, grey wastewater, sugar industry effluent, and even pre-treated sweater as shown in Table 3.

One of many effluents successfully treated with chitosan is grey wastewater. Grey wastewater is present within approximately 75% of resident wastewaters and is considered a cleaner effluent of bath tubs, sinks, laundry appliances, and schools. Despite the nonreactive nature of this effluent, it still poses tenable threats to ecosystems and must be treated effectively. Batch testing was used with varying agitation speed, pH, chitosan dose, and settling time were used. As predicted, pH efficiencies increased with increasing pH to 4. The maximum efficiency settling time was determined at 15 minutes due to shear stress and compaction of flocs. Upon optimization, NTU, BOD, and COD were determined to be 96%, 91%, and 73% reduced (Thirugnanasambandham et. al, 2013).

With superior removal and reduction efficiencies of many types of effluent, the natural question is to consider what chitosan cannot effectively treat. In "Influence of Effluent Type on the Performance of Chitosan as a Coagulant", authors Ritha Pambi and Paul Musonge considered that within the scope of food processing plants. Chitosan with a 75% DD was purchased through Sigma-Aldrich and dissolved in 20 mL of 0.1 M hydrochloric acid. Sugar Processing effluent, Milk Processing Effluent, and Brewery processing effluent were all tested with jar-test apparatus and rapid mixing for 3 minutes at 100 rpm. The COD removal for sugar, milk, and brewery effluents were 11%, 54%, and 50% respectively. The Total Suspended Solids (TSS) were much more significant at 98%, 95%, and 95%. Significant factors which influenced the removal efficiencies include dissolved solids (TDS), initial TSS, and a pH value maximum of 9. The dissolved solids (TDS) were notably higher in the milk effluent. Moreover, the optimal pH value varied with effluent type. It can be concluded from this study that chitosan's coagulation and flocculation efficiency is dependent upon the effluent type and TDS.

Biosorption Properties

Beyond antimicrobial and coagulation-flocculation applications, chitosan and magnetic nanoparticles grafted with chitosan have proven effective at adsorption of Cobalt II, Copper II, Zinc II, and cation or anionic dyes. This adsorption ability is due to amino groups as well as hydroxyl groups. These amino groups are positively charged and attract dyes electrostatically. A wide range of adsorption studies was summarized in Table 4 which includes various types of chitosan and adsorbates.

Dye Adsorption

Due to the inert properties and low concentrations of dyes, they are difficult to be removed effectively and economically. Many other methods are currently being employed; however, they remain ineffective and expensive alternatives. These methods include adsorption, coagulation and flocculation, reverse osmosis, and others. Common chitosan composites that are used to remove dyes are chitosan/montmorillonite composites, chitosan/polyurethane composites, chitosan/activated clay composites, chitosan/bentonite composites, chitosan/oil palm ash composites, and chitosan/kaolin/γ-Fe_2O_3 composites. Each composite type, naturally, has different adsorption properties. For example, a chitosan/montmorillonite composite has an increasing adsorption capacity with respect to the molar ratio of chitosan and the composite, but

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Table 3. Bioeffluents successfully treated with chitosan

Effluent	Purpose	Experimental Details	Results	Reference
Food waste	Coagulation of high fat and protein milk waste	Chitosan-treated sludge is considered for feed supplement of cleaning in place wastewater.	25 mg/L at pH 7.0 yielded optimum efficiency showing that the material could be recycled at no extra cost.	(Chi & Cheng, 2006)
Seafood and fish processing wastes	Crawfish shell chitin tested for pigment extraction of seafood processing streams	150 mg/L Chitosan at pH 6.0 (commercial and synthetic)	97% SS removal and 83% tubidity removal. 150 mg/L at pH 6 resulted in 45% reduction in COD.	(Hong & Meyers, 1989)
Brewery wastewater	Coagulation of wheat dregs in wastewater	120 mg/L in 4.5 pH for optimal removal efficiency; increasing pH decreased turbidity	Maximum removal efficiency was observed at ~85% with a pH of 4.5, pH 7 at ~65%, and pH 8 at ~65%.	(Cheng, Chi, Yu, & Lee, 2005)
Surimi washes water	Protein adsorption and turbidity reduction of surimi wash water	20, 40, and 100 mg/L chitosan-alginate complexes were tested; 100 mg/L for maximum protein removal; 20 mg/L for maximum turbidity removal	Maximum 86% removal of protein, Minimum 73.1%; Maximum 95.7% turbidity removal, minimum 85.5%	(Wibowo, Velazquez, Savant, & Torres, 2007)
Bentonite suspensions	Chitosan coagulation with bentonite suspensions using varying degree of deacetylation (DD), MW, viscosity, and polydispersity	Tap water (TW)–deionized water comparison at varying pH and concentration; maximum efficiency at 0.10 mg/L in TW pH 7.0	The efficiency of coagulation was observed with both TW and DW at pH 5 or 7. With concentration 0.02 mg/L and lower, less than 10 NTU was observed.	Roussy, Cooren, Dempsey, & Guibal, 2005)
Organic suspensions	Varying DD and MW tested using coagulation/ flocculation	Mushroom powder TW mixes were tested for pH 5, 7, and 9	DD was shown to have little effective on coagulation.	(Roussy, Vooren, & Guibal, 2005)
Kaolinite	Chitosan flocculation of kaolinite particles	Distilled water with TW was tested with highly refined kaolinite powder	A maximum turbidity removal was observed as ~85% with a 0.75 mg/L dosage.	(Divakaran & Pillai, 2004)
Bacterial suspensions	To determine antibacterial properties in sterile water	Maleic acid sodium grafted onto hydroxypropyl chitosan was tested using cut plug method and viable cell counting	All concentrations tested yielded maximum 99.90% at removal of *S. aureus* and *E. coli*	(Xie, Xu, Wang, & Liu, 2002)
Particulate and Dissolved Contaminants	Determine removal efficiency of bentonite suspensions, organic suspension, anionic dye solutions, and humic acid solutions	Both sorption and coagulation/ flocculation were effective at removal of dyes; charge destabilization effectively coagulated humic acid and kaolin	Multiple coagulation mechanisms were determined for (a) bentonite, (b) organic suspensions, (c) anionic dye solutions, and (d) humic acid solutions which were charge destabilization for a, b, and d. However, sorption was observed for c.	(Guibal, Vooren, Dempsey, & Roussy, 2006)
Effluents containing humic substances	Chitosan hydrochloride (CH) and glutamate (CG) were tested for flocculation in dissolved humic solutions	CH and CG solutions were prepared using air-dry chitosan flakes and tested for color removal	CH yielded maximum effectiveness of >95%	(Bratskaya, Schwarz, & Chervonetsky, 2004)
Effluents containing dyes	Dye removal at differential pH and concentrations	Chitosan samples were ground and dissolved in acetic acid; agitated aqueous solutions of 2% acetic acid, 98% deionized water were incubated overnight. Experiments were done using Jar-Test apparatus at room temperature.	100% efficiency was observed for multiple dye concentrations and chitosan concentrations at pH 3	(Guibal & Roussy, 2007)
Pulp and paper mill wastewater	Coagulation/flocculation of post-bleaching effluent of the paper industry	Coagulation then photo catalysis determined properties such as biodegradability and through absorbance	100% reduction in absorbance for chromophores at 500 nm	(Rodrigues et. al., 2008)

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Table 3. Continued

Effluent	Purpose	Experimental Details	Results	Reference
Oily wastewater	Adsorption of oily wastewater was tested with differential concentrations, sedimentation times, and pH values	Palm oil mill effluent was tested using Jar-Test equipment at ~2000 mg/L of residue	~97-99% removal of residue was obtained at 0.5 g/L of chitosan powder, 15 minute contact time, 5.0 pH, and 30 minute sedimentation time	(Ahmad, Sumathi, & Hameed, 2004)
Oil-in-water emulsions	Flocculation of oil-in-water emulsions was tested with differential pH as well as SDS-stabilized emulsion and surfactant-free emulsion	0.05% diesel oil emulsions with an average droplet diameter of 200 nm were mixed with chitosan using ultrasonic treatment	Removal efficiencies decreased with increasing pH possibly due to chitosan's low solubility; complete phase separation was achieved at pH values greater than 7.5 through SDS-stabilized schema	(Bratskaya, Avramenka, Schwarz, & Phillippova, 2006)
Aquaculture wastewater	Aquaculture wastewaters were tested for turbidity, SS, chemical oxygen demand, ammonia, and phosphates after being treated with varying deacetylation degree, pH, and concentrations of chitosan	Chitosan leaves beneficial bacteria while removing *Edwardsiella itctaluri*	Optimal removal efficacies were 90% turbidity, 61% SS, 69.7% COD, 89.2% NH_3, and 95.6% PO_4^{3-}.	(Chung, 2006)
Effluent containing metal ions	Adsorption of heavy metals Hg(II), Fe(II), Ni(II), Pb(II), Cu(II), and Zn(II) were tested at pH 5, 6, and 7	0.1 g of chitosan mixes were added to 50 mL of wastewater; these samples were left in room temperature for 3 hours followed by a 5 min centrifuging process	Chelation capacities for each heavy metal were 94.1% Fe(II) at pH 5, 22.9% Mn(II) at pH 7, 26.3% Co(II) at pH 7, 62.8% Ni(II) at pH 7, 64.9% Cu(II) at pH 7, 50.3% Zn(II) at pH 7, 15.6% As(II) at pH 5, 19.9% Mo(II) at pH 7, 39.1% Cd(II) at pH 7, 97.5% Hg(II) at pH 7, and 91.0% at pH 7 for Pb(II). Most of these maximums were with a 91.3% DD.	(Gamage & Shahidi, 2007)
Effluent containing phenol derivatives	Chitosan was tested alongside tyrosinase and two synthetic polymers polycondensate and polyethlenemine	Industrial wastewater removal involving a color change from clear to dark brown was tested using tyrosinase and different polymers.	Synthethic polymers were observed to be more effective due to lack of coagulation but precipitation of phenol and aromatic amines. However, all cationic polymer coagulants produced a precipitation. Retention of immobilization and storage stability were 80%.	(Wada, Ichikawa, & Tatsumi, 1995)
Partially purified sewage	Chitosan flocculation composites were compared with traditional flocculation solutions	Raw sewage waters were added to differential dosages and stirred for 10 minutes then transferred to separating funnels and settled for 30 minutes	Chitosan composites were shown to optimize COD by 1.8-23.7%, SS by 50%, and Al^{3+} by 61.2-85.5%.	(Zeng, Wu, & Kennedy, 2007)
Brackish water	Differential pH of 4-9 with a varying SS was tested on flocculation and settling time of river silt.	Turbidity was tested using Jar-Test apparatus with a 0.1 M HCl or $NaCO_3$. Solutions were stirred for 30 minutes and allowed a 30-minute settling time.	Maximum flocculation occurred at a pH of 7.0 while SS vs. NTU relationship was linear. 90% removal efficiency was observed.	(Divakaran & Pillai, 2002)
Lead and chromium wastewater	Comparing chitosan to aluminum sulfate for removal of metal salts and *Daphnia magna* with differential pH in actual conditions and humic acid spiked surface water.	Jar Test apparatus with 1 L high alkalinity water tested from 0.5-10 mg/L chitosan solutions. 1 g/L chlorine solution was added with a 24-hour contact time.	Increased toxicity of *Dapnia magna* was effectively 0% immobilization in some conditions.	(Rizzo, Gennaro, Gallo, & Belgiomo, 2008)

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Table 3. Continued

Effluent	Purpose	Experimental Details	Results	Reference
Poultry waste	Chitosan combined with dissolved air flotation were tested at multiple poultry effluent sites for SS and COD.	Poultry processing wastes were coagulated with chitosan and dissolved air flotation at sites such as the chiller and scalder	Composite SS effluents were reduced by 74-94% at different sites; COD of effluents were reduced by up to 82%.	(Bough, Shewfelt, & Salter, 1975)
Coal mine wastewater	Chitosan grafted N-vinyl formamide were tested with varying concentration of N-vinyl formamide, bromate ions, and chitosan.	Experimental setup involved a 1 L beaker of 1% weight coal with stirring apparatus for 15 minutes and 30 minute settling time.	Chitosan had little effect on NTU reduction; however, approximately 10% was the maximum for both coking and non-coking coal.	(Mishra, Tripathy, Srivatstava, Mishra, & Behari, 2008)
Algal waters	Chitosan with ultrasound flocculation was compared with aluminum sulfate rapid mix flocculation of algal turbid waters.	Batch testing with 25 kHz ultrasonic frequencies followed by 50 rpm rapid mix for 20 min at a range of 10 to 40 NTUs.	Turbidity removal efficiencies of chitosan ranged from 84.1%-90.5% for rapid mix and 84%-97% for ultrasound.	(Fast & Gude, 2015)
Egg industry effluent	Differential COD concentration, adsorbent dose, pH, and settling time were tested.	Batch studies performed from 0.7-1.3g/L of wastewater in 100 mL of wastewater with 2-7 pH range. The supernatant was then centrifuged and filtered. A three-level, four-factor Box-Behnken design (BBD) studied each variable.	Optimal pH 4 1.1g/L chitosan with a 40 min settling time was determined. Maximum reductions were 94%, 88%, and 83% for turbidity, COD, and BOD respectively.	(Thirugnansambandham, Sivakumar, & Prakash, 2014)
Grey wastewater	Differential COD concentration, adsorbent dose, pH, and settling time were tested.	Batch studies were carried out using 1-3 min agitation time, 2.5-5.5 pH, 0.3-0.5 g/L chitosan, and 10-20 min settling time. The supernatant was centrifuged and filtered following settling time.	Optimal reduction efficiencies for turbidity, BOD, and COD were 96%, 91%, and 73% respectively.	(Thirugnanasambandham, Sivakumar, Prakash, & Kandasamy, 2014)
Sugar Industry Effluent	Resin effluent and final effluents were tested of a sugar refinery using chitosan for coagulation.	Both effluents were tested at varying pH using chitosan powder with aqueous hydrochloric acid. Sodium hydroxide was used to adjust pH.	Final effluent turbidity reduction was more successful than resin effluent yielding 97% suspended solids, 61% color, and 35% COD removal efficiencies versus 68% suspended solids, 30% color, and 15% COD.	(Pambi & Musonge, 2015)
Pre-treated Seawater	The pre-treated sweater was tested using chitosan coagulation at the differential dosage, initial pH, solvents, and compared to metal coagulants.	Jar test apparatus was performed on Red Sew waters as well as distilled water. Turbidities were 50 NTU in order to duplicate natural rainwater induced turbidity. The samples were flash-mixed for 5 min and flocculated at 50 rpm for 30 min with a 30 min settling time. Lastly, a multiple layer filtration column was used consisting of dry sand, glass wool, and gravel.	Removal efficiencies ranged from 95.8% to 97.6% within a 6 mg/L to 60 mg/L dosage. Tests also showed that chitosan performs better in a hydrochloric acid solvent.	(Altaher, 2012)

this property plateaus at a 1:1 ratio. It is also noted that chitosan/montmorillonite composites closely follow a Langmuir isotherm (Wang & Wang, 2007). In contrast, a chitosan/polyurethane composite acts as a matrix due to the high surface area which immobilizes dyes similarly to granular activated carbon. Moreover, chitosan/activated clay was shown to have the highest adsorption capacity when used with the reactive dye RR222. Chitosan/activated clay yielded an absorbance of 1912 mg/g compared to an average of 342 mg/g average adsorption for the other composites.

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Table 4. Adsorbent properties of chitosan and chitosan composites (Kamble et. al, 2007) (Bhatnagar & Sillanpää, 2009)

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
Dye Adsorbent			
Chitosan/montmorillonite	Congo Red	53.42	(Guzman, Saucedo, Navarro, Revilla, & Guibal, 2002)
Chitosan/polyurethane	Acid Violet 48	30	(Guibal, Milot & Roussy, 1999)
Chitosan/activated clay	Methylene blue	330	(Guibal, Milot & Tobin, 1998)
Chitosan-activated Clay	Reactive dye RRR22	1912	(Moret & Rubio, 2003)
Chitosan/bentonite	Tartrazine	294.1	(Dambies, Roze, & Guibal, 2000)
Chitosan/bentonite	Malachite Green	435	(Chen & Chung, 2006)
Chitosan/palm oil	Reactive blue 19	909.1	
Chitosan flakes	Reactive red 222	293	(Gupta, Chauhan & Sankaramakrishnan, 2009)
Chitosan beads	Reactive red 222	1103	(Adyun & Aksoy, 2009)
Chitosan-ECH	Reactive red 289	1802-1840 (g/kg)	(Schmul, Krieg & Keizer, 2001)
Chitin	Reactive yellow 2	28	(Hasan et. al, 2003)
Chitin	Reactive black 5	65	(Boddu, Abburi, Talbott, & Smith, 2003)
Chitin	synthetic reactive dye wastewater	133-167	(Spinelli, Laranjeira & Favere, 2004)
Chitin modified by sodium hypochlorite	synthetic reactive dye wastewater	59-124	(Rojas, Silva, Flores, Rodriguez, Ly, & Maldonado, 2005)
Quarternary chitosan salt	Reactive orange 16	1060	(Geng, Jin, & Qi, 2009)
Chitosan	Remazol black 13	91.47-130	(Yan, Haijia & Tianwei, 2007)
Powdered cross-linked chitosan grafted with acrylic acid	Remacryl Red TGL	204.2-510.7	(Kim, Benedetti & Boulegue, 2004)
Chitosan beads	Malachite green	74.83-93.55	(Niu & Volesky, 2003)
Chitosan-g-poly(acrylic acid)montmorillonite	Methylene blue	1859	(Ngah & Liang, 1999)
Chitosan-based adsorbent	Basic blue 3	166.5	(Arrascue, Garcia, Horna, & Guibal, 2003)
Disulfonate derivates of chitosan	Basic blue 9	121.9	(Lasko & Hurst, 1999)
Chitosan	Acid green 25	645.1	(Zou, Liu & Liu, 2009)
Chitosan	Acid orange 10	922.9	(Metwally, Elkholy, Salem, & Elsabee, 2009)
Chitosan	Acid orange 12	973.3	(Wang, Liu, Wang, Xie, & Deng, 2009)
Chitosan	Acid red 18	693.2	(Juang, Tseng, Wu & Lin, 1996)
Chitosan	Congo red	93	(Juang, Tseng, Wu & Lee, 1997)
Poly(methylmetacrylate) grafted chitosan	Procion Yellow mx	250	(Annadurai & Krishnan, 1997)
Poly(methylmetacrylate) grafted chitosan	Remazol Brilliant Violet	357	(Annadurai, Chellapandian & Krishnan, 1997)
Poly(methylmetacrylate) grafted chitosan	Reactive Blue H5G	178	(Wu, Tseng & Juang, 2000)
Cross-linked chitosan beads	Metanil yellow	1334	(Wu, Tseng & Juang, 2001)
Cross-linked chitosan beads	Reactive blue 15	722	(Chiou & Li, 2002)
Chitosan grafted with amide groups	Remazol Yellow Gelb 3RS	1211	(Choi & Li, 2003)

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Table 4. Continued

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
Chitosan grafted with carboxyl groups	Basic yellow 37	595	(Chiou, Ho & Li, 2004)
Metal Ion Adsorption			
Chitin	Cd(II)	14	(Akkaya, Uzun, & Guzel, 2007)
Chitosan	Cd(II)	5.93	(Dolphen, Sakkayawong, Thiravetyan & Nakbanpote, 2007)
Chitosan	Hg(II)	815	(Rosa, Larajeira, Riela & Favere, 2008)
Chitosan	Cu(II)	222	(Annadurai, Ling, & Lee, 2008)
Chitosan	Ni(II)	164	
Chitosan	Zn(II)	75	(Chao, Shyu, Lin & Mi, 2004)
Chitosan	Cu, Zn, As, Cr	137, 108, 58, 124	(Lazaridis, Kyzas, Vassilou, & Vikiaris, 2007)
Porous-magnetic chitosan beads	Cd(II)	188-518	(Bekcia, Ozveria, Sekia, & Yurdakoc, 2008)
Chitosan-coated on perlite	Cu(II)	196.07	(Wang, Zhang, & Wang, 2008)
Chitosan coated on perlite	Ni(II)	114.94	(Crini et. al, 2008)
Chitosan from silkworm chyrsalides	Pb(II)	72	(Crini, Martel & Torri, 2008)
Chitosan from silkworm chyrsalides	Cu(II)	87	(Monvisade & Siriphannon, 2009)
Carboxylgrafted chitosan	Cu(II)	318	(Wong, Szeto, Cheung & McKay, 2004)
Amido-grafted chitosan	Cr(VI)	935	(Chatterjee, Chatterjee, Chatterjee & Guha, 2007)
Chitosan coated on polyvinyl chloride beads	Ni(II)	120.5	(Chatterjee, Lee, Lee, & Woo, 2009)
Chitosan coated on polyvinyl chloride beads	Cu(II)	87.9	
Chitosan	Al(III)	45.45	(Azlan & Saime, 2009)
Molybdate-impregnated chitosan gel beads	As(V)	ca. 160 mg/g	
Chitosan beads	As(III)	1.83 mg/g	(Singh, Sharma, Tripathi, & Sanghi, 2009)
Chitosan beads	As(V)	1.94 mg/g	(Wu, Tseng, & Juang, 2001)
Chitosan flakes	Cr(VI)	22.09-102	(Vachoud, Zydowicz& Domard, 2001)
Non-cross-linked chitosan	Cr(VI)	78	(Juang, Wu, & Tseng, 2002)
Cross-linked chitosan	Cr(VI)	50	
Chitosan coated on nonporous ceramic alumina	Cr(VI)	154 mg/g	
Quatenary ammonium salts of chitosan	Cr(VI)	30.2-68.3	(Figueriedo, Loureiro, & Boaventura, 2005)
Cross-linked chitosan	Cr(II)	6	(Chiou & Chang, 2006)
Cross-linked chitosan	Cr(VI)	215	(Kyzas & Lazaridis, 2009)
Aminated chitosan	Ni(II)	30.2	(Zheng, Yang, Jo, & Park, 2004)
Chitosan	Ag	42	(Durshun & Kalayci, 2005)
Chitosan benzoyl thiourea derivative	Co(II)	29.47	(Pang, Ng, Chung, & Wong, 2007)
Chitosan benzoyl thiourea derivative	Eu(III)	34.54	(Nadavala, Swayampukala, Boddu & Abburi, 2009)
Cross-linked chitosan	U(VI)		(Li, Meng, Hu & Du, 2009)

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Table 4. Continued

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
Phenol Adsorption			
Chitin	Phenol	21.5	(Zhang, Xua, Chena, & Zong, 2009)
Magnetite-immobilized chitin	Pentachlorophenol	5.4	(Kumar, Subbaiah, & Reddy, 2009)
Beads of chitosan-sodium alginate	Phenol	108.6	(Chatterjee & Woo, 2009)
Chitosan	Phenol, p-nitrophenol and p-chlorophenol	1.9-2.5	(Chatterjee, Lee, Lee, & Woo, 2009)
Functional chitosan, chemically modified by β-cyclodextrin	Phenol, p-nitrophenol and p-chlorophenol	20.5-179.7	(Sundaram, Viswanthan, & Meenakshi, 2009)
Chitosan-abrus precatorius	Phenol	156	(Sundaram, Viswanthan, Meenakshi, 2009)
Chitosan-abrus precatorius	2-chlorophenol	204	(Jagtap, Thakre, Wanjari, & Kamble, 2009)
Chitosan-abrus precatorius	4-chlorophenol	278	(Viswanathan, Sundaram, & Meenakshi, 2009)
Anion Removal			
Chitosan hydrobeads	Nitrate	92.1	(Viswanathan, Sundaram, & Meenakshi, 2009)
Chitosan beads modified by cross-linked with epichlorohydrin	Nitrate	104	(Sundaram, Viswanathan & Meenakshi, 2009)
Neodymium modified chitosan	Flouride	11.4-22.3	(Xie, Li, Wang, & Liu, 2009)
Magnesia/Chitosan composites	Flouride	11	(Yoshizuka, Lou & Inoue, 2000)
Titanium-incorporated chitosan	Flouride	7.2	(Sismanoglu, 2007)
Protonated chitosan beads	Flouride	4.7-7.3	(Ngah & Musa, 1998)
Nanohydroxypatite/chitin	Flouride	3840	(Zhang & Bai, 2003)
Protonated cross-linked chitosan	Perchlorate	45.45	(Sun, Wang, Liu, Gong, Bao, & Ma, 2008)

Note. Adapted from "Applications of chitin-and chitosan-derivatives for the detoxification of water and wastewater-a short review" by Bhatnaga, & Sillanpää, 2009 Advances in Colloid and Interface Science 152(1), p. 26-38.

Heavy Metal Adsorption

Toxicity of heavy metal ions released daily by industry has not yet accumulated to become a public health concern; however, a long-term risk is present both for the environment and society. Similarly to dye adsorption, chitosan produces the best adsorption as a composite. A few examples of heavy metal adsorption composites are chitosan/ceramic alumina, chitosan/perlite, chitosan/magnetite, chitosan/cotton, chitosan/sand, chitosan/cellulose, and chitosan/montmorillonite. Chitosan composites are much less sensitive to acidic environments than chitosan alone. Magnetite composites, in particular, attract heavy metals magnetically using nanoparticles such as iron oxide and maghemite. These magnetic nanoparticles are not only lower toxicity but can also be produced cheaply. Furthermore, they have been effectively used for removal of Pb(II) through ultrasound enhanced agitation.

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Desalination

Foam biosorbents consisting of hemicellulose grafted with diethylene triamine pentaacetic acid (DTPA) and cross-linked with chitosan successfully removed ~0.3 g of salt per gram of biosorbent (Ayoub et al, 2013). The absorption properties of this solution can be attributed to the swelling of the biosorbent and also the effect salinity has upon the polyelectrolyte complexes. As the concentration of NaOH in the solution increases, the gel swells in response. This same biosorbent material was also used for uptake of heavy metals; however, a much different absorption mechanism took place.

A more popular surface modification for desalting and salt rejection purposes employs chitosan for nanofiltration. Nanofiltration is used as a pretreatment for desalination through reverse osmosis in decreasing the pressure necessary. The primary mechanism for rejection of the salt solutions is due to ion valency. Due to the interaction between electrolytes and the nanofiltration surface, different feed solutions produced a range of removal efficiencies varying from 12.7% to 92.8% (Ming, Chen, & Gao, 2005). Many recent studies have been conducted to better understand and assess chitosan's nanofiltration properties through further surface engineering and membrane modification. In studies conducted by Wang et. al, an O-(Carboxymethyl)chitosan nanofiltration membrane was functionalized with graphene oxide to optimize desalination. After characterization and testing, the membranes exhibited better rejection capabilities than "pristine membranes and the commercial [nanofiltration] membranes". These were seen to definitively enhance desalination capabilities of the media (2015). Furthermore, Shenvi, Rashid, Ismail, Kassim, and Isloor synthesized a composite chitosan-poly(1,4-phnylene ether sulfone) (PPEES/CH) membrane which was then crosslinked by glutaraldehyde. Following characterization and water flux studies, the salt rejection was shown as a positive correlation with glutaraldehyde concentration of up to 34% and 53% for NaCL and $MgSO_4$ while simultaneously decreasing flux (2012). In another study, sulfated chitosan was cross-linked with polysulfone ultrafiltration membrane and epichlorohydrin which exhibited salt rejections of 90.8% for Na_2SO_4 and 32.5% for NaCL solutions. Another example of chitosan as an active layer for nanofiltration is exhibited by Zhou, Gao, Li, and Gao (2013) through a composite nanofiltration membrane from O-carboxymethyl chitosan an epoxy chloroprpone with a polyacrylonitrile supporting layer. Optimal concentrations were determined through studying salt rejection and permeation flux. The optimal membrane exhibited 94.36% Na_2SO_4 removal.

ENVIRONMENTAL IMPACT OF CHITOSAN IN WATER TREATMENT

Studies have been done on chitosan to determine potential toxicity after coagulation and flocculation of different surface waters. While some high turbidity levels with an excessive dosage of chitosan can create chitosan flocculation, the appropriate dosage naturally would not increase the NTUs. In addition, higher pH values generally cause a decrease in efficiencies which can sometimes be seen as drastic. Although chitosan's purpose is to decrease toxicity, some studies have shown increased toxicity compared to alum and ferric acid or NOM removal and *Dapnia magna* toxicity removal of humic acid spiked samples (Rizzo et. al., 2008). However, all coagulants decreased the toxicity in unspiked samples. Moreover, chlorination increased toxicity with chitosan being more toxic than traditional coagulants. Thus, surface water type is highly important to determine if chitosan could potentially increase toxicity.

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Of course, it must be considered that the lower toxic material in some cases is not always so in others. For example with chitosan use in the well treatment fluid, replacement of phenols and formaldehyde absolutely decrease toxicity to the consumer (Eoff & Reddy, 2004). Moreover, potential cationic polyelectrolytes could possibly contribute to toxicity leading to an increased use in bioflocculants.

COST OF WATER TREATMENT

Many studies show that chitosan can be a less toxic, more economical option compared to traditional coagulants. Chitosan was proven to be more economical than aluminum sulfate and polyaluminum chloride when used as a coagulant for palm oil mill effluent and residue oil (Ahmad, Sumathi, & Hameed, 2006). For the most effective, least toxic alternatives, composites may provide optimal results. Polyaluminum chloride and silicate chitosan composite effectively enhanced COD, SS, and Al^{3+} by 1.8-23.7%, 50%, and 61-85.5% respectively. It also reduced costs by 7-34% (Zeng, Wu, & Kennedy, 2007). Furthermore, chitosan proved an efficient and cost-effective adsorbent for dozens of dyes such as AB25, AB40, AB62, AB113, AB193, AR73, RR24, RY2, RB74, and RY18 in alkali solution (Shen et. al., 2011). It has long been seen as a cost-effective alternative to activated carbon (Gupta & Imran, 2004). Beyond cost-efficiency for water treatment properties, its coagulation capabilities can allow further profitability for companies through recycling materials such as milk and poultry industry effluents (Chi & Cheng, 2006).

SUMMARY

Chitosan and its derivatives provide numerous opportunities for potentially sustainable water and wastewater treatment. Presently, the EPA has approved chitosan for use of point-of-use coagulation of bacteria among other uses with an aim at developing countries as a sustainable and economical alternative. Future research could include cost-benefit analysis as well as the implementation of successful antimicrobial, coagulation and flocculation, and adsorption functionality. Considering the environmental and social need for more drinking water alternatives, cost efficiency for biosorbent capabilities of salts should also be further studied and combined with other leading desalination initiatives such as microbial desalination cells. Environmental and aquatic toxicity of chitosan should be evaluated in detail as well.

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Chapter 15
Life Cycle Costing on Waste Management

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ABSTRACT

Sustainability is the essential key point in every aspect of our life. It cannot be successful when it is limited to some certain issues in daily life. It is a revolutionary step for continuous development without any impact to the nature that should be adapted to the economy, manufacturing, urbanization, industrialization, etc. Increasing population and increasing wealth causes increase in the necessities of the human being. If it is considered as inevitable to give many bad impacts to the environment, this type of perspective is more dangerous and harmful to the environment and society than giving unconscious damages. This point of view might make these impacts to be accepted as legal, and this is what should be strongly discarded. There should be a new concept which enlarged our sphere of concern to include the entire physical environment including animals, plants, and landforms.

INTRODUCTION

There should be a new concept which enlarged our sphere of concern to include the entire physical environment including animals, plants, and landforms. Assuming responsibility for other individuals, society, whole environment (plants, animals, soil, water, atmosphere, etc.) should be the main idea in sustainable development and manufacturing. An ethic, of course, cannot prevent the alteration, management, and use of these 'resources,' but it does affirm their right to continued existence, and, at least in spots, their continued existence in a natural state.

This chapter will focus on the necessity of sustainability for the future of humanity by highlighting the environmentally friendly manufacturing technologies by explaining the methodology of life cycle assessment and costing to choose the correct production and marketing techniques.

Manufacturing and technology make life easier, more comfortable and more accessible. The production is inevitable for that reason; the production systems and processes should be more logical and gentler to the human and nature. Uncontrolled increase in human population with exponential growth is one

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of the essential problems. As the world is facing with limited resources in the limited regions and the necessities are also increasing not only because of the population increment but also because of growing demand for the welfare & wealth, the technological development should be long-running status not to exploit all the resources from today. Sustainability should be the environmental objective for everyone and especially for the major decision makers. Renewable and nonrenewable resources should be applied to the sustainable global economy with the balance of nature approach. Finite resources cannot support an exponential increase of people forever.

Related to the increasing population and industrial activities; the convergence of three entities of 'resources, needs and wastes' is the crisis. Crisis is inevitable with;

1. Absence of moral direction in treatment of natural resources,
2. Inability for social institutions to adjust to reduce environmental stress,
3. Abiding faith in technology.

It will be impossible to supply resources and a high-quality environment in the next century for the entire world's population. Besides that; overpopulation, urbanization, industrialization trigger the size of the crisis. Increased awareness, changes in political, social and technological systems can only be the solution for this problem. The main motto is hidden in the maximum benefits with the minimum of disturbance to the natural environment. Regardless of personal profits, it is important to achieve a sustainable global economy with an integrated approach by;

- Changing the bulky, useless technologies that disturb the nature and resources (A resource utilization plan for nonrenewable resources that does not damage the global environment, and provides for future generations),
- Adopting new environmentally friendly manufacturing technologies (A utilization plan or renewable resources such as water, forests, grasslands, fisheries that don't deplete the resource or destroy the ecosystem),
- Completely restructuring energy programs (An energy policy is needed that does not pollute, and cause climatic change),
- Developing an effective population control strategy (Populations of humans and other organisms must live in harmony with natural support systems such as air, water, and land),
- Instituting economic planning, financial aid and tax incentives (careful management and wise use of the planet and its resources),
- Instituting social, legal, political, and educational changes with a goal to maintain environmental quality (A legal, social, and political system dedicated to sustainability and a socially just global economy).

Earth is the only suitable habitat we have, and the resources are limited. Some resources are renewable, but many others are not renewable. For this reason, there is a huge necessity for large-scale recycling of many materials. The recycling can be achieved only by an integrated waste management. In fact, some economists have the idea of 'finding resources is less problematic than finding ways to use existing ones and technology and ingenuity will overcome lack of resources', however it is a great fact that resources

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are finite, so this type of reasoning is fallacious because the population increase with a finite resource base cannot be sustained, and it is not cheap and easy to rehabilitate the damaged environment. You need not only the money for rehabilitation but also extremely long time.

The key to sustainable development is effective environment management. Inputs and outputs should be balanced with no disturbance of the natural equilibrium of earth systems. Wastes are causing a tremendous impact on the environment as they pollute the nature but also the limited resources come to nothing easily if they are not used again. Integrated waste management including recycling or gaining the raw materials again is very relevant in that sense and will save the earth's resources.

Environmental resources should be sustained; waste management is one of the leading factors for sustainability that will supply the quality of human environment. The issues related with the sustainable development should be discussed in this chapter, because the present is the key to the future.

WASTE MANAGEMENT

Protecting public health and the environment becomes the crucial problem, due to the increasing population around the world. Increasing population and wealth also means, increasing garbage which is technically described as "solid waste" or only as "waste." Semisolid food wastes and municipal sludge may also be included in solid waste. Liquid wastes such as lavatory and bathroom wastes are termed as "grey-water" or "waste water," which should also be handled and removed from the public life through sewer system (Goren, 2015).

Waste management is directly related to the amount and the content of the waste. Each attempt for collecting, transporting and treating the waste has a direct and indirect influence on the environment and depending upon this; it has a significant effect on human health. Any waste itself and all the operations to get rid of the waste have environmental scope such as emission to land, emission to water and emission to air and also have effect on the economy. The use of energy, occupational health and safety issues, noise, vibration, heat, and odor are also the biggest problems that the community should have to face. In the past 20 years, the sheer numbers of humans and their increasing demand for material goods have done the following:

- Lead to severe degradation of the natural environment that supplies our renewable resources such as food, wood, and water,
- Lead to rapid exhaustion of non-renewable resources,
- Placed humans in competition with other species for necessary resources such as space, food, and water,
- Forced people to live in areas of significant natural hazards.

The '4 R' system, consisting of Reduction, Reuse, Recycling, and Recovery is the core step for an integrated waste management system that supports the sustainable development. Reduction of waste is imperative in case of toxic wastes.

All the waste treatment processes have not only effect on life quality but also have a significant impact on the economy by having an influence on the workload and work capacity for that community.

The effect of this cycle can be estimated by the help of "LIFE CYCLE ANALYSIS" also known as "LIFE CYCLE ASSESMENT" or shortly named as "LCA."

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LCA has a great relationship with the "Process Chain Analysis," by enabling to analyze the entire life cycle of the products or services concerning their environmental impacts and to display these analyses in a transparent way (Goren, 2015).

It is a necessity especially in this century, to choose the correct manufacturing and marketing techniques, in order not to cause environmental impact. This process depends on identifying and documenting all the costs related to the production which is known as "LIFE CYCLE COSTING (LCC)" (Australian National Audit Office, 2001). This is not related only to the manufacturing duration of a product but also directly linked to transporting, advertising, launching and even connected with the whole lifetime of that product. It is inevitable to mention; life cycle also involves the management and treatment costs of that product after finishing its life as a product. Future costs are nonignorable facts about a product or a process; usually, they are much more than the expenses of manufacturing and ownership period. For this reason, it is also paramount to estimate the future costs correctly.

1. Functioning
2. Expenditures
3. Maintenance
4. Repairment
5. Recycle or disposal

The cost of the waste management system has a direct and indirect effect on the inhabitants (Reich, 2005). The immediate effect is related to the budget used for collection, transportation, and disposal; however, the indirect effect is much more important as it has an effect through emissions. The emissions have short term and long term effect. Cost Benefit Analysis (CBA) can be employed for evaluating the economical methods for waste management. CBA's main idea is to cover all positive and negative impacts of a policy or project in monetary terms (Reich, 2005). Long term health effects should be the most important factor for CBA, which is usually neglected for short term budgets. Economic analyses are used for different scenarios for waste management. These scenarios can be presented including all the methods by changing the rate of that process, compared to the total system. However, this evaluation should start by integrating the analysis of economic and environmental aspects of waste management which have mostly opposite effect.

Municipal solid waste -more commonly known as trash or garbage- consists of everyday items such as food wastes, product packaging, garden wastes, durable & nondurable goods like furniture, clothing, containers and miscellaneous inorganic wastes. This is regularly generated from peoples' homes, but it also comes from commercial, institutional and some industrial sources (Goren, 2011). To understand what types of wastes are generated, "waste characterization process" is applied to the wastes. This will help to estimate what will come across during the waste management which is very important in the sense of treatment costs. The cost is directly correlated with the technology that is chosen. However, it is also related to dealing with normal situation or an unexpected situation. Each community may have different types of wastes according to their lifestyles, culture, tradition and social activities. Each region, even in the same city may have different characteristics. Not only the region but also the seasons can show diversity in the content of the waste. For that reason, the characterization processes should be done every season for each and every single community. This helps to control the waste, by understanding the content and the varieties.

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EVERYTHING AFFECTS EVERYTHING ELSE

In the sense of environment friendly technologies; all the attempts should be in favor to human health. Environmental health directly means of human health. Without human comfort and human health, anything has no meaning. There may be a common misconception that natural resources are plenty around the world. In fact, we have many but they are not limitless, and the "regenerate" power of nature is limited. Also, the "regenerate" speed is very slow. For that reason, there should be a "balance" between consuming (polluting) and preserving (protecting). Consuming less can be a solution to this large-scale problem; but because of the increasing population and growing needs, this cannot be effectively accomplished. This should be performed by the manufacturing processes which is well-planned by the life cycle analysis by taking into account of the lifetime, consumption rate and life cycle cost of the product. This type of manufacturing and consuming is a part of sustainable development. This means of using the resources for today, not for tomorrow. The development should not use "tomorrow's resources." Tomorrow's resources will be necessary for the future and should be utilized by the generations to come.

Waste is everywhere because the human being is everywhere. It is normal to have waste if there is a human activity anywhere. The type of the waste depends on the kind of the activity, such as domestic or industrial. Whatever the type; increasing amount of wastes requires, not only recycling and reuse but also the technologies with "zero-waste." These types of technologies are called as "green technologies" that produce less waste or zero-waste. This is a necessity not only for the environment but also for the economic issues. This type of green technologies may allow increasing the manufacturing benefits by gaining maximum benefit from the manufacturing and marketing process. Whenever the correct feasibility is performed, this new type of manufacturing technologies can generate good business opportunities. The dilemma of protecting the environment and gaining money will be fade out by the help of this type of planning by correct life cycle costing. This is a process of having interaction with technical, economical and social disciplines.

The environmental problems, which we are facing today, are diversified due to the context and the generation. Likewise, the diversity of the source, the factors affecting the environmental problems are also diverging. These are, mainly, intense industrialization, irregular urbanization and the lack of infrastructure. There are also some specific reasons based on the regions. Domestic wastes increase in the amount and complexity as a result of rising standards of living. Industrial wastes are the main sources of pollution and threat to public health. However, domestic wastes can also be as dangerous as the industrial wastes because of the many chemical materials used in daily life and also due to the formation of new by-products by decomposition of organic wastes. If the wastes are not treated properly, they cause soil pollution and water pollution for surface, sub-surface & underground water. Furthermore, the landfill gas occurred at the dump sites, cause air pollution, contribution to global warming and even in some cases they may cause explosions.

The removal and elimination of the wastes are not only related to public health but also related to the economy. The recyclables cause lost in the economy by not being used as a resource. The production from raw material also causes loss of energy. The main problem for not a good waste management is mainly from the economic concern and also from the lack of the needed technical background about pollution and basic waste management information.

To solve the environmental pollution caused by the wastes, only one approach is not enough. All the possible and feasible techniques and technologies should be used to form an integral, efficient management. This active management is called as integrated waste treatment. It should start from preventing the

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generation of the waste; every individual should do his/her best to reduce the waste he/she is producing daily by cooking less and do not waste food, by using durable containers, by reusing some materials for other purposes, etc. Of course, this is not limited to an individual. The most significant breakthrough should come from the industry. They should review and renew their technology to produce less waste, less polluted water, less air pollution, less energy while manufacturing, servicing, transporting and marketing. During all kinds of industrial activities, there should be less consumption and the environment should be less affected.

The second most important step for integrated waste management is source reduction by separating the wastes according to their types. Especially the package wastes should not be mixed with organic wastes. This will help to decrease the amount of costly treated, troublesome wastes. Moreover, may cause an income from the package wastes which are completely recyclables. It's a fact that; package wastes are not 'garbage'. They are a good input for further production with less energy and cost. If the paper becomes wet by the organic wastes, those papers will have no more economic value. The main earning is from nature by using less resource. This point is important than ever, in the sense of both environment and economics.

In the economic approach of waste management, usually, there are two methods (Massarutto, de Carli, & Graffi, 2011). The first one is focusing on only one type of technology such as incineration, etc. and does the comparative assessment of technologies for example; incineration vs. composting, anaerobic digestion vs. landfilling, as if they are the alternatives to each other.

This kind of comparison is useful for evaluating the range of application of each technical solution but unsatisfactory for assessing the management system as a whole since no single technology can address the 100% of waste flows and all of them generate residues that should be treated in some other points of the system (Massarutto, de Carli, & Graffi, 2011).

The second economic approach is related to the integrated management scenarios. The models are used for the materials balance, considering the bulk of waste flows generated and following them through the management system, with the aim of optimizing the choice of decision makers (Pires, Martinho & Chang, 2011). The analyses are executed by over simplifying the cost of different techniques with a primary approach to average costs remaining constant. However, the costs for collection depend on the parameters like daily collected amount, the method of collection, the frequency of emptying the containers, whether it is a curbside collection or source separation method. The unit-cost for collection also depends on the target of 10% or 90% of the total amount of each recyclable material. In this case, the quality of the collection is also important. The different types of materials should be completely separated from each other to have high income from the recycling activity; however, this generates higher sorting costs. On the other hand, if the paper or cardboard package wastes become wet, they lose their economic value as should be. The savings from the less landfilling amount might be calculated correctly; however, it is difficult to calculate a social cost for source separation with this type of approaches.

The method that was put into practice by life cycle analyses, all the above uncertainties disappear by the concept of "from cradle to grave" through adopting to waste management. The market value of the materials could be considered as a practical indicator of when something begins and ends to be a waste (Cleary, 2009). The "cradle" should be the moment when a certain good acquires negative value like disposing something to the garbage. The "grave" could be the moment when some materials return to the productive system with a positive value, like using it as a raw material in any manufacturing process (Cleary, 2009).

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International Standard Organization has explained this type of life cycle assessment in ISO 14040 as follows; "The heightened awareness of the importance of environmental protection, and the possible impacts associated with products) manufactured and consumed, has increased the interest in the development of methods to comprehend better and reduce these impacts. One of the techniques being developed for this purpose is Life Cycle Assessment (LCA)" (Porter, 1992).

In this standard, the principles and framework for conducting and reporting LCA studies are also described. The method for assessment is explained as follows;

"LCA is a technique for assessing the environmental aspects and potential impacts associated with a product, by

- Compiling an inventory of relevant inputs and outputs of a product system;
- Evaluating the potential environmental impacts associated with those inputs and outputs;
- Interpreting the results of the inventory analysis and impact assessment phases about the objectives of the study.

LCA studies the environmental aspects and potential impacts throughout a product's life (i.e. cradle to grave) from raw material acquisition through production, use, and disposal. The general categories of environmental impacts needing consideration include resource use, human health, and ecological consequences (Cleary, 2009).

In this standard, the "cradle" is taken as the raw material, and the disposal is named as "grave." This type of approach seems as opposite to the previous idea for cradle & grave. However, they become identical in the sense of transformation to air and water emissions.

While this general rule is conceptually clear, applying it in concrete is not straightforward; in order to decide whether to incorporate a certain cost in the analysis or not, we previously need to clarify the perspective of the analysis: whether private or social, and in the latter case whether referred to the optimization of a particular local management system or having an holistic vision. For example, materials collected for recycling often have a positive market value only because the set of incentives provided by extended producer responsibility enable industry-funded compliance schemes to pay the price to collectors; yet these systems have to bear further costs after collection, even if these will not be paid in the waste bill, but rather through the market price of goods incorporating charges levied by compliance schemes. In other cases, benefits may be overrated because waste-derived outputs (such as energy) receive an extra above the market price (for example, incentives to non-fossil energy sources paid by many EU governments, revenues from so-called ''green certificates''). Other prices may be distorted by taxation (e.g. landfill) or market power of operators (ISO 14040: 2006).

The basic stages of conducting an LCA are as follows;

1. The definition of goals and scopes (study model which defines the methodological framework which all other LCA phases must comply with)
2. Inventory analysis (Inventory of all the inputs and outputs related to the product system)
3. Impact assessment (Assessment of the potential impacts associated with these inputs and outputs)
4. Interpretation of the inventory data and impact assessment results related to the goal and scope of the study.

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According to the International Standard Organization, some phases of the LCA technique, such as impact assessment, are still in relative infancy. Considerable work remains to be done, and practical experience gained to further develop the level of LCA practice. Therefore, it is important that the results of LCA should be interpreted and applied appropriately. In this step, the most important point is to understand that what we are trying to learn. Otherwise, the entire attempt becomes meaningless.

GOAL AND SCOPE DEFINITION

Within the standard, ISO 14041 covers Environmental management - Life cycle assessment - Goal and scope definition and life cycle inventory analysis. The standard series continues with ISO 14042 by covering life cycle impact assessment while ISO 14043 covers life cycle interpretation.

As with other assessments, the first step involves clarifying the purpose and extent of the LCA. This entails formally determining the functional unit, impacts of interest, and system boundary—elements from the "First Choice".

While LCA "light" approaches have been described above, a "full" LCA includes actual primary environmental impact data gathered once the product's full lifecycle has been determined. Such detailed LCAs take, on average, three months and cost $10,000-$60,000 (Reich, 2005), and are only possible to complete once the product is in use and has gone through all stages of its life cycle. This increased accuracy is worth it for benchmarking or external reporting (such as green marketing) purposes.

LIFE CYCLE INVENTORY ANALYSIS (LCI)

The next phase entails creating a list of all of the components of the products life cycle that fall within the defined system boundary. It has three major steps:

1. **Construct a process flowchart that shows the following:**
    a. Raw materials
    b. Manufacturing processes
    c. Transports
    d. Marketing
    e. Users
    f. Waste management
2. **Collect data for:**
    a. Material inputs
    b. Products and by-products
    c. Solid waste, air and water emissions
3. **Calculate the amounts of each in relation to the functional unit:** Essentially, this is the process flow diagram with detailed mass and energy values. The resulting Life Cycle Inventory (LCI) provides a breakdown of all of the energy and materials involved in a product's system at a level of detail that provides a basis for evaluation.

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IMPACT ASSESMENT

Once a detailed LCI is created, environmental impacts can be ascribed to its parts, and if desired to the whole system. There are four steps to the Life Cycle Impact Assessment (LCIA) process, the first two of which are considered mandatory, while the last two are optional (Massarutto, de Carli & Graffi, 2011).

Classification

Classification involves assigning specific environmental impacts to each impact categories (component) of the LCI. It is here where decisions made during the scope and goal phase about what environmental impact categories are of interest come into play.

Characterization

Once the impact categories have been identified, conversion factors – known as characterization or equivalency factors – use formulas to convert the LCI results into directly comparable impact indicators.

Normalization (*Optional*)

In this step, a basis is provided for comparing different types of environmental impact categories. Some practitioners choose to normalize the impact assessment by scaling the data by a reference factor, such as the region's per capita environmental burden. This helps to clarify the relative impact of a substance in a given context. For instance, if global warming contributions are already high in the context in which the product is being assessed, a reference factor would normalize whatever the product's global warming contributions are to clarify its relative impacts.

Weighting (Optional)

The process of weighting is assigning a weighting factor to each impact category depending on the relative importance. It is related to the energy consumption of manufacturing and the quantity of the product. This will help to calculate the equivalence of carbon footprint.

INTERPRETATION

Although listed fourth, life cycle interpretation occurs throughout the whole LCA. It involves the ongoing process of clarifying, quantifying, checking, and evaluating the information used by, and resulting from, the life cycle inventory (LCI) and impact assessment (LCIA) phases. The standard that covers the LCA process, ISO 14044, gives two main objectives:

1. Analyze results, reach conclusions, explain limitations, and provide recommendations based on the findings of the preceding phases of the LCA, and to report the results of the life cycle interpretation in a transparent manner.

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2. Provide a readily understandable, complete, and consistent presentation of the results of an LCA study, following the goal and scope of the study.

To achieve these objectives, the ISO standard states that interpretation should cover at least three major elements of the following.

1. Identification of the significant issues based on the LCI and LCIA. Which life cycle stages or components stand out as major contributors to overall impact? What are the anomalies?
2. Evaluation which considers completeness, sensitivity, and consistency checks. Is all the information needed for interpretation present in the LCI and LCIA? How reliable is the information related to any identified significant issues? How much do changes in such factors influence the overall results? Are all of the assumptions, data, characterization factors, etc. that were used in the assessment consistent internally and with the overall goal and scope of the LCA?
3. Conclusions, recommendations, and reporting. As discussed in later sections of this guide, a great deal of an LCA's value depends on how its results are communicated to people involved in making relevant decisions, whether other designers, engineers, management, marketers, or other parts of the supply chain.

CONCLUSION

It is very important to note that no matter how carefully assembled, analyzed, assessed, and measured; LCAs are never the "real" answer. They require interpretation, which is turn requires transparency and judgment. The data sources, assumptions, and all other relevant information need to be transparent to decision makers so that they can understand the full context of the results of the life cycle inventory assessment. Deciding among design options is not as easy as just comparing LCIA numbers, whether single- or multi-factor, weighted or not. LCIA results can be a source of insights, but do not stand alone in guiding product development choices. Engineers will need to take them in the context of the other attributes they are trying to optimize, including cost, manufacturability, performance, and so on. Besides, there are myriad other factors guiding product development decisions not covered by LCAs, including social impacts and acceptance, pricing, political agendas, and regulations.

The major stages in an LCA study raw material acquisition, materials manufacture, production, use/reuse/maintenance, and waste management (Curran, 2006). This way is the only scientific method to analyze the environmental impacts of production.

Adding life cycle assessment to the decision-making process provides an understanding of the human health and environmental impacts that traditionally is not considered when selecting a product or process. This valuable information provides a way to account for the full effects of decisions, especially those that occur outside of the site that are directly influenced by the selection of a product or process.

Remember, LCA is a tool to inform decision-makers better and should be included with other decision criteria, such as cost and performance, to make a sensible decision.

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Chapter 16
A Decision Support System for Sustainable Waste Collection

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ABSTRACT

This paper presents a decision support system (DSS) for making the waste collection process more sustainable. Currently, waste collection schedules and routes are created manually in most waste management organizations. This is both very time consuming and likely to result in poor solutions, as the task is extremely difficult due to the large number of bins combined with the many parameters to be considered simultaneously. With a sophisticated DSS, it becomes possible to address the complexities of optimal waste collection and improve sustainability—not least from the environmental perspective. The DSS proposed here is designed to be used on the operational level in the waste management organization and supports daily operations and activities. System evaluation indicates that it can reduce truck operating time by approximately 25%, corresponding to a saving of approximately 21,300 kg of carbon dioxide and 187 kg of nitrogen oxides per year and truck.

INTRODUCTION

An important part of our welfare concerns ensuring properly functioning and environmentally sound waste management in both cities and rural areas. This is becoming increasingly important with the use of new raw materials and steady yearly increases in the total amount of waste. Over the past decade, the amount of household waste in Sweden has increased by 15 percent and in 2015 more than 4.3 million tonnes of household waste were generated – approximately 460 kilograms per person (Swedish Waste Management Association, 2016). One consequence of the increasing amount of waste is an increased

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number of waste collection trucks, which release greenhouse gas (GHG) emissions that contribute to climate change and cause health problems for people in urban areas. From the environmental and health perspectives, there is a strong need to optimize the procedures of planning and executing waste collection routes. From the societal and civic perspectives, there are also reasons to consider the economic aspects of household waste collection, as it is financed by taxes and/or fees.

This paper presents a decision support system (DSS) for improving the waste collection process and optimizing it from a sustainability perspective. The main focus is on the environmental aspect, as waste collection is associated with large GHG emissions from garbage trucks, each of which consumes an average of approximately 30,000 liters of diesel per year. We propose a DSS that helps the waste management organization optimize its truck operations and increase their efficiency, making them more environmentally sustainable. The DSS is designed to be used on the operational level in the waste management organization and supports the daily operations and activities. Note that, although various waste collection systems have been proposed in the literature (see, e.g., Giribone et al., 2002; Abeliotis et al., 2009; Caballini et al., 2010; Revetria et al., 2011; Chang and Lin, 2013), as far as the authors are aware, none of these focuses on a complete DSS for operational use with an explicit focus on optimization from a sustainability perspective.

Waste collection schedules and routes are currently created manually in most waste management organizations. Manually planning truck operations is very difficult due to the large number of bins combined with the many parameters to be considered simultaneously. Parameters include driver working hours and breaks, truck capacity (in terms of both weight and volume), and time windows at offload facilities. Even greater difficulties are created by the temporal constraints that must be considered, meaning that some bins preferably should, or should not, be emptied at certain times (e.g., bins at daycare centers should be avoided when children are outside playing). Furthermore, the problem of route optimization is a highly complex mathematical problem: finding the shortest route between a number of points (in this case represented by bins) is classified as an "NP-hard" problem in its simplest form. This means that the time it takes to solve the problem grows exponentially with the problem size, i.e., number of nodes. Finding the optimal route is possible, but might take a very long time because all possible routes must be evaluated to find the best one. Even for small-sized problems of this sort, a huge number of possible routes must be considered; for example, in a problem with only 15 nodes to visit, there are 6,227,020,800 possible routes.

The high complexity of efficiently optimizing the waste collection process, in combination with the obvious need to reduce emissions from garbage trucks, has motivated this study and the development of a DSS for sustainable waste collection. The next section describes the research method used in the study. In Section 3, the conceptual modeling of the waste collection problem used as a basis of the DSS is presented. Sections 4 and 5, respectively, present the optimization algorithms and simulation used in obtaining sustainable solutions. The DSS is presented in Section 6, followed by an evaluation of the system in Section 7. Finally, conclusions from the study are presented in Section 8.

RESEARCH METHOD

The research method chosen for this work may be characterized as an action case method (Vidgen & Braa, 1997). The action case study can be described as a hybrid between interpretative case studies and interventional action research (Vidgen & Braa, 1997). The action case method aims to balance the po-

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tential contradiction for the researcher in being both the observer of a particular case and simultaneously interfering with the process by contributing knowledge and ideas as part of bringing the process forward. This balance can also affect the generality of the results. The action case method has been criticized (Baskerville & Wood-Harper, 1996), and to alleviate some of these criticisms, an iterative approach has been applied. The iterative approach is inspired by Susman's (1983) generic model, which comprises the following five cyclic activities guiding the process: diagnosing, action planning, action taking, evaluation, and specifying learning. Here, it is also worth mentioning that although the activities are sequentially connected, some parallelism normally occurs, especially in relation to the specifying learning activity.

The action case study, which started in 2010 and is still ongoing, has been conducted at a waste management company. The company is responsible for collecting household waste in nine municipalities in western Sweden from a total of approximately 134,000 bins. Each bin is emptied once or several times during a 14-day period according to a predefined schedule. The company has 50 employees and an annual turnover of EUR 8.5 million. Currently, 25 trucks are needed to collect the waste and most of them are fueled with diesel. During the study, and following Creswell's (2009) advice, a lot of empirical material has been collected from various sources. Thirty-five interviews were conducted with transportation planners and garbage truck drivers, as well as with managers in several positions. In addition, observations, document analysis, internal company as well as external system analysis, and DSS prototyping have contributed material used in developing and analyzing the DSS and in related processes.

PROBLEM MODELING

In the study, we approach the overall waste collection problem as a pickup and delivery problem, while the lower-level optimization problem of finding the best possible route linking a number of selected bins is approached as a traveling salesman problem (TSP). The basics of these two problems are explained in the next two subsections.

Pickup and Delivery Problem

The general pickup and delivery problem (GPDP) concerns creating routes for carrying out a number of transportation requests using a fleet of vehicles (Savelsbergh & Sol, 1995). Each vehicle has a given maximum capacity, starting point, and endpoint. A transport request defines the quantity of goods to be transported and the locations where the goods are to be picked up and delivered. Each request is fulfilled by a single vehicle without intermediate transshipment.

The pickup and delivery problem (PDP) is a specialized version of GPDP in which all vehicles start and stop at a central depot (Montané & Galvão, 2002). Furthermore, for each transport request, only one location is defined for pickup and delivery, respectively. Another common problem is the vehicle routing problem (VRP), which is identical to PDP except that either all pickup or all delivery locations are located at the depot (Tan et al., 2006). An example of a VRP problem is shown in Figure 1. This problem illustrates a realistic situation in which there are multiple vehicles with different capacities serving multiple locations with heterogeneous time windows, priorities and load to be picked-up.

Based on GPDP, PDP, and VRP, further specialized problems can be defined and divided into two categories: static and dynamic. A problem is static if all transport requests are known when the routes are constructed (Savelsbergh & Sol, 1995). In a situation in which transport requests may be added

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Figure 1. Example of VRP problem (adopted from OptaPlanner.org)

while running routes, meaning that routes have to be changed on the fly, the problem is instead dynamic. Besides static and dynamic problems, it is also meaningful to distinguish between problems involving one and several operating vehicles, i.e., single- and multi-vehicle problems. Furthermore, problems can also be categorized according to whether or not they involve time constraints. For example, vehicles are often only available during the drivers' working hours or, if people are being transported, pickups must be performed at specific times. Such restrictions are called time windows.

The above problems have several possible optimization objectives (Savelsbergh & Sol, 1995). Some common examples are minimizing the total time for the route, minimizing the distance driven, or meeting the time windows as closely as possible. A problem may be either a single-objective problem, i.e., involving only one aspect to be optimized, or a multi-objective problem, i.e., involving several, often conflicting, aspects to be optimized simultaneously. Various solution techniques are used depending whether the problem is a single- or multi-objective one.

In this paper, we model the problem of waste collection as a static multi-vehicle pickup and delivery problem with time windows and multiple optimization objectives. The lower-level optimization problem of finding the best possible route between bins that have been allocated to a truck is modeled as the TSP, as described in the next subsection.

Traveling Salesman Problem

The traveling salesman problem (TSP) is an optimization problem belonging to the NP-complete class of combinatorial problems (Russell & Norvig, 2003). The definition of the problem is that, given a finite graph, the goal is to find the shortest Hamiltonian circuit. A Hamiltonian circuit is a path in a graph that visits each node exactly once except the start node, which is also the end node. A graph is

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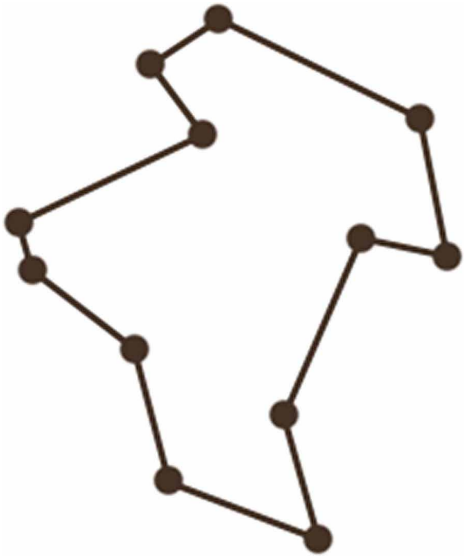
Figure 2. An optimal Hamiltonian circuit in a graph consisting of 12 nodes



a structured set of nodes and edges, where edges connect the nodes. Figure 2 illustrates a Hamiltonian circuit. As TSP is NP complete, and finding the optimal circuit entails calculating every possible circuit in the graph, the complexity of the problem grows exponentially with the number of nodes in the graph (Gen & Chen, 2000).

TSP is one of the most studied problems in combinatorial optimization due to its simple definition and field of applications (Applegate et al., 2006). A typical example application of TSP is in the industrial manufacturing of circuit boards. When manufacturing circuit boards, holes are usually drilled or stamped through the board in a specific pattern. The mean time of drilling or stamping is constant and cannot be altered by improving the manufacturing process. The time spent moving the drill or stamping cylinder can, however, be improved by optimizing the order in which the holes are processed, thus optimizing the distance traveled by the drill or stamping cylinder. Using the same concept, TSP can be also applied to problems related to finding the shortest possible path through a number of geo-locations, as in the case of waste collection.

The next section describes the software algorithms used in solving the optimization problem on the technical level.

DEVELOPMENT OF THE OPTIMIZATION ALGORITHM

Due to the general complexity of PDPs and TSPs, optimization techniques that are not guaranteed to find the optimal solution, but a sufficiently good one in a short time, are often used rather than exact methods (Zbigniew & Fogel, 2000). Evolutionary algorithms are a class of such inexact optimization techniques that can be used to approach these problems (Jozefowiez et al., 2008), and such a technique is used in this study.

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Evolutionary Algorithms

Evolutionary algorithms are essentially based on Darwin's theory of the "survival of the fittest" (Darwin, 1859). According to this theory, in a population of individuals (i.e., solutions), those having the most desirable characteristics will obtain the best opportunities to mate and carry on their genes. In this way, Darwin argued, genes promoting fitness will propagate through generations and the population will increase in fitness over time. In this study, a solution represents the fleet of vehicles and provides a set of routes each specifying what bins should be visited each day, in what order and by what trucks.

In evolving a population of solutions, evolutionary algorithms apply biologically inspired operations for selection, crossover, and mutation (Pham & Karaboga, 2000). The operators are applied in a loop, an iteration of the loop being called a generation. The following pseudo code presents the basic steps of this evolutionary process:

Step 1: Initialize population
Step 2: Evaluate the fitness of solutions in the population
repeat
Step 3: Select solutions to reproduce
Step 4: Form a new generation of population through crossover and mutation
Step 5: Evaluate the new solutions
until terminating condition

The solutions in the initial population are usually generated randomly (step 1). The solutions in the population are evaluated and assigned fitness values, representing a quantification of their optimality (step 2). In each generation, a proportion of the solutions in the population is selected from which to breed offspring for the next generation of the population (step 3). Solutions are selected based on their fitness and those having a high fitness typically have a higher probability of being selected, but to prevent premature convergence, it is common for a small proportion of solutions with worse fitness also to be selected. From the solutions selected, new solutions are created to form the next generation of the population (step 4). To create each new solution, two parent solutions are chosen and, through mating (called crossover), an offspring is produced (see Figure 3).

Occasionally, the new solution can undergo a small mutation to maintain high diversity in the population and avoid local minima. A mutation usually involves changing an arbitrary part of a solution with a certain probability, in this case changing the order in which two collection sites are visited, as shown in Figure 4.

When the new population is formed, the solutions are evaluated and the average fitness will have generally increased (step 5). After evolving populations for some time, near-optimal collections of routes have been found. The process of evolving generations continues until a user-defined termination criterion has been fulfilled, for example, that the best solutions in the last n generations have not changed or that a certain time has elapsed.

Two fitness values (optimization objectives) are considered in the optimization, as specified by the waste management organization: 1) minimal carbon dioxide emissions and 2) minimal violations of temporal constraints. These two objectives conflict with each other, as considering temporal constraints negatively affects the driving distance. The difficulty with conflicting optimization objectives is that there is usually no single optimal solution with respect to both objectives. Instead of a single optimum,

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Figure 3. Example of a crossover

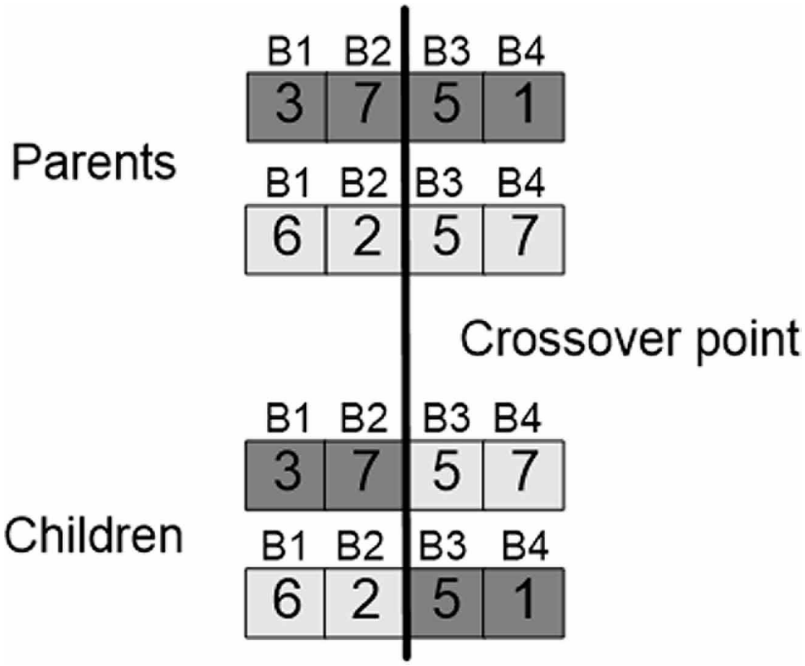

Figure 4. Example of a mutation

there is a set of optimal tradeoffs between the conflicting objectives, called Pareto-optimal solutions (Deb, 2004). To manage multiple objectives, specific optimization algorithms have been suggested. Instead of seeking only a single optimum, these algorithms maintain a set of Pareto-optimal solutions. One of the most efficient algorithms for Pareto optimization is the elitist non-dominated sorting genetic algorithm (NSGA-II) (Deb et al., 2000). Due to the algorithm's proven efficiency, this is the optimization algorithm selected for the study.

NSGA-II is basically an evolutionary algorithm extended with features for handling multiple tradeoff solutions. To deal with conflicting objectives, NSGA-II selects solutions for the next generation of the population based on Pareto ranks: rank 1 includes the Pareto-optimal solutions in the complete population, and rank 2 the Pareto-optimal solutions identified when temporarily discarding all solutions of rank 1, and so on. More specifically, solutions for the next generation are selected from set *R*, which is the union of the parent and offspring populations (both of size *N*). Pareto-based sorting (also called

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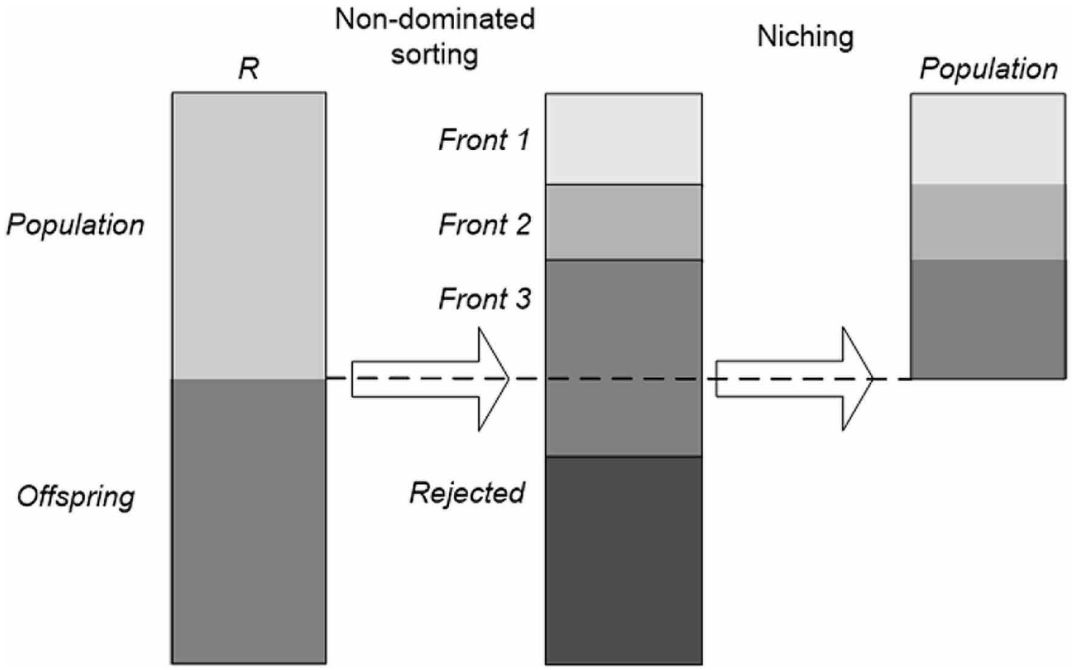
Figure 5. Selection procedure of NSGA-II



non-dominated sorting) is applied to *R* and the next generation of the population is formed by selecting solutions from one Pareto front at a time. The selection starts with solutions in the best Pareto front, then continues with solutions in the second-best front, and so on, until *N* solutions have been selected. If there are more solutions in the last front than there are remaining to be selected, niching is applied to determine which solutions should be chosen. All the remaining solutions are discarded. The selection procedure is illustrated in Figure 5 (adapted from Deb, 2004) and the pseudo code is presented below:

```
Initialize Population
Generate N random solutions and insert into Population
for (i = 1 to MaxGenerations) do
Generate ChildPopulation of size N
Select Parents from Population
Create Children from Parents
Mutate Children
Combine Population and ChildPopulations into CurrentPopulation with size
2N
for each individual in CurrentPopulation do
Assign rank based on Pareto – Fast non-dominated sort
end for
Generate sets of non-dominated vectors along PF_known
Loop (inside) by adding solutions to next generation of Population starting
from the best front
```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```
until N solutions found and determine crowding distance between
points on each front
end for
Present results
```

To evaluate the fitness of solutions, the algorithm uses a simulation model that represents the real-world bin collection. This model is described in the next subsection.

DEVELOPMENT OF THE SIMULATION MODEL

To simulate a waste collection procedure, a discrete-event simulation model was constructed. A discrete-event model was used instead of a traditional analytical (mathematical) representation of the problem because analytical methods require simplifications, as these methods do not provide means for modeling complex behavior (Al-Nory & Brodsky, 2008). Furthermore, the concepts of event order and timing are usually not explicit in analytical models, making it difficult to achieve a correct representation of the real-world system (Al-Nory & Brodsky, 2008). For a complex problem like that considered here, discrete-event simulation is a powerful alternative to analytical methods and provides better means for incorporating complex relationships using easier methodologies and tools than does mathematical programming (Law, 2007).

Discrete-Event Simulation Model

A simulation model essentially consists of a set of system states and transitions between these states, which correspond to elements and event sequences in the real system (Banks, 1998). The execution of an event-driven simulation model is controlled by the time points of the scheduled events. After an initialization phase in which the simulation clock is reset and the state variables, statistical variables, and event list are initiated, the simulation cycle, i.e., the simulation main loop, is started (Law & Kelton, 2000). In each iteration, the type of the next event in the event list is determined (i.e., the event with the first start time). Subsequently, the simulation clock is advanced to the start time for this event and a routine for handling the current event type is run. An event routine first updates the state variables and then the statistical variables; finally, future events are generated and added to the event list. The last thing that happens in the simulation cycle is testing whether the condition for when the simulation is considered completed has been satisfied. If it is not, a new simulation cycle is run. If the condition is met, the simulation is terminated, and output parameters are calculated and reported.

Data for the simulation model used in the study were collected for two months in cooperation with the waste management company. Validation of the simulation model indicates that it represents reality very well, with an average deviation from reality of only 7%.

The next subsection describes how the simulation model and the evolutionary optimization algorithm have been integrated in a simulation-based optimization procedure.

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Simulation-Based Optimization

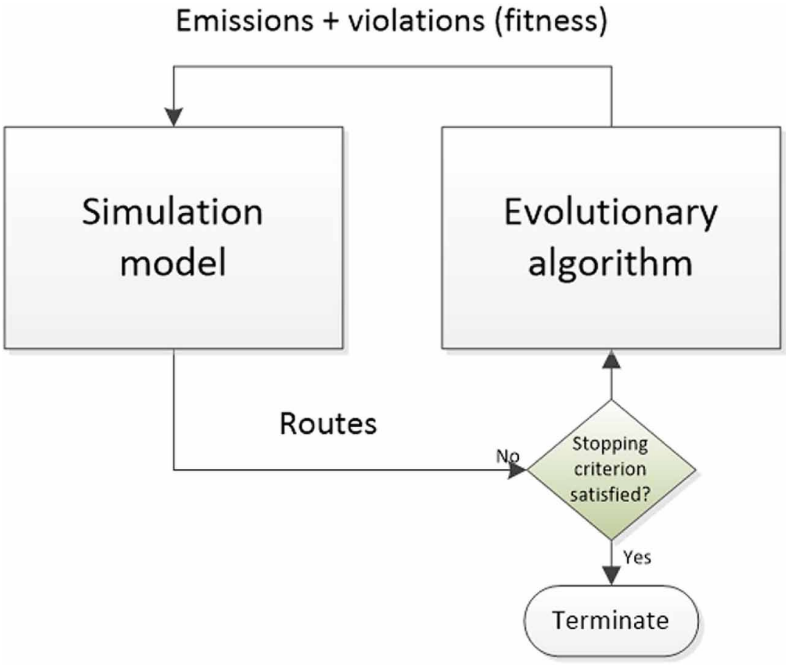
Simulation-based optimization is an iterative process (see Figure 6): the evolutionary algorithm generates a solution (in this case, a set of routes) and feeds it to the simulation model, which computes the fitness (in this case, carbon dioxide emissions and violations of temporal constraints). Based on the evaluation feedback obtained from the simulation model, the optimization algorithm generates a new set of parameter values and the generation–evaluation process continues until a user-defined stopping criterion is satisfied (April et al., 2004). Such a criterion may, for example, be that a certain amount of time has passed or that specific objective values have been achieved (Boesel et al., 2001).

The next section describes how the simulation-based optimization is integrated in a DSS for improved waste collection from a sustainability perspective.

DEVELOPMENT OF THE DECISION SUPPORT SYSTEM

The DSS was designed in close collaboration with the Swedish waste management company AÖS to ensure the system's real-world usability. An iterative prototyping approach was used in which the system was gradually developed based on feedback from domain experts (i.e., its future users). From a conceptual perspective, the system consists of three parts: (a) the back-end, (b) the driver's front-end, and (c) the transportation planner's front-end. All parts share a software infrastructure and use the same database for accessing information to ensure that all users can always access complete and consistent data. The common software infrastructure handles basic data such as information about customers, trucks, facilities, routes, users, etc. It also provides services to view and manipulate data.

Figure 6. Simulation–optimization process



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DSS Back-End

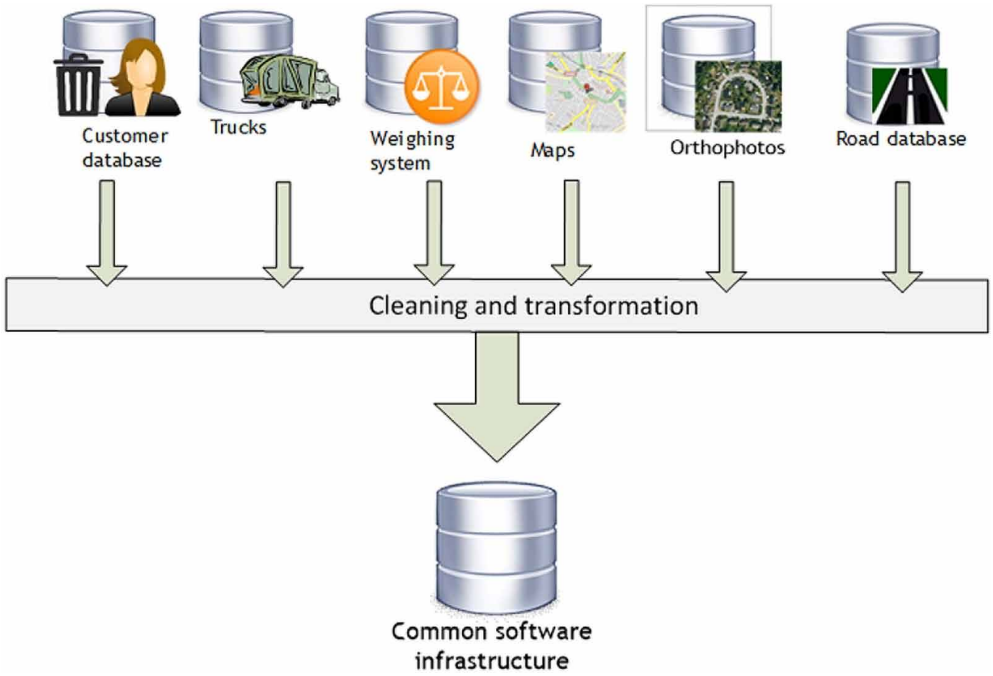
To provide complete, dynamic, and updated information to the users, the DSS programmatically integrates various data sources (Figure 7). These include map services, orthophotos (similar to satellite photos), road data, vehicle tracking systems, weighing systems, and customer databases. The various data sources are both on-line and off-line in nature and data synchronization occurs either regularly based on a synchronization schedule or on-demand as follows:

- **Maps and Orthophotos:** Synchronized on-demand when needed (e.g., when new buildings or roads appear in the community), approximately twice per year;
- **Road Data:** Synchronized on-demand when the Swedish Transport Administration releases major updates;
- **Vehicle Tracking:** Automatically synchronized every second;
- **Weighing Data:** Automatically synchronized as soon as a vehicle unloads at a recycling facility;
- **Customer Databases:** Automatically synchronized every 15 minutes.

Transportation Planner's Front-End

The transportation planner's front-end includes all the functionality needed to plan, optimize, and operate the waste collection process. An early decision in the development process was to make the system web-based so it would be accessible from anywhere with an Internet connection, and not only from a specific computer with specific software installed. An important part of the transportation planner's front-end

Figure 7. DSS back-end



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is the display of dynamic information and the opportunity to constantly monitor what is happening in real time. To facilitate this, current status information is the first thing viewed when the user logs into the system (see Figure 8). The status view shows, for example, the location of each truck, how much of each collection route has been completed, and the locations where problems have arisen.

The system also shows all routes for all trucks on the current day, as well as past and future routes. All routes are generated using the previously described simulation-based optimization system. An example of a route of one truck is shown in Figure 9. Each blue/purple dot on the map indicates a bin to be visited, which are also shown in an ordered list on the left.

On the current day, the route of an individual truck can also be monitored and manipulated in real time. Figure 10 shows a route currently being traversed by a vehicle. A green dot (and its corresponding row in the list to the left) indicates that the bin has been emptied without any problem. A red dot indicates that the bin could not be emptied and more information about the reason for this is given if the user clicks on the dot. Blue dots are bins that have not yet been visited. The position of the truck in relation to the bins is also shown on the map and updated in real time, making it possible to monitor the progress of the route in detail.

Several times per day, customers call the transportation planner to say that their bins have been overfilled and must be emptied immediately, although the bin is not part of any route on that day. To help the transportation planner handle suddenly arising requests and ensure that they add as little extra environmental load as possible, the DSS includes a real-time optimization function. This function checks where all the trucks are located, their current loads, their planned routes for the rest of the day, and their current progress in relation to what is left of the workday. Based on this information, the real-time optimization function automatically assigns the request to the truck that is optimal in terms of minimal emissions. The request is immediately communicated to the driver's front-end, which is described in the next subsection.

Figure 8. Real-time overview of current status

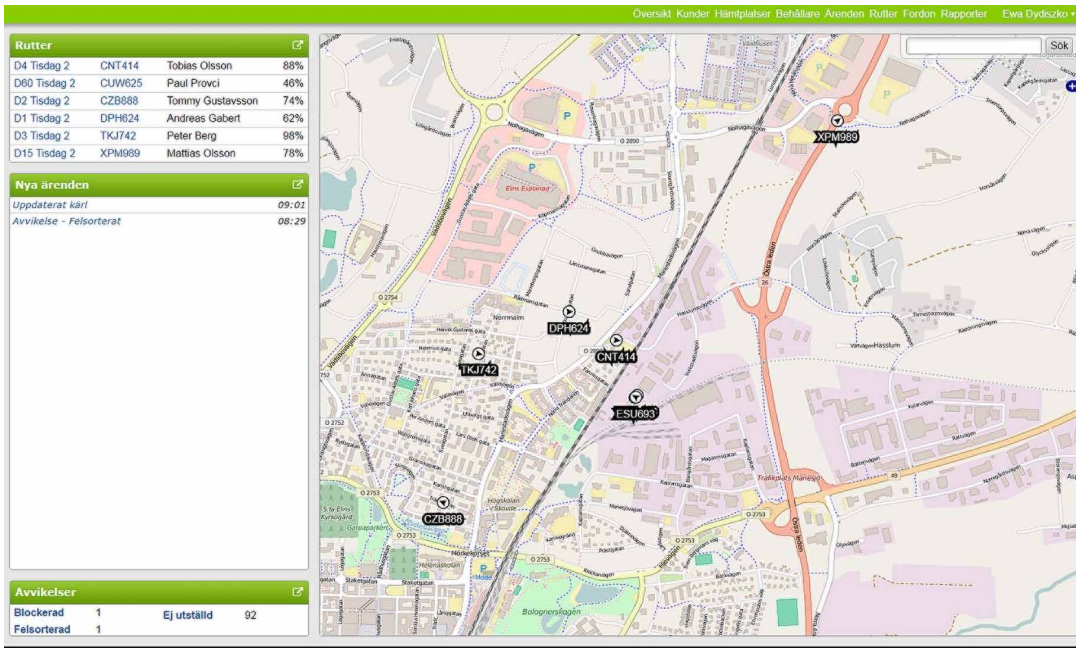

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Figure 9. Overview of a route

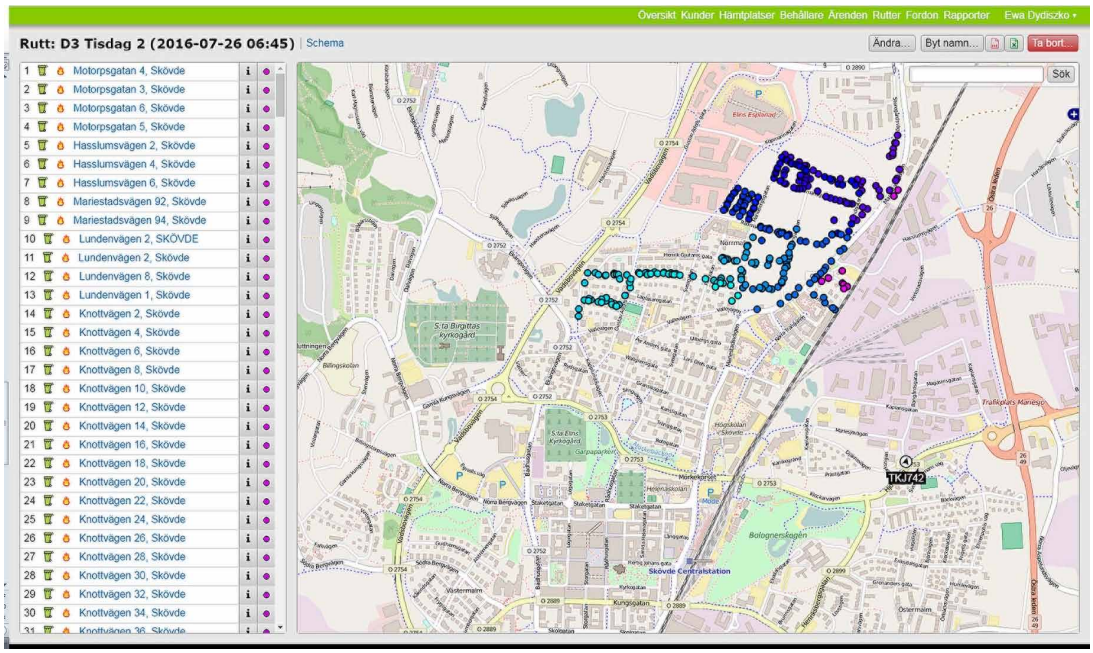
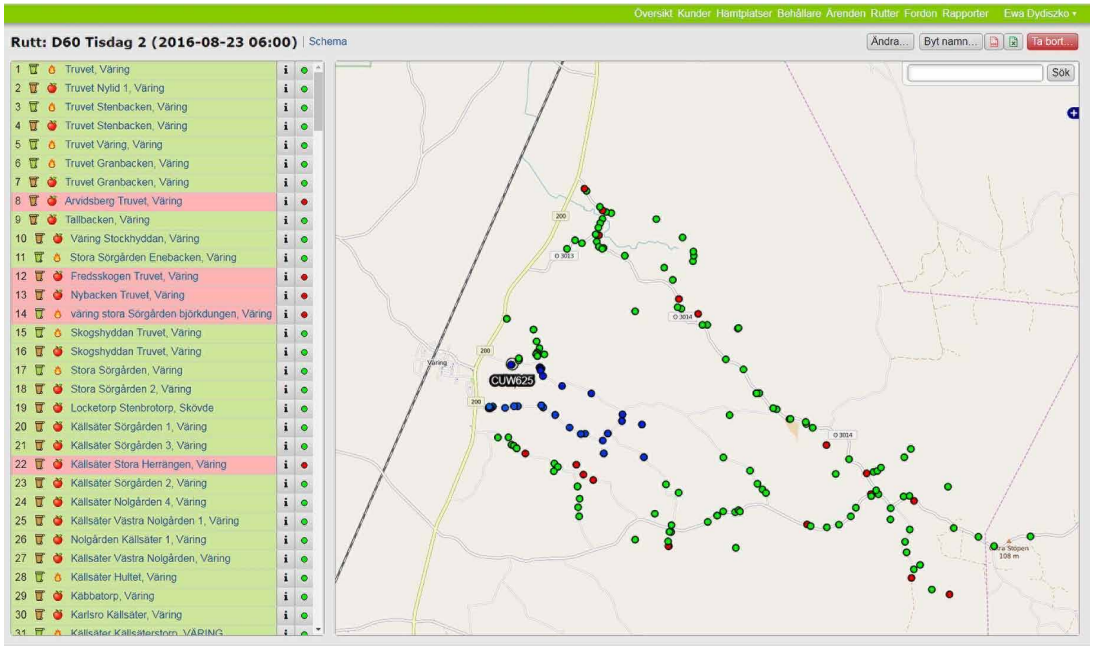


Figure 10. Overview of a route currently being executed



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Driver's Front-End

The driver's front-end is Android based and accessed through a 10" tablet available in the truck. The front-end has been designed in close collaboration with drivers, starting with a "blank slate" and successfully adding functionality according to driver requirements. The front-end shows what bins to visit during the day, in what order, and the current status of each bin—similar to the transportation planner's front-end shown in Figure 11. Through the tablet, the driver can also report when a bin has been emptied and also various problems encountered when traversing the route. Problems might, for example, be related to parked cars blocking bins, traffic accidents, or hidden bins. A screenshot of the driver's front-end is shown in Figure 11.

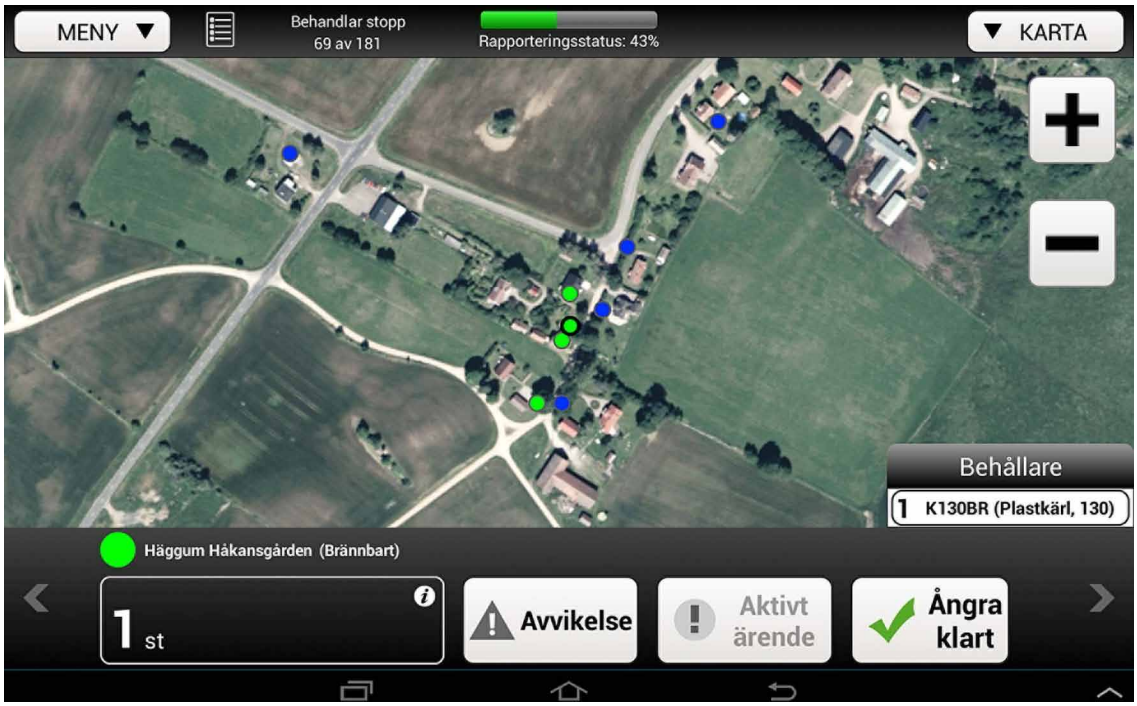
The truck is equipped with a communication unit that provides access to the mobile network, allowing the vehicle to communicate with the base system in real time. This enables direct communication between the driver and the transportation planner, who can instantly send information to each other.

The next section evaluates the sustainability gains made using the described DSS.

EVALUATING THE DSS FROM A SUSTAINABILITY PERSPECTIVE

To assess the sustainability gains made using the DSS, a case study was conducted. For the case study, we selected one of the nine municipalities served by AÖS, which includes approximately 17,000 unique bins spread over an area of approximately 40 × 50 km. For the reader to grasp the problem, the geographical locations of the bins are plotted on maps shown in Figure 12 and Figure 13 (the latter zooms in on part of

Figure 11. Driver's front-end



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the former). Three trucks are available for emptying the selected bins, and each of them empties on average approximately 550 bins per day. This means that a unique route should be created for each truck and each workday during a 14-day period (excluding Saturdays and Sundays). If successful, the optimization will reduce the driving distance and possibly also free one or several trucks for one or several days, which would save a great deal in terms of both the emissions and costs associated with the collection process.

Each truck has a limited capacity in terms of both weight and volume, and when this capacity is reached must be emptied. Emptying is done either at a recycling center (for compostables and corrugated cardboard) or at a heating plant (for combustible waste). Because different kinds of waste must be deposited in different places, different types of waste cannot be mixed in the truck. All these constraints are fed into the simulation-based optimization process and labeled mandatory, meaning that a route that violates any of the constraints is considered invalid and of no value.

The routes resulting from the most successful optimization runs were presented to domain experts in the waste management organization, who carefully studied and evaluated them. The domain experts estimated that the optimized routes would reduce the operating times of the trucks by approximately 25% compared with the operating times for the routes created manually by the transportation planner. The operating time of a truck denotes the time its engine is running (either in motion or stationary) and corresponds directly to the amount of emissions from the truck. As mentioned in the Introduction, a garbage truck consumes on average approximately 30,000 liters of diesel per year, corresponding to approximately 85,200 kg of carbon dioxide and 747 kg of nitrogen oxides. A 25% reduction in emissions therefore means that 21,300 kg of carbon dioxide and 187 kg of nitrogen oxides per truck and year can be saved using the DSS, which is a substantial environmental saving.

Figure 12. Garbage bins included in the optimization

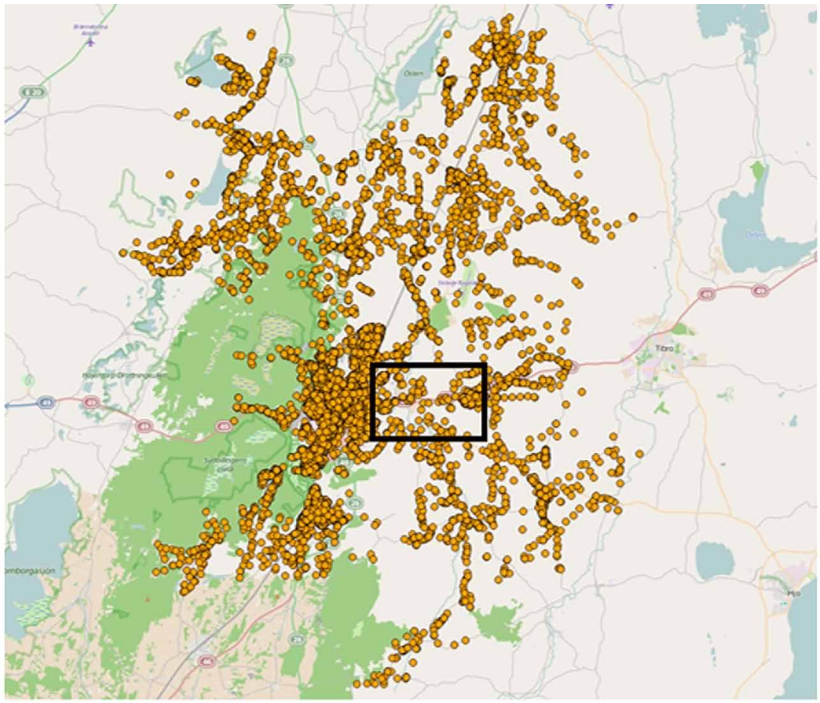

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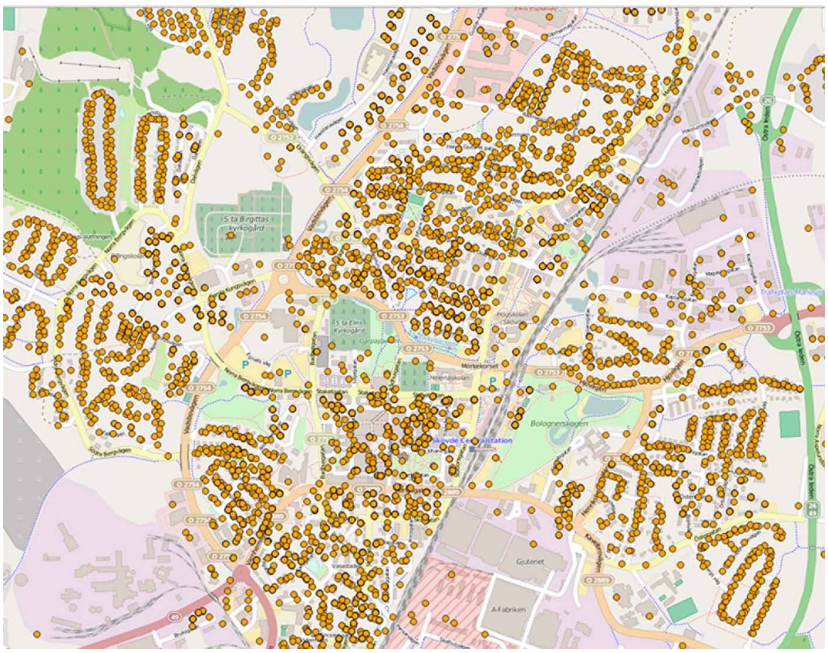
Figure 13. Zoomed-in view of the area corresponding to the black square in Figure 5



Considering the economic aspect of sustainability, a 25% reduction in the operating time of the trucks also represents substantial economic savings, not least related to staffing. The trucks are operated by one or two drivers and, because labor costs are very high in Sweden, as in most industrialized countries, reduced staffing needs correspond to substantial financial savings. Furthermore, less driving also means that considerable money can be saved on fuel.

Considering the social aspect of sustainability, this is improved mostly through the real-time optimization function in the DSS. This function can improve customer service, ensuring that all urgent customer requests are handled promptly. Reduced waste collection costs also mean that the associated fee could be reduced for citizens.

CONCLUSION

This paper presents a decision support system (DSS) for improving the waste collection process from a sustainability perspective. Currently, waste collection schedules and routes are created manually in most waste management organizations. This is both very time consuming and likely to result in poor solutions, as the task is extremely difficult due to the large number of bins combined with the many parameters to be considered simultaneously. With a sophisticated DSS, it becomes possible to address the complexities of optimal waste collection and improve sustainability—not least from the environmental perspective.

In the proposed DSS, the overall waste collection problem is approached as a pickup and delivery problem (PDP), while the lower-level optimization problem of finding the best possible route linking a number of selected bins is approached as a traveling salesman problem (TSP). To solve the problem, i.e., find optimal solutions, a multi-objective evolutionary algorithm is implemented. The evolutionary

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algorithm uses a discrete-event simulation model to evaluate and assess the feasibility of various solutions. This model closely mimics the real waste collection process and can be used for testing various scenarios.

The proposed DSS was designed to be used on the operational level in waste management organizations, where it supports daily operations and activities. From a conceptual perspective, the system consists of three parts: (a) the back-end, (b) the driver's front-end, and (c) the transportation planner's front-end. All parts share a software infrastructure and use the same database for accessing information to ensure that all users can always access complete and consistent data. To ensure the real-world usability of the DSS, it was designed and evaluated in collaboration with the Swedish waste management company AÖS.

To assess the sustainability gains made using the DSS, a case study was conducted examining one of the municipalities served by AÖS, which includes approximately 17,000 households. An optimization was run in the case study and domain experts estimated that the truck operating time would be reduced by approximately 25% compared with the operating times for the routes created manually. For an average garbage truck, using the proposed DSS would prevent the release of approximately 21,300 kg of carbon dioxide and 187 kg of nitrogen oxides per year. There are also considerable cost savings, not least related to staffing and fuel costs. Besides the environmental and economic improvements, the system would also provide improved customer service and the opportunity to handle urgent customer requests efficiently.

From a broader perspective, the potential sustainability gains with a DSS like the one proposed here are enormous. In Sweden, approximately 2000 garbage trucks serve households, in Europe approximately 90,000, and in the rest of the western world approximately 400,000. Although a 25% improvement might not be reached in all waste management organizations, even a small improvement means a huge reduction in carbon dioxide emissions if the DSS were broadly adopted. For example, assuming an average improvement as low as 5%, over two billion kg of carbon dioxide emissions would be prevented every year. It should also be noted that the numbers of trucks mentioned include only trucks serving households; the total number of garbage trucks is much larger if we also include trucks serving industries and recycling facilities.

To large extent, the results of the study are generic and can be applied in other domains as well. Many examples of pickup and delivery problems are encountered in everyday life, such as parcel, dial-a-ride, and postal services. The underlying simulation and optimization approach implemented in the DSS is generic and can be applied to essentially any PDP. The technical infrastructure of the system is also generic and can be reduced for other applications. The front-ends, however, need to be tailored to each specific application domain, although many concepts can certainly be reused.

Future work will concentrate on the possibility of incorporating additional data sources in the back-end of the DSS to improve system efficiency. With more information available, it will be possible to improve the optimization results and it might also be possible to realize real-time optimizations with a one-to-one mapping to the real world. Both internal company and external public data sources will be considered for inclusion.

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Chapter 17
SCOR Model and the Green Supply Chain

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ABSTRACT

Supply chain management (SCM) is a continually evolving field, relying on breaking down internal and external organizational barriers to gain efficiencies, improve customer support and increase flexibility, thereby resulting in lower costs and increased market share. An emerging area in supply chain practice is green SCM, which integrates environmental management with traditional SCM. Green supply chain management is seen as an important step companies need to take on the road to sustainable practices. SCOR Model (Supply Chain Operations Reference) has been developed by the Supply Chain Council (SCC now merged with APICS) in order to guide companies applying SCM principles. The GreenSCOR model was also developed as an integrated green SCM tool that allows companies to manage their supply chain's environmental impacts, resulting in more efficient operations which have minimal impact on the environment. This chapter will talk about how SCM principles can be modified to reduce the adverse effects of company operations on the environment, especially using the GreenSCOR model.

INTRODUCTION

Supply chain management (abbreviated as SCM) is a continually developing field, relying on breaking down internal and external organizational barriers to gain efficiencies, improve customer support and increase flexibility, thereby resulting in lower costs and increased market share. An emerging area in supply chain practice is green supply chain management, which incorporates environmental management with traditional supply chain management. Green supply chain management is seen as an important stride companies need to take on the road to sustainable practices. SCOR Model (Supply Chain Operations Reference) has been developed by the Supply Chain Council (SCC is now merged with APICS) in order to guide companies applying SCM principles. The GreenSCOR model was also developed as an integrated green supply chain management tool that allows companies to manage their supply chain's

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environmental impacts, resulting in more efficient operations which have minimal impact on the environment. This chapter will talk about how SCM principles can be modified to reduce the adverse effects of company operations on the environment, especially using the GreenSCOR model.

Supply chain management involves all facilities, functions, and activities associated with flow and transformation of goods and services from raw materials to customer, as well as the associated information flows (Russel & Taylor, 2008). SCM can be regarded as an integrated group of processes to "source," "make," and "deliver" products. Namely SCM deals with the corporate functions of procurement, production and distribution. SCM can be applied in service industries (hospitals, fast food, supermarkets, retail), petroleum industries, chemicals industries (continuous processes), textile industries (ready to wear clothing) and many others. The specific SCM applications are influenced by type of process (continuous, batch, project, mass production), number of stock keeping units (SKU's) and government regulations among other factors.

Sustainable supply chains are becoming more important as firms focus on the resource consequences of the operations that they carry out. The three P's of sustainability can be listed as People, Profits and Planet. These concepts can easily be applied to supply chain operations as well. As the world population is increasing the waste generated also increases. The growing waste problem can be reduced by applying the principles of 4R many of which are related to the operations of the supply chain:

- **Reduce:** For example, designing concentrated detergent that uses less packaging,
- **Reuse:** Using reusable packaging,
- **Recycle:** Packages used in transportation can be recycled and turned into new packages,
- **Recover:** Energy can be gained from waste.

Creating a sustainable supply chain can start with the design of the products. Products can be designed in such as way so as to consume less materials, result in less transportation costs and be easily disassembled so that parts can be used for remanufacture or refurbishing. As an example, polyester fabric 100% recyclable, polar fleece may be made by recycled soda bottles, also the new BMW i30 interior is made from recycled materials. Firms can generally follow these principles for design for the environment or DFE:

- Use fewer materials.
- Use recycled materials or recovered components.
- Don't assume that natural materials are always better.
- Don't forget energy consumption.
- Extend the useful life of the product.
- Involve the entire supply chain so they share the responsibility in terms of the environmental impact.
- Change designs, some consumers' solutions may require services rather than products, an example could be using laundry services rather than selling washing machines.

We can see Walmart as an example of applying the above principles. Package reduction in certain toy lines reduced transportation costs by $2.4 M/year which is equivalent to 3800 trees and 1 billion barrels of oil. Stores use solar panels, windmills, and skylight thereby reducing the power consumption. Spoiled food is composted and resold as fertilizer using a 0% waste policy. Stores sell power saving light bulbs such as Compact Fluorescent (CFL) or LED lights.

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Recycling can be defined as the process to change (waste) materials into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution (from incineration) and water pollution (from landfilling) by reducing the need for "conventional" waste disposal, and lower greenhouse gas emissions as compared to plastic production. The following materials and more can be recycled (EPA, 2015):

- **Iron:** Ferrous Metals include iron and iron-containing metal scrap. Ferrous metal is handled in the same manner as non-ferrous metal, but generally has lower market value.
- **Steel:** Tin-Coated Steel Containers Includes cans used for food packaging (i.e., canned foods). Some local recyclers might require cans to be cleaned and crushed with labels removed. Bimetal Containers: A typical example includes tin-plated steel cans with aluminum "pop top" (e.g., peanut cans). These containers can be separated from aluminum cans by using a magnet. Many recyclers accept bimetal containers with tin-coated cans.
- **Copper:** Non-Ferrous Metals include most types of scrap metal which do not contain iron (such as copper and brass). This scrap can be a relatively valuable commodity, depending on quantity. It is often recycled through scrap metal dealers, although some general recyclers will handle it with other materials.
- **Aluminum:** Included in this category are aluminum beverage cans, as well as clean aluminum scrap and aluminum foil. Currently, aluminum is a highly valued material for recycling.
- Lead.
- **Batteries:** Lead-acid batteries are used in automobiles, back-up lighting systems, lawn mowers, and computers. Lead-acid batteries contain lead, a toxic metal and sulfuric acid. Many US states prohibit disposal of lead-acid batteries in municipal solid waste, and many require either retailers, wholesalers, or distributors to take back batteries. Currently, about 90 percent of lead-acid batteries used in automobiles are recycled. Household batteries come in a variety of types including alkaline, carbon-zinc, mercuric-oxide, silver-oxide, zinc-air, and nickel-cadmium. Currently, only button catteries containing mercury and silver or nickel-cadmium batteries can be recycled, often at net cost.
- **Paper:** High-Grade Paper is usually generated in office environments and can earn recycling revenues when present in sufficient quantity. Types of high-grade paper include:
    - Computer paper (also known as Computer Print Out or CPO). Can be all white or have a white main fiber with bright green or blue bars.
    - White ledger. Most white office paper, including white computer paper, copy machine paper, letterhead, white notebook paper, and white envelopes. Common contaminants include glossy paper, wax-coated paper, latex adhesive labels, envelopes with plastic windows, and carbon paper.
    - **Tab Cards:** Usually manila-colored computer cards; may be other colors but must be separated by color to be valuable as a high-grade paper.
    - **Other Papers:** These papers are less valuable than high-grade paper in terms of recycling, although they still can be cost effective to recycle in many cases. Examples of other types of paper include:
        - **Colored Ledger:** Most non-white office paper, including carbonless paper, file folders, tablet paper, colored envelopes, and yellow legal paper.

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    - **Corrugated Cardboard:** Also known as Old Corrugated Cardboard or OCC. Includes unbleached, unwaxed paper with a ruffled (corrugated) inner liner. It usually does not include linerboard or pressboard, such as cereal boxes and shoe boxes. For most business, cardboard is a cost-effective material to recycle.
    - **Newspaper:** Also known as Old News Print or ONP. It is most valued when separated from other paper types, but can be recycled as mixed waste paper.
    - **Miscellaneous Waste Paper:** Encompasses most types of clean and dry paper which do not fall into the categories mentioned above, including glossy papers, magazines, catalogs, telephone books, cards, laser-printed white ledger, windowed envelopes, paper with adhesive labels, paper bags, wrapping papers, packing paper, sticky-backed notes, and glossy advertising paper. This mixed paper has limited value in existing markets.
    - **Mixed Waste Paper:** Paper that is unsegregated by color, quantity, or grade (e.g., combination of white ledger, newsprint, colored paper, envelopes without windows, computer paper, glossy paper, etc.) Mixed paper generally sells below the price of the least valuable paper in the mix.
- **Plastics:** There are 7 types of plastics that are identified by a Society of Plastics Industry (SPI) code number ranging from 1 to 7. These numbers are usually found on the bottom of plastic containers inside a three-arrow recycling symbol. A description of each kind of plastic is presented below.
    - **PET (SPI = 1):** Polyethylene terephthalate (PET) is the most readily recyclable material at this time. It includes 1- and 2- liter clear soda bottles, as well as some bottles containing liquor, liquid cleaners, detergents, and antacids.
    - **HDPE (SPI = 2):** High-Density Polyethylene (HDPE) is currently recyclable in some areas. This class includes milk, juice, and water jugs, base cups for some plastic soda bottles, as well as bottles for laundry detergent, fabric softener, lotion, motor oil, and antifreeze.
    - **PVC (SPI = 3):** Polyvinyl Chloride (PVC, also referred to simply as "vinyl") includes bottles for cooking oil, salad dressing, floor polish, mouthwash, and liquor, as well as "blister packs" used for batteries and other hardware and toys.
    - **LDPE (SPI = 4):** Low-Density Polyethylene (LDPE) includes grocery bags, bread bags, trash bags, and a variety of other film products. LDPE is currently being recycled by some of the major retail chains.
    - **Polypropylene (SPI = 5):** Polypropylene includes a wide variety of packaging such as yogurt containers, shampoo bottles, and margarine tubs. Also cereal box liners, rope and strapping, combs, and battery cases.
    - **Polystyrene (SPI = 6):** Polystyrene includes Styrofoam coffee cups, food trays, and "clamshell" packaging, as well as some yogurt tubs, clear carry-out containers, and plastic cutlery. Foam applications are sometimes called EPA, or Expanded Polystyrene. Some recycling of polystyrene is taking place, but is limited by it low weight-to-volume ration and its value as a commodity.
    - **Other (SPI = 7):** Can refer to application which use some of the above six resins in combination or to the collection of the individual resins as mixed plastic (e.g., camera film can include several types of plastic resins). Technology exists to make useful items such as plastic "lumber" out of mixed plastic resins, but generally the materials are more useful and valuable is separated into the generic resin types described above.

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- Rubber.
- Engine oils.
- Other oils.
- Textiles.
- Tires.
- Concrete.
- X-ray films.
- Electronics.
- **Organic Waste:** There are several types of organic waste commonly recycled.
    - **Compostables:** Usually, compostable materials include food scraps and yard trimmings. Paper that cannot be recycled also can be composted.
    - **Food Scraps:** Includes grease-free organic scraps from restaurants, cafeterias, motels, and other places producing food waste. It is technically possible to compost food waste in a manner similar to yard trimmings, although additional problems with rodents and other scavengers need to be addressed. Some sates allow farmers to sterilize food waste and use it as animal feed.
    - **Yard Trimmings:** Includes landscaping debris, grass clippings, branches, and leaves. There are large-scale facilities which compost yard trimmings, producing a product that can be used for mulch, potting soil, landfill cover, and soil amendment. Also, composting can be performed directly on site or in backyards.
- **Glass:** Recycling can involve Color-separated glass. This includes all container glass that is separated into clear, green, and brown. When this glass is broken or crushed for recycling, it is called "flint," "green," and "amber" cullet, respectively. Also Mixed Color recycling can take place. This is the same as color-separated glass except clear, green, and brown glasses are mixed together. It generally has very limited market value.

To give an example of textiles or apparel, factory waste can be made into yarn or fiber, can be combined with other raw materials and made into paper, can be used as insulation material, can be burned, made into banknotes, glue and other useful products. In apparel and textile industries, "Green Marketing" efforts also force companies into using recycling as a competitive marketing tool. In effect these campaigns promote the habit of recycling among customers and promote an environmentally friendly image and help boost sales. Intimissimi as part of a global campaign started a recycling/recollection program. Similar promotional materials (adapted to culture of course) were used in different countries. With 800 stores in US and Canada American Eagles Outfitters company started a recycling and recollection effort. Boxes named "I:CO" were placed in stores and consumers were given credit for donating their clothes. Clothes are sorted into 350 different categories.

All of these activities involve the firm having a good reverse logistics infrastructure. Reverse logistics can be defined as the operations related to the reuse of products and materials. It is the process of planning, implementing, and controlling the efficient, cost effective flow of raw materials, in-process inventory, finished goods and related information from the point of consumption to the point of origin for the purpose of recapturing value or proper disposal. More precisely, reverse logistics is the process of moving goods from their typical final destination for the purpose of capturing value, or proper disposal. Remanufacturing and refurbishing activities also may be included in the definition of reverse logistics. Examples of reverse logistics can be found in:

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- Water bottles.
- Netflix (DVD movies).
- Previously mentioned textile examples.
- Soda bottles.
- Electronics (EU mandates a certain fraction be recollected by the companies).

Some concerns reverse logistics mainly deals with would be whether or not to use reusable packaging, having a returns management (RM) system, and administering the returns management systems (maybe blacklisting consumers who return too much). Also what to do with the reverse logistics flow is another problem, several options may be donating to charity, auction, selling via outlet, remanufacture, refurbish, or send to landfill. Some terminology in reverse logistics could be summarized as follows:

- **A Channel:** Primary channel of sales.
- **B Channel:** Secondary channel for goods that have been through a reverse flow.
- **Centralized Return Center (CRC):** Facility where returns are processed.
- **Design for Disassembly (DFD):** Designing a product so it can be easily disassembled.
- **Returnable Tote:** Packaging that can be reused.

SUPPLY CHAIN COUNCIL (SCC) AND APICS

The Supply Chain Council, otherwise known as SCC, originated as Supply Chain Council, Inc. The SCC was organized in 1996 by Pittiglio Rabin Todd & McGrath (PRTM) and AMR Research, and initially included 69 voluntary member companies. SCC now has closer to 1,000 corporate members world-wide and has established international chapters in North America, Europe, Greater China, Japan, Australia/New Zealand, South East Asia, Brazil and Southern Africa. Development of additional chapters in India and South America are underway. SCC membership consists primarily practitioners representing a broad cross section of industries, including manufacturers, services, distributors, and retailers. In April 2014, it was announced that the Supply-Chain Council would merge with APICS. This merger was completed on 5 August 2014 (APICS-SCC, 2015; APICS, 2015).

SCC is an independent, non-profit global association. Formed in 1996 to create and evolve a standard industry process reference model of the supply chain for the benefit of helping companies rapidly and dramatically improve supply chain operations. SCC has established the supply chain world's most widely accepted framework – the SCOR process reference model – for evaluating and comparing supply chain activities and their performance. It can be used to describe supply chains that are very simple or very complex using a common set of definitions and enabling a common understanding. It lets companies quickly determine and compare the performance of supply chain and related operations within their company or against other companies. SCC continually advances its tools and educates members about how companies are capitalizing on those tools. With membership open to all interested organizations. In August 2014 SCC merged with APICS – American Production and Inventory Control Society.

APICS Supply Chain Council (APICS SCC) is the world's largest nonprofit supply chain organization that advances supply chains through research, benchmarking, and publications. Business leaders, academia and global enterprises gain valuable insights, information and actionable data through APICS SCC's wide supply chain network, frameworks and resources. APICS SCC maintains the Supply Chain

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Operations Reference (SCOR®) model, the supply chain management community's most broadly accepted framework for evaluating and comparing supply chain activities and performance. APICS SCC, was formed through the 2014 merger between APICS and the Supply Chain Council. APICS is the leading professional association for supply chain and operations management and the leading provider of research, education and certification programs that elevate end-to-end supply chain excellence, innovation and resilience. The APICS Certified in Production and Inventory Management (CPIM), APICS Certified Supply Chain Professional (CSCP) and APICS SCOR-P certifications are viewed as the industry standard.

SUPPLY CHAIN OPERATIONS REFERENCE (SCOR)

The SCC or APICS-SCC maintains the SCOR standard which is a supply chain process reference model containing over 200 process elements, 550 metrics, and 500 best practices including risk and environmental management. Organized around the five primary management processes of Plan, Source, Make, Deliver and Return. SCOR was developed by the industry for use as an industry open standard. Any interested organization can participate in its continual development.

SCOR model has business categories including:

- **Plan:** Processes associated with planning, scheduling, and coordinating supply chain activities.
- **Source:** Processes associated with procuring material, physically receiving material, and storing raw materials.
- **Make:** Processes associated with transforming raw material into a finished product. In defense maintenance, repair, and overhaul operations, the Make category is used to model maintenance activities.
- **Deliver:** Processes associated with storing, packaging, and delivering finished products to the customer.
- **Return:** Processes associated with delivering and receiving material from a customer to a supplier, commonly called reverse logistics.
- Enable.

Based on these processes the SCOR model defines metrics at five levels, starting from strategic level all the way to transaction level. SCOR metric can be grouped as internal facing or customer facing. In terms of level 1 strategic metrics we can talk about reliability, responsiveness and agility related metrics. Internal facing metrics are grouped into cost and asset related metrics. Some examples are given below:

- **Reliability:** The ability to deliver, on-time, complete, in the right condition, packaging and documentation to the right customer, an example is perfect order fulfillment rate.
- **Responsiveness:** The speed at which products and services are provided, for example order fulfilment cycle time.
- **Agility (Flexibility):** The ability to change (the supply-chain) in order to support changing (market) conditions, for example upside and downside supply chain adaptability metrics.
- **Cost:** The cost associated with operating the supply chain, for example Cost of Goods Sold (COGS) and supply chain management cost.

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- **Assets:** The effectiveness in managing assets in support of demand satisfaction, for example cash to cash cycle time, return on supply chain fixed assets, return on working capital.

The SCOR processes are defined in increasing levels of details beginning with a description of the overall process. The processes are further separated into process elements, tasks, and activities. Each basic supply chain is a ``chain'' of source, make, and deliver execution process elements. Each interaction of two execution processes (source-make-deliver) is a defined as a ``link'' in the supply chain. Planning sits on top of these links and manages them all. The SCOR model contains three levels of process details. Level I is the top level that handles process types, these are strategic decisions. Level II is the configuration level and deals with process categories, mainly dealing with tactical level problems. Level III is process element level and is the lowest level in the scope of the SCOR model, mainly operational day to day tasks. By providing a complete set of supply chain performance metrics, industry best practices, and enabling systems' functionality, the SCOR model allows companies to perform very thorough fact based analyses of all aspects of their current supply chain (Huang, Sheoran & Wang, 2004). Table 1 provides a list of SCOR process categories.

GREEN SUPPLY CHAIN AND SCOR

The field of Supply Chain Management evolved over the years. Initially the focus was on improving collaboration between the departments, now the focus is on increasing collaboration and information

Table 1. SCOR process categories (Huang et al., 2004)

Code	Explanation
P0	• Plan infrastructure
P1	• Plan Supply Chain
P2	• Plan Source
P3	• Plan Make
P4	• Plan Deliver
S0	• Source Infrastructure
S1	• Source Stocked Products
S2	• Source Make-To-Order Products
S3	• Source Engineer-To-Order Products
M0	• Make Infrastructure
M1	• Make-To-Stock
M2	• Make-To-Order
M3	• Engineer-To-Order
D0	• Deliver Infrastructure
D1	• Deliver Stocked Products
D2	• Deliver Make-To-Order Products
D3	• Deliver Engineer-To-Order Products

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sharing between trading partners such as suppliers or retailers. Efficiency gains are made possible by the channel partners acting towards a common goal rather than trying to maximize their own profits. To help managers achieve these efficiencies the SCOR model was developed by the Supply Chain Council (now merged with APICS). The SCOR model offers metrics and best practices for each function of the Supply Chain. The managers responsible for the supply chain can use these metrics to continuously monitor their performance and identify areas for process improvements.

Likewise the concept of environmental management has evolved from the 1960s to the 1990s. Initially the focus was simply on building treatment plants and minimizing pollution resulting from factory operations. Now the focus is on minimizing pollution upstream in the supply chain, at the sources, suppliers, transportation and other components. Concepts such as design for environment, and life cycle analysis have evolved from this pollution prevention attitude.

Finally the goal of promoting a holistic approach to minimizing waste and harm to the environment in the supply chain resulted in the green supply chain and the green SCOR model. The Green SCOR modifies the original SCOR model to consider the environmental aspects as well. Table 2 provides the environmental impacts of the five SCOR processes.

SCOR metrics are aligned with five specific supply chain performance attributes defined by the model. Because SCOR was developed as a supply chain model, these attributes do not directly address environmental concerns. To effectively develop environmentally oriented metrics, the performance attributes should be linked to environmental impacts. Several options were investigated for managing the placement of environmental metrics, including creating a sixth attribute, Environmental Impact, which would have its own definition. In a report prepared by the Logistics Management Institute (LMI, 2003) it was stated "we wanted to avoid changing any of the fundamentals of SCOR, however, and needed to avoid creating an attribute that would be too easy to dismiss when performing analysis, thus negating the purpose of our efforts." As a compromise, parallel environmental definitions were established to use as a framework for developing environmental metrics. Table 3 (taken from LMI, 2003) shows the SCOR

Table 2. SCOR Process environmental impacts (LMI, 2003)

SCOR Process	Potential Impact
Plan	• Plan to minimize energy consumption and hazardous material usage. • Plan the handling and storage of hazardous materials. • Plan for the disposal of ordinary and hazardous waste. • Plan compliance of all supply chain activities.
Source	• Select suppliers with positive environmental records. • Select materials with environmentally friendly content. • Specify packaging requirements. • Specify delivery requirements to minimize transportation and handling requirements.
Make	• Schedule production to minimize energy consumption. • Manage waste generated during the Make process. • Manage emissions (air and water) from the Make process.
Deliver	• Minimize use of packaging materials. • Schedule shipments to minimize fuel consumption.
Return	• Schedule transportation and aggregate shipments to minimize fuel consumption; prepare returns to prevent spills of hazardous materials (oils, fuels, etc.) from damaged products.

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Table 3. SCOR performance attribute environment linkage (Taken from LMI, 2003)

Performance Attribute	SCOR Definition	Environmental Definition
Reliability	The performance of the supply chain in delivering: the correct product, to the correct place, at the correct time, in the correct condition and packaging, in the correct quantity, with the correct documentation, to the correct customer.	The ability to deliver the correct product reduces waste from product discards; reduces air emissions and fuel use from extra transportation for returned products. Proper documentation enables all players of the supply chain to keep better track of hazardous materials or toxins that are embedded in certain products; thus allowing them to arrange for proper storage, handling, and disposal.
Responsiveness	The velocity at which a supply chain provides products to the customer.	The environmental impacts that affect the speed of material movement, including regulatory or pollution control steps within a process.
Flexibility	The agility of a supply chain in responding to marketplace changes to gain or maintain competitive advantage.	The degree to which a firm can meet the environmental demands of its customers. This pertains to the products, their production, transportation and recyclability, etc.
Costs	The costs associated with operating the supply chain.	The costs of environmental compliance and cleanup as well as energy costs.
Asset Management Efficiency	The effectiveness of an organization in managing assets to support demand satisfaction. This includes the management of all assets: fixed and working capital.	Managing assets in a manner that reduces environmental impacts and reduces internal costs.

performance attribute definitions with their corresponding environmental definitions. The environmental definitions assist only as a guide to assist the development of metrics. They ensure the metrics for each process element are consistent; they are not endorsed for addition to the SCOR model itself.

There might be some obstacles to implementing a green supply chain in some industries, as explained by Luthra et al. (2011) "Market Competition and Uncertainty; Lack of Implementing Green Practices; Cost Implications; Unawareness of Customers and Supplier Reluctance to Change Towards GSCM have been identified as dependent variables. Lack of Government Support Systems; Lack of Top Management Commitment and Lack of IT Implementation have been identified as the driver variables. Resistance to Technology Advancement Adoption; Lack of Organization Encouragement and Poor Quality of Human Resources have been identified as the linkage variables. No barrier has been identified as autonomous variable. Market Competition and Uncertainty; Lack of Implementing Green Practices; Cost Implications; Unawareness of Customers have been identified as top level barriers and Lack of Government Support Systems as most important bottom level barrier. Removal of these barriers will be helpful in implementing GSCM in Indian automobile industry."

As it is well know some forms choose to use third party companies for running their logistics operations. 3PL logistics has grown in importance as firms like to focus on their core skills. Logistics industry itself contributes heavily to greenhouse gasses. Considerable efforts are under way in order to green the industry. Vural (2015) provides the following examples presented in Table 4 at three levels of greening for the logistics industry.

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Table 4. Examples for greening strategies of logistics service providers (taken from Vural, 2015)

	Tactical Greening	Quasi-Strategic Greening	Strategic Greening
Targeting	Participating ecological and industrial fairs to catch environmentally conscious logistics customers	Adoption of an environmental management system (EMS) for industrial customers that set this as supplier selection criteria.	Launching a new service line that offers a seamless logistics solution with lowered carbon emission impact.
Green Design	Changing the existing truck fleet with new generation trucks with low emission motors.	Transforming the delivery process into a consolidated system in order to avoid empty haulage through extensive use of information technology	Conducting a life cycle analysis for logistics services provided by the company and developing solutions for the environmentally harmful processes within them
Green Positioning	Giving an interview to a sector periodical to emphasize the green aspects of its transportation services	Communicating the number of trees that a logistics service provider plants for every unit of carbon emission that its services produce	Integrating corporate environmental objectives with values, vision and mission statements and communicating them with the stakeholders
Green Pricing	Reducing the cost of packaging through designing backhaul transport for reusable containers	Offering incentives for customers who prefer a slower but less harmful transportation solution such as intermodal transport	Initiating carbon trade with customers who save carbon emission units at one logistics service they purchase for future use in other logistics services they will buy
Greening Logistics	Changing the raw material for pallets into recyclable plastics from wood	Reducing the number of warehouses and consolidating the inventory at larger stock points	Converting all of the offices located in different parts of the world into green offices
Marketing Waste	Reducing carbon emission waste by using environmentally friendlier transportation modes such as rail and sea	Collecting and selling old truck tires to recycling organizations	Establishing a reverse logistics branch as a separate business unit and providing services through reverse channels
Green Promotion	Sending tree plantation certificates as gifts to industrial customers that exceed a specific transportation volume with the company	Issuing annual environmental performance reports via the website and other frequently followed channels	Launching a CSR campaign with a non-profit organization like Greenpeace to share a percentage of logistics service sales with the elimination of adverse environmental impacts of logistics industry accidents
Green Alliances	Cooperating with a university in order to minimize its energy usage in one of its warehouses	Making an agreement with an accreditation company in order to transform all its warehouses into green buildings	Joining green logistics associations or research groups in order to foster new solutions and innovation for environmental problems

CONCLUSION

It is getting more and more important for firms to realize that the resources the earth can provide us are limited and that production and distribution operations consuming large amounts of resources are responsible for air, land and sea pollution and global warming. One way that companies can reduce their negative impact on the environment is through the application of green supply chain and Green SCOR model. Companies are under extreme competitive pressures in order to act in an environmentally responsible way. Greening their supply chains is gaining fast ground as an alternative to achieve this purpose (Sarkis, 2006).

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Firms are generally held accountable for the labor practices and environmental impact of their suppliers as well (Bacallan, 2000). Companies may have nothing to do with the practices of their suppliers and legally they may not be challenged, however the public opinion will change against them dramatically. Controlling all parts of the supply chain upstream and downstream may prove to be a valuable technique in terms of reducing such negative backlash.

Manufacturers are increasingly recycling and remanufacturing their post-consumer products due to higher levels of public awareness, strict legislation and extended producer responsibility (McGovern & Gupta, 2011). There are also economic incentives for reusing parts or subassemblies instead of throwing them away. Recycling can be seen as a method to extract the useful content from used or nonfunctioning products. Remanufacturing is a method to bring some used parts to like-new condition. Product recovery tries to use recycling and remanufacturing in order to minimize the amount of waste sent to landfills. Disassembly systems are designed in order to extract these parts as efficiently as possible from the used parts. Issues such as modular design and identification pf parts by color codes makes the disassembly process easier and these issues need to be considered in the design of the products.

We should also talk about the long term impact of green laws passed in some western countries including the European Union. The EU has been heavily focused on the development and adoption of green laws intended to reduce or eliminate adverse environmental impact of companies (Blumberg, 2005). The initial focus was in Germany and in Northern European countries such as Norway and Denmark where environmental impact is an important issue. Much of the focus was concentrated on waste materials and recycling, but in the recent years focus has shifted to disposal of products and technology. The essence of the new laws was that the Original Equipment Manufacturer (otherwise known as OEM) would take the final responsibility for the disposal of that product. Laws could hold the OEM responsible for any physical or economics damage resulting from the improper disposal of that technology.

Waste of electrical and electronic equipment (WEEE) such as computers, TV-sets, fridges and cell phones is one the fastest growing waste streams in the EU, with some 9 million tons generated in 2005, and expected to grow to more than 12 million tons by 2020. WEEE is a complex mixture of materials and components that because of their hazardous content, and if not properly managed, can cause major environmental and health problems. Moreover, the production of modern electronics requires the use of scarce and expensive resources (e.g. around 10% of total gold worldwide is used for their production). To improve the environmental management of WEEE and to contribute to a circular economy and enhance resource efficiency the improvement of collection, treatment and recycling of electronics at the end of their life is essential. To address these problems two pieces of legislation have been put in place: The Directive on waste electrical and electronic equipment (WEEE Directive) and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive). The first WEEE Directive (Directive 2002/96/EC) entered into force in February 2003. The Directive provided for the creation of collection schemes where consumers return their WEEE free of charge. These schemes aim to increase the recycling of WEEE and/or re-use. In December 2008, the European Commission proposed to revise the Directive in order to tackle the fast increasing waste stream. The new WEEE Directive 2012/19/EU entered into force on 13 August 2012 and became effective on 14 February 2014 (EC, 2015).

Taking into consideration all of the important developments concerning green manufacturing, green marketing and a generally increased level of green consciousness it is evident that firms will receive payoffs for implementing green practices in their supply chains. The SCOR model turns out to be a useful tool that environmentally conscious firms can implement to make their supply chain greener. The most

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important reason for this is that the SCOR model provides a common supply-chain framework, standard terminology, common metrics with associated benchmarks, and best practices. The model can be used for evaluating, positioning, and implementing supply-chain application software. This paper argued that the SCOR model should consider the green supply chain and discussed issues related to the use of SCOR performance metrics for greening the supply chain. It is intended to serve as a facilitator for SCC and APICS to further enhance the Green-SCOR model and eventually make it an industry standard for environmentally conscious companies.

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KEY TERMS AND DEFINITIONS

APICS: Acronym for the American Production and Inventory Control Society, APICS is the premier professional association for supply chain and operations management and the leading provider of research, education and certification programs that elevate supply chain excellence, innovation and resilience.

DFE: Acronym for Design for Environment, DFE-design for environment-involves designing products from recycled materials, using components that can be recycled, designing a product easier to repair than discard, and minimize unnecessary packaging.

EPR: Acronym for Extended Producer Responsibility, EPR-extended producer responsibility- producers are responsible for their products even after their useful life.

Green SCOR: An extension of the SCOR model to cover environmental areas and sustainability issues for the logistics and production related areas.

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LCA: Life Cycle Analysis is a technique to assess the environmental aspects and potential impacts associated with a product, process, or service, by (1) Compiling an inventory of relevant energy and material inputs and environmental releases, (2) Evaluating the potential environmental impacts associated with identified inputs and releases, (3) Interpreting the results to help you make a more informed decision.

LCEA: Life cycle energy analysis is an approach in which all energy inputs to a product are accounted for, not only direct energy inputs during manufacture, but also all energy inputs needed to produce components, materials and services needed for the manufacturing process.

Recycling: Series of activities by which discarded materials are collected, sorted, processed and used in the production of new products.

Refurbishing: To renovate and recondition a used product to a certain level, perhaps not as high as in remanufacturing.

Remanufacturing: To disassemble a used product completely and inspect all modules and parts. Worn out parts are replaced to bring the quality standard of final product to like-new condition.

SCC: Acronym for the Supply Chain Council now merged with APICS.

SCM: Acronym for Supply Chain Management, Supply chain management involves all facilities, functions, and activities associated with flow and transformation of goods and services from raw materials to customer, as well as the associated information flows.

SCOR: Acronym for Supply Chain Operations Reference, a set of guidelines providing metrics and best practices for supply chain functions of procurement, production, delivery, and return.

Sustainable Operations: Performance measures and continuous improvement are the components necessary to translate sustainable corporate strategy into sustainable operations, using an integrated quality, environmental and safety management system. Sustainable operations entail total quality management, sustainability, environmental stewardship and process safety.

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Chapter 18
Participation Framework to Sustainability:
The Undercurrents in Bottled-Water Production and Consumption

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ABSTRACT

The topic of bottled water is particularly timely since water crisis and waste plastics are shifting from one of problem-framing to what is much more concerned to climate agenda. As plastics are everywhere to make life possible for a faster and convenient pace of society, bottled water has become one of the most disposable products to be consumed and disposed of, on a regular basis, both at and away from home. These eventually translate to consumer wastes causing a profound impact to the environment. The more bottles mean more greenhouse gases from production, transportation, waste bottles management, including fresh water supply. These adverse impacts are compounding a framework to justify as to how producer and consumer apply, individually and within the whole product life cycle, to sustainable consumption and production practice (SCP).

INTRODUCTION

The world has been pushing the planet away from sustainability. Humanities are shaped their lives on materially intensive economies and consumerist lifestyle regardless of living in a finite world. Many disposable products are developed to make life possible for a faster and convenient pace of society. Bottled water has become one of the most common plastic products to be consumed and disposed of, on a regular basis, both at and away from home. These bottles eventually translate to consumer wastes (Amano & Ness, 2004; Chamornmarn, 2008; Huber, 2010). Water and plastics are two major materials of bottled water. More bottles mean more greenhouse gases from production, transportation and waste

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management, including continued risk of ecological vulnerability and water conflict with commercializing a public resource. Without greater understanding of how to produce and how to consume bottled water in sustainable ways, it may even worsen the most disagreeable impacts to the planet and future livelihoods.

Thailand was ranked near the top in bottled-water consumption in Southeast Asia and is among the top 9 consumers globally (Rodwan, 2010) In global context, bottled water has been the top end-used application of Polyethylene terephthalate (PET) plastic since its introduction into beverage packaging (Willett, 2003) According to the survey during 2008-2010, bottled-water business in Thailand maintains annual growth by 15 percent in total volume terms, with the consumption of 40,000 tons of PET plastic and 2.4 billion liters of water (Chamornmarn, 2008; Euromonitor International, 2010; Ratthanin, 2010).

The bottles can constitute various pollutions to air, water and soil quality as carbon substance is the key element of PET resin formulation. Increasingly, the ways to capture surface water supplies and underground sources are compounding the problem of water inadequacy into environmental degradation. Precisely, this chapter deals with an evidence-based case of sustainable consumption and production (SCP) implementation for PET-bottled water. Consumers' environmental awareness is evaluated whereas an input-output approach to bottling system is included to address the role of bottlers in an SCP. The undercurrents of bottled-water production and consumption are therefore closely examined for filling the gaps between socio-economic development and environmental protection.

The presumption is that if enough bottlers implement sustainable production whereas more and more consumers are aware of sustainable consumption, they can drive change towards a sustainable consumption and production of PET-bottled water. The guiding research questions are as to

1. Whether the bottled-water businesses and the consumers perform the SCP for PET-bottled water?
2. How the practice is? and
3. What the differences are in terms of resource efficiency and impact reduction?
4. How is an LCM approach contributed to the SCP success?
5. What is the most practice for bottling drinking water done in Thailand?
6. What are the environmental and health consequences occurred from PET bottles?
7. Is there any different impact compared between virgin and recycled bottles?

BACKGROUND

Sustainable Consumption and Production

In 2002, all the nations facing the climate crisis agreed not only to develop a 10-year framework of the SCP programs (the Marrakech Process)[1], but also had the SCP addressed as a prerequisite for sustainable development. The vision of sustainability was first referred to in *Our Common Future* in Bruntland Report defining sustainable development as a pathway to meet the present needs without compromising the ability of future generations to meet their own needs (Elliott, 2006).When environment lost capacity to continuously support the overexploitation placed upon it, a stronger and sensitive linkage between sustainability and socio-economic growth is truly required (Akenji & Bengtsson, 2009). Hence, sustainable practices in resource efficiency from less material consumption and less pollution have been universally addressed to handle the consequences of economic globalization and bring about sustainable development (Jones, Hillier, & Comfort, 2014).

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Definitions of SCP have been internationally discussed in many respects. SCP is linked to the adoption of sustainable lifestyle to meet the increasing demand for goods and services of both present and next generations, while improving the level of emissions and energy used or released over a product lifecycle (Giljum, Burger, Hinterberger, Lutter, & Bruckner, 2011). SCP implies the ways that humanities who live in a finite world protect the planet away from sustainability (United Nations Department of Economic and Social Affairs [UNDESA], 2010). SCP becomes an effective framework for improving resource efficiency and impact reduction occurred from the production and consumption of products and services (Cellura, Longo, & Mistretta, 2011). As such, SCP is not only essential for decoupling socio-economic growth from environmental degradation, but is also behind the success of sustainable development (Economic and Social Commission for Asia and the Pacific [ESCAP], 2011; United Nations Environment Programme [UNEP], 2015).

Many empirical studies exhibit the outcomes of SCP approach. The interaction analysis of consumption and production in China revealed that consumer's demand for energy-intensive product was the driving force of pollutant emissions (Liu, Wang, Yang, & Shi, 2010). It was substantial to apply the SCP framework for identifying energy and environmental impacts from household consumption (Cellura, Longo, & Mistretta, 2011; Zhao, 2009). An SCP offered better solution for impact management and sustainability objectives (Tukker, 2008). Resource efficiency and pollutant emission reduction were the basis of energy sustainability under the SCP domain (Sampattakul, 2010).

In completing the SCP of products and services, the roles are shared among four parties: producer (business), consumer, government and other stakeholders like retail and distributer (ESCAP, 2011). Businesses and consumers can apply individually and within the entire product life cycle for a reach of SCP (Hoff et al., 2014; Parent, Cucuzzella, & Reveret, 2013). The contributions involve responsible industrial development from supply side as well as an individual change to sustainable lifestyle in demand side (Brodhag, 2010; Raskin, Electris, & Rosen, 2010). State entity is a regulator to deliver a top-down policy to the concerns, facilitate the treatments and enforce the law and regulation. The other three elements those from supply and demand sides stand for bottom-up participation. Businesses can respond to the SCP of PET-bottled water at the early stage of product design, during bottling processes, product distribution, or even extend to the end of the useful life of product (Akenji & Bengtsson, 2009). Consumers can adopt the SCP through the patterns of use and waste handling.

A trade-off between resource efficiency and impact reduction targets is referred to in every step of SCP implementation because the valuation of resource efficiency is actually linked to a reduction of environmental impacts. Thus, the approach to impact prevention and reduction is often discussed as a component of resource consumption practice.

1. **Resource Efficiency:** On an everyday basis, natural resources are extracted and transformed to provide goods and services for supporting all social and economic activities. When people use fewer resources and generate fewer emissions, they minimize natural resource consumption as well as maximize its all benefits (Niccolucci et al., 2011; Prakash, Yogesh, Viraja, & Shilpa, 2015). Resource efficiency could be expressed in accordance with the domestic environment and import materials and goods. Consumption efficiency is based on a reduction of resource intensity, material and product flexibility, utilization of all resource benefits and applying saving technology (ESCAP, 2011). The adoption also deals with possibilities of reuse, recycling and recovery approaches, reduced risk to resource scarcity, lower environmental cost on less wastes and pollution generation and lower prices for materials and products (Liu et al., 2010; Pogutz & Micale, 2011).

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Eventually, resource efficiency can deliver the rebound effects not only to increase a demand for the goods and a growth in resource consumption, but also contradict efforts to save resources for greater efficiency.

2. **Impact Reduction:** Treatment on impact reduction implies the ways of utilizing resources and processes to eliminate pollutants and wastes generation both at the source and within the use (Vasami, 2010). Environmental and human health impacts are caused by both natural events and human activities those involving with procedures in producing and consuming goods and services. Reducing environmental impact profile includes the attempts to conserve finite resources and prevent natural resource depletion together with decreasing possibilities of greenhouse gases emission, pollutants and wastes generation (Brodhag, 2010; Veshagh & Obagun, 2007). Additional is energy used or released over the life cycle of goods and services. Potential impacts could decrease if businesses prioritize clean technologies in producing goods and services, whereas societies are aware of the precedent consumerist-lifestyle (Raskin et al., 2010; Termpittayapaisith, 2011).

PET-Bottled Water

1. **Life Cycle Management:** On a linear basis, a product is developed, produced, distributed, consumed and disposed. A product life cycle management (LCM) is very close to a reduction of carbon and ecological footprints by minimizing socio-economic burdens as well as maximizing environmental value and sustainability (Power, 2009). When LCM is reconciled with products and services, a set of activities and processes is applied to the whole product life cycle for improving impact reduction, environmental protection and sustainability (Ramani et al., 2010). LCM helps in improving the impact profile generated from every interaction with environment, directly or indirectly, both at present and in future (Harris, 2011; Hertwich, 2005; Kuczenski & Geyer, 2010).

LCM can be diversified to three perspectives: a cradle to gate, a cradle to grave, and a cradle to cradle (DuPont, 2011; Gironi & Piemonte, 2010) A cradle-to-gate LCM involves with the stages of material acquisition and manufacture as belonging to inputs and outputs from production operation in factory only. A cradle-to-grave LCM, which is an extension of the cradle-to-gate boundary, includes contributions to the retail, the use and the end of the useful life of the product. When businesses possess a partnership with customers and suppliers, the LCM is implemented from a cradle of product to a grave by thinking about sustainable processes to access sources of raw materials, to deliver materials and products and to foster environmentally-friendly practices for the end-of-useful life management. Towards a cradle-to-cradle LCM, the involvement with all stages in a product life cycle is required so that all wastes are sustainably discharged and recovered for starting a new product life cycle.

In identifying potential impacts from PET-bottled water, the LCM begins with an initial stage of material extraction (plastics and water) to material processing (productions of PET bottles and water disinfection), product manufacture (bottling system), distribution (retail of bottled water), use and reuse (bottled water consumption) and end-of-useful life management (waste bottles management) (Nestlé Waters North America, 2010). A profile of impact inventory relates to certain amount of finite resource, a series of transformations and releasing emissions of diverse natures from landfill, burning, incineration, recycling and recovery used for handling the wastes (Hauschild, Jeswiet, & Alting, 2005; Huber, 2010; Song & Hyun, 1999; Takahashi, 2010).

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In view of many researchers, toxic substances, such as antimony, aldehydes and carcinogenic chemicals, are reasoned to health consequences caused by improper use and multiuse (Schmid, Kohler, Meierhofer, Luzi, & Wegelin, 2008; Shotyk & Krachler, 2007; Westerhoff, Prapaipong, Shock, & Hillaireau, 2008). The cause relates to direct contact between mouth and bottle after leaving it in sunlight exposure at longer time because time is dominant factor to the organic substances leaching out from PET bottle (Mutsuga et al., 2006). Logistics and transportation in distribution management are also the inclusive factors to reach efficient use of fuel energy and carbon dioxide emission reduction in the LCM of PET-bottled water (Amano & Ness, 2004; Coelho, Castro, & Gobbo, 2010; Foolmuan & Ramjeeawan, 2012; Huber, 2010; Takahashi, 2010)

a. Life cycle inventory of PET bottles. Basically, PET resin is a thermoplastic condensed between ethylene glycol with terephthalic acid forming long chains of repeating units of carbon, oxygen and hydrogen. When producing PET bottles, the resins are melted and polymerized till feasible for a pre-form injection in latter conjunction with a blow molding process. The processes consume both materials and energy while emitting much of chemical substance, including dust and debris of pollutions and acetaldehyde from the polymer degradation (Foolmuan & Ramjeeawan, 2012). Much of the fossil fuel used in the PET bottle derives from feedstock energy, which is truly bound within the product (Zhang & Kimura, 2007).

Referring to ISO 14040[2] and 14044[3], life cycle inventory (LCI) deals with the interpretation of impact categories. It means LCI implies all input-output unit processes quantified along with a product system so that environmental impact profile can appear in classification and characterization (Gironi & Piemonte, 2010). Hence, LCI refers to a compilation and quantification of input-output data against the environmental profile of a product. For examples, the impact category of global warming represents the inventory item of carbon dioxide (CO_2) while cadmium (Cd) and lead (Pb) inventories stand for the impact category of eco-toxicity and human toxicity when exposed to toxic substances.

As with the data in many researches, the LCI of PET bottles increased to the highest level when 100 percent of used bottles went to landfill (Takahashi, 2010) The waste bottles approximated 14 percent of post-used bottles were recycled (Huber, 2010) The balances ended up in landfills, lakes and streams leading to many impact consequences. PET bottles could be recycled in multiple times and into a variety of end products (Hurd, 2000) The production processes and transportation of PET polymerization and PET bottles generated higher impact on global warming than did the categories of nonrenewable energy, acidification and eutrophication (Gironi & Piemonte, 2010).

b. Recycled PET. Among all plastics types, PET resin is defined as the most recyclable plastic corresponding to the symbol of number 1 in the loop of chasing arrows. In early 1978, PET bottle was first recycled into a fiber product (Willett, 2003). It is evident that recycled-PET plastic is possibly used as 100 percent virgin material for new applications as the scraps from PET bottles could recapture resin properties for a second life either in bottles or new applications (Coelho et al., 2010; Shen, Nieuwlaar, Worrell, & Patel,2011; Vakili & Fard, 2010). In case of bottle to bottle application, the outcomes are based on the efficient use and cost effectiveness, except environmental profile (Amano & Ness, 2004; Vasami, 2010).

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LCI of recycled PET can be changed towards many conditioning factors those including recycling rates, recycling system, sorting process, modes and distances for transport of the wastes (Vakili & Fard, 2010). Recycled PET could be optimized within three recycling trips. The multiple-recycling trips (the useful number of lives of the material) also influenced on the LCIs of both fuel energy and electricity used for processing operation and greenhouse gases emissions (Gleick & Cooley, 2009; Song & Hyun, 1999). However, there was no difference of CO_2 released from producing 10,000 units of 12-ounce PET bottle compared between virgin PET and a mix of recycled resin (Franklin Associates Ltd [FAL], 2010a, 2010b). It was revealed that the recycled resin alternated better consequences than the reuse, in terms of cheaper recycled cost and easier recycling process (Gironi & Piemonte, 2010)

c. Recycling system. Recycled PET is actually processed by two methods: mechanical recycling and chemical recycling (Hurd, 2000; Ida, 2006). Mechanical recycling is defined for material recycling, whereas chemical recycling serves feedstock recycling. Both methods have a typical processing sequence beginning with a collection and transporting, sorting and separation, and reprocessing.

In mechanical system, PET plastics are crushed and grinded into small flake for further contaminants separation. The flakes are washed and dried before feeding into an extruder where they are heated to melting state and converting into recycled PET manufacturing.

Feedstock recycling, which waste PET is chemically recycled, refers to a de-polymerization process, in which plastic polymer is broken down into the constituents-monomers. There are three main methods in PET chemical recycling: glycol for glycolysis, methanol for methanolysis, and water for hydrolysis (Vakili & Fard, 2010). In identifying the best device, the results of desired products yield and environmental impact profile are first accounted. Particularly, the category of global warming is the major impact from chemical recycling because the inventory of CO_2 derives from fuel-related emissions, not process emissions (Hurd, 2000; Vasami, 2010).

Mechanical recycling is best to recover the waste bottles for textile and yarn applications whereas the bottle application is limited to chemical recycling. A standardized procedure also influences to have waste PET recycled effectively. Development of recycling technology for waste bottles is still continued in demand to be reconciled with the growing market of PET-bottled water.

2. **Bottling System:** Upon a basis of bottling processes, the inputs of plastics and water resources are required, including utilities of electricity and fuel energy, while delivering the outcomes of bottled water and the impacts. The bottling system featured in Figure 1 displays the used resources and the outcomes against the input-output approach to PET-bottled water. Bottling system of drinking water in PET container is technically classified as the open-loop and the closed-loop processes. The difference is that the close loop begins with producing PET stretch-blow-molding bottles from PET pre-forms while the open loop sets the production of PET bottle apart.

Towards the closed-loop process, production lines of bottles manufacture and filling stage are automatically connected together. In filler room, the closed loop begins with using PET pre-forms appearing in tube-formed objects as intermediate materials to produce the formed-bottles. Then, the bottles fed by electronically-automatic system are moved forward to dust detection and elimination with an infrared light scanner and a high speed blower before filling. The infrared light is also equipped to limit

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the volume of filled water in every bottle prior capping and labeling stages. The closures and labels are generally sourced from plastic molders, instead of the bottler's own production. Label application is an intermediate step following capping stage in the closed-loop process.

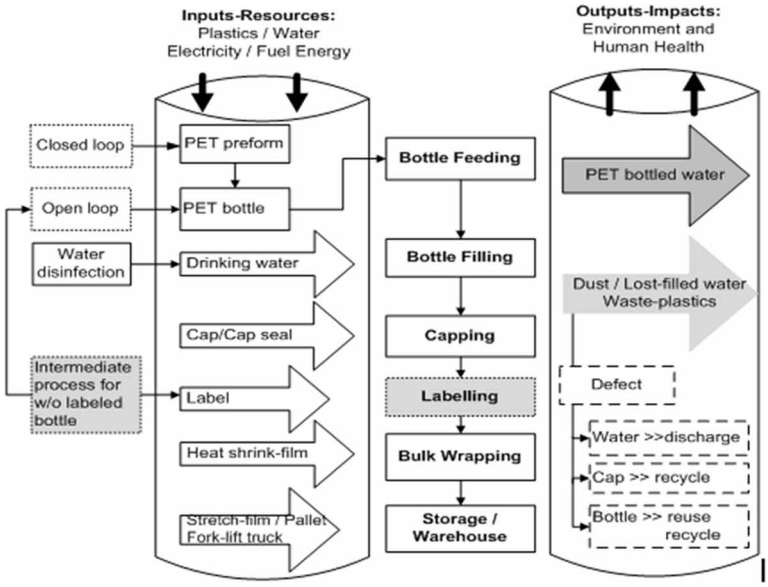
The open loop is a semi-manually-conventional process, in which returnable bottles are possibly refilled. The loop initially proceeds with a feeding of the formed-bottles, which are usually hand fed onto a conveyor to be filled with drinking water passing through orifice at a continual rate of flow. As would be true, the open loop produces the lost-filled water approximates 30 percent compared to the close loop. On the other, the bottlers investing in the open-loop process can both exclude PET bottles production from bottled-water business, or separate filling and capping stages (filler room) from labeling and bundle packaging. In case that closure wrapper is specially required, the open loop enables a separate operation of cap-sealing. It means the open loop allows the bottle to be labeled either before or after filling step. The water is also shared for cleaning the inside of the bottles before filling.

ENVIRONMENTAL AWARENESS

Environmental impacts and human health risk would decrease when societies are aware of the precedent consumerist-lifestyle for daily pleasure. Humanities generally behave to satisfy the opportunity to consume and the sense of fulfillment and satisfaction upon the experience of social life. Consumer behavior is therefore mediated through the consumption and production practices those certainly covering emissions, energy and water use, and waste produced.

When unsustainable consumption and production pattern stands out in public realm, environmental awareness becomes a stronger and sensitive device to sustain the planet. A consumption and production pattern exhibits the degree to which the market economy has shaped the surroundings and eventually

Figure 1. Bottling system of PET-bottled water on the input-output approach
Source: Author, doi:10.4028/www.scientific.net/AMR.807-809.2897



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the way of living (Shobeiri, 2005). In contemporary society, humanities are induced in adjusting their lifestyle towards low-carbon pattern by consuming reduced material and less energy of functional utility. This is due to the fact that consumption activities are demanding nature's resources and producing greenhouse gases at a faster rate than nature regenerated and reabsorbed (Liu et al., 2010; Sze, 2010)

Consumer behavior is not simply about the act of purchase but is rather a thoroughly cultural phenomenon that serves to legitimate capitalism on an everyday basis (Poonuchaphai, 2010) . The social experiences eventually constrain a wider recognition of sustainable lifestyle. When asked to rank what was most important to Thai people aged 13-18, playing LINE application in smart phone came first. Saving environment employed the lowest interest (Suwajittanont & Chai-ittipornwong, 2011). A sense of responsibility to care, protect and enhance environmental quality can be concerted to people if more and more environmental issues are documented through mass media, with the eco-journalism basis those relevant to verifying, informing, educating and giving a warning to news receivers. (Kaweeya, 2006).

Humanities are actually shaped their lives on social action with various factors, including the external influences of norms and values as everyone wants to be inside the mainstream behavior (Berger & Corbin, 1992) Level of environmental awareness can interpret as to how people view themselves on social agenda. The more people have education and information, the more they could account for environmental protection and a change in behavioral perception (Larijani, 2010). Environmental awareness can be expressed in the manners of environmental prevention and protection on waste and pollutant emissions, coupled with the increasing efficiency in resource consumption (Harris, 2011; Peattie, 2010). A new kind of consumers' relationship with the public realm could be constructed if environmental protection and management are truly converged with economic and humanistic values those within bio-geophysics, way of thinking and social interaction in a social system (Flor, 2004).

In psychological view, the stages of covert and overt activities and experiences, which individuals engage in their behavioral patterns, are conceptualized for an interplayed set of thought and action (Peacocke, 2006). A conceptual form of human behavior is actually linked between perception and action. Person's actions are expressed with the intention to environmental protection can represent an individually-environmental behavior linked between areas of action and the readiness to act (Brodhag, 2010). Thus, the gap between bodily action and mental action belongs to the interplay of awareness and action against consumption behavior.

In business scale, the institutional attributes to environmental issues deal with a corporate social responsibility expressed in the formats of policy, plan, project and activity. The responsibilities determine the level of environmental awareness consistent with reducing unnecessary resource depletion and sustaining resource benefits together with creating social value along a product LCM (Power, 2009; Schultz, W., Nolan, J.M., Cialdini, R.B., Goldstein, N.J., & Griskevicius, V., 2007). When businesses are conscious to reducing environmental disruption and integrating environmental care into a corporate vision, a product value chain is simultaneously reconciled with business sustainability (Po gutz & Micale, 2011; Raskin et al., 2010).

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MAIN FOCUS OF THE CHAPTER

Potential Impacts from PET Bottles

Within characteristics of food container, PET bottle is considered a safe, healthy and convenient packaged food product as much as a more sustainable container, in terms of CO_2 emissions and energy consumption, compared to aluminum can and glass bottle (Feron, Jetten, De Kruijf, & Van Den Berg, 1994; Lehmann, Vilaplana, Strömberg, Suliman, & Rodriguez, 2005). In this section, the author set an assessment against a content ratio of resin quality for greater understanding of the impact variation from PET bottles. A tested scenario was simply arranged to three parameters: virgin PET resin, half-by-half between virgin and recycled resin, and 100 percent recycled PET resin, with functional unit of one kilogram of 500-milliliter bottle. As it was an additional part in this chapter, the parameters of virgin resin and recycled PET were based on the literature LCIs from the SimaPro 7.1 software supported by the National Metal and Materials Technology Center in Thailand. These data were computed to support the half-by-half parameter (a mix ratio of virgin-PET resin and recycled PET by 50 percent for each). Three potential impacts were focused on the categories of global warming potential (GWP), eco-toxicity and human toxicity. GWP was expressed as kg CO_2 eq. inventory (kilogram of CO_2 equivalent), while contamination of para-dichlorobenzene (1,4-DB) substance in fresh water aquatic, marine aquatic and terrestrial ecologies were translated to inventory data of both eco-toxicity and human toxicity.

As drawn in Table 1, producing PET bottles with the virgin PET delivered better result in impact reduction of every category whereas the recycled PET valued for finite resource efficiency. The highest amount of GWP (2.8108 kg CO_2 eq.) came from the recycled PET, while the mix ratio was highly sensible for the impact categories of eco-toxicity (675.5046 kg 1,4-DB eq.) and human-toxicity (0.9852 kg 1,4-DB eq.). Towards the eco-toxicity result, the marine aquatic resource was much more vulnerable than did the fresh water aquatic and terrestrial ecologies, in all parameters. It was obvious with regard to the test that PET bottles from 100 percent of virgin resin exhibited better environmental profile. Nevertheless, the discrepancy in the parameters is possibly due to quantities and types of input resources; material and utilities used upon the recycling methods. Either are selection of assigned functional unit and the coverage on PET recycling method. Sources of CO_2 emission those including process energy, transportation and non-process emissions during material management can also differ the impact profile of recycled PET. The chemical recycling requires a lot of energy in spite that there is no energy possibly recovered by landfill. The impact category of GWP between the energy use in landfill operation and the recycling system are different. That's why waste-PET bottles are mostly valuable for recycling to new applications of textiles, sheeting for vacuum packaging, office stationery and detergent bottles, instead of bottle to bottle in drinkable water application. However, LCI data varies within five percent is not considered significantly different (FAL, 2010a).

Role of Bottlers in SCP

As could be expected, bottled-water manufacturing is one of the fastest-growing businesses in Thailand. The business value approximates USD 300 million has the growth rate maintained by 15 percent since 2007. Among 6,000 bottlers throughout nation, 65 percent of the market is captured by four leading brands consisting of two local entities; Crystal and Singha, and two international brands; Namthip and Purelife. The remaining 35 percent are shared by the bottlers regarded as small and medium enterprises (SMEs) that partly own their brands and also provide bottling service as an original equipment manufacturer (OEM).

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Table 1. A test scenario of potential impacts from PET bottles based on content ratio of resin quality set for three parameters: virgin PET resin, half-by-half between virgin and recycled resin, and recycled PET

Parameters (% of Quality Resin)	Impact Sensitivity (Functional Unit:1 kg of 500 ml-PET BOTTLES)					
	GWP ($KgCO_2$ eq.)	Eco-toxicity (Kg 1,4-DB eq.)				Human-toxicity (Kg 1,4-DB eq.)
		Fresh water aquatic	Marine aquatic	Terrestrial	Total	
Virgin PET	0.0494	0.0014	11.5351	0.0003	11.5368	0.0088
Virgin + Recycled 50:50 (%)	2.7364	0.0962	675.3979	0.0105	675.5046	0.9852
Recycled PET	2.8108	0.0033	544.8582	0.0022	544.8637	0.9210

PET-bottled water has widely dominated Thai consumers, and caused the decline in returnable glass bottles and the opaque bottles made of high density polyethylene polymer (HDPE bottles). The SME bottlers are most likely to produce a 500-milliliter-water weighted bottle. Either are the individual cups by 150 milliliter, or smaller bottle sizes of 330-350 milliliter. The larger pack sizes of 1000-1500 milliliter serve the highest sale volume of leading brands.

It is interesting that varieties of sustainability framework are particularly addressed for bottled-water businesses in Thailand. The measures to say exclude the FDA registration and good manufacturing practice (GMP) certification as they are mandatory bottled-water manufacture. Global quality certifications, such as ISO (International Standards Organization) 9001 for quality management system, ISO 14000 for environmental management, ISO 22000 for food safety and ISO 26000 for social responsibility, are accounted by all leading brands and some SME brands.

1. Resource efficiency:
    a. Plastics. In PET-bottled water business, efficiency in plastics consumption mostly begins with a lighter-weight bottle. A bottle with thinner wall, shorter neck (from 18 to 12 millimeter) and narrow cap (from 32 to 28 millimeter) is primary designed for reducing PET plastic consumption. PET-bottled water can employ a sustainable design or design for environment from the initial stage of development of bottle to bottling process and logistic operation. In drinking water business, the design in bottle shape and bottle body together with bottling process really compromise with the efficiency in reducing waste-in-process plastics, which can be caused by several threats, such as bottle-mold quality, uneven thickness, deviations in the spiral neck, bottle clarity, leakage and off-centered bottoms.

As results, the efficient use of plastics material is initiated from bottle-mold preparation. The design in bottle neck is also advantageous for common cap of all bottle shapes and size. Included is increasing toughness of bottle bottom for better stiffness, which is beneficiary for multi-layer stacking and storage of bundle packaging normally holding twelve bottles. The design for multi-layer stacking can helps in decreasing trip of distribution that affects reduced fuel energy consumption and distribution cost.

Among the SMEs, a device of bottle-shape harmonization across brands is another efficiency to enhance sustainability in plastic resource consumption. The leading brands do the contrary. The varieties of bottle shape and sizes, which are not valued by the SMEs, are used among the leading brands to manage

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consumer perception to brand identity and satisfy the requirement at all aspects. Neither leading nor SME brands own the accessory production of closures, films, labels and bulk-wrapper though some SMEs experience in plastic molding. Selection of bottling process also affects the success of SCP implementation for PET-bottled water. The open loop is generally worthwhile for the brands familiar with plastic injection and blow-molding production. They can utilize their knowledge and skills to establish a cross-sector business regarding plastics injection and blow-molding and bottled-water manufacturing service.

Additionally, the most lighter-weight bottle approximates 12-13 grams for reduced plastics consumption by 30 percent and easier squeezing after use for reduced space of landfill volume. This green bottle is neither attractive nor feasible for the bottlers, except a leading brand. Due to the thinnest wall and the slightest bottle bottom, these special bottles require additional investment in nitrogen feeding connected to the bottling system. The process deals with an installation of gas feeding system and nitrogen gas reserve in a tank those requiring a more safety operation.

Recovering waste-PET bottles to new applications is less taken. The interest in advancing the recycling technology is quite low, too. A huge demand for PET-bottle scraps can distort the bottlers' interest in renewable PET technology. Thus, waste PET is less frequently recycled among Thai bottlers, with remarking on the relevant laws and regulations prohibiting use of recycled plastics for food packaging. As waste plastics are a major concern in the bottling system, amounting to 2.0 percent of all materials, the limitation of waste-in-process bottles is arranged at 0.2-0.3 percent. These wastes are sorted and sold to recycling agents since these flakes are mostly required for export market in China and India. Indeed, there is no difference between the leading brands and the SME bottlers in handling waste plastics from bottling system. The wastes are directly turned to money, instead of renewal approach.

b. Water a rapid growth of bottled water business is truly related to depletion of surface-water supplies and groundwater sources. The leading brands in Thai market mainly use underground water to produce bottled water while the SMEs bottle tap water. Efficiency in water resource is not the major concern among Thai bottlers because of the low cost of water acquisition. Nevertheless, tap water is the option providing insurance against shortages, as does a reserve of underground water that should supply the companies for approximately five years.

The open loop processes 65 -70 percent drinkable water ends up in the bottle. The rest is wasted. The lost-filled water can be reused for chilling the process before drainage, however, it cannot be recirculated to clean empty bottles or bottled and sold. The bottlers using the open loop should be aware of the substantial waste of drinkable water, which can reach 30-35 percent, which can be reduced through the close loop.

The other sensible point of water efficiency in bottling system is that the water is both a final product and a cleaning product. The open loop consumes drinking water for cleaning the inside of the bottles while the close loop processes with a high-speed blower. The discharged water is treated as clean is not appropriate for filling bottles under food-contact regulations. The closed-loop process, which seems newly for Thai-based bottling manufacturing, is equipped for all the leading brands. The SMEs, including every branch of leading brands, are common to the open loop. However, it would be inconceivable for thousands of the SMEs to switch to a closed-loop system.

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2. Impact Reduction:
    a. Plastics. The amount of PET plastics used in bottled-water businesses in Thailand is quite interesting. The SME bottlers consume PET plastic amounting to 120 tons per month, while the leading brands approximate 400 tons, excluding the peak period in the hot season (when consumption reaches 500 tons per month). It is evident that reduced use of plastics and reduced defects are major concerns to the bottlers. Except for a multi-plant policy taken by all leading brands, a truck-loaded management is accounted by the manufacturers who prefer the efficiency in reduced energy consumption and unit cost reduction to impact reduction from uses of electricity and fuel energies.

Most bottlers assert that the bottling system generates no CO_2 emissions to the air, water and soil. In case of PET pre-form blow-molding in the filler room, the closed-loop process is equipped with a cleaner technology because it enables use of electrometers and infrared device for debris and dust elimination, instead of emitting to the air. For the open loop, the bottles are supplied by PET-bottle manufacturing. The outsource supply becomes an excuse by the bottlers that no emission is generated in the open-loop bottling system.

Based on LCM perspective, the attempts to impact reduction direct to a cradle-to-grave module. The cap-seal wrapper is modified to every bottle to ensure a primary use in health concern. Additional is the communicated information via the bottle label about sustainable use for environmental protection from the waste bottles. However, recycling the post-used bottles for new purposes is slightly accounted, either encouraging the consumers or by the bottlers themselves. A legal constraint on using recycled material for food packaging, enforced by the Food and Drug Administration (Thailand) is addressed for a low literacy in recycling technology in bottled-water businesses. Precisely, reduced use of plastics and reduced defects in bottling system that are the major concerns to the bottlers can be converged with the corporate contribution to environmental prevention and protection.

    b. Water. Bottled-water business requires a shift to the SCP. In Thailand, most bottling plants are located in the provinces along the Chao Phraya River and its tributaries that can cause the profound impact on ecological system. The water is mostly extracted from underground water or artesian wells, with a fee paid per cubic meter to the office of municipal affairs or to the Ministry of Natural Resources and Environment at USD 0.40 per cubic meter for the right to capture the water. The water of any quality discharged from factories in the provinces near the Chao Phraya River and its tributaries must legally undergo filtration before drainage. Increasingly, PET-bottled-water manufacturing is simply established for the SMEs because they bottle tap water, with a normal filtration.
    c. According to unsustainable water resource management spread over the country for many years, the surface water supplies are currently limited as well as groundwater sources are highly vulnerable to depletion. The belief that the discharged drinking water is neither hazardous nor wastewater is not considered justified by those aware of the water crisis.

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Consumer Behavior of SCP

Consumer behavior towards the SCP of PET-bottled water is evaluated by the strength of agreement to avoid the manners, which are known to be damaging to the environment. The analysis contains comparative statements about the contributions to improving greater efficiency in consuming PET-bottled water and decreasing the impact from the post-used bottles.

In most cases, Thai consumers moderately perform the SCP, with more emphasis on the resource efficiency rather than the impact reduction. In their opinion, PET-bottled water is purified, clean and safe for drinking. Increasing use of tap water is totally declined due to negative perception of the impurity. Meanwhile, the refrigerated water from coin-machine and freezer services, which is tap water, is considered appropriate for drinking due to a filtration in chilling step. The convenience in use of PET-bottled water, either in or away from home, becomes the normal practice in working days and during shopping and travelling.

The idea of zoning gas station and shopping mall is most credited for improving waste bottles management. A forbidden use in the offices is totally declined, so does the enactment of the Polluter Pays Principle (PPP) when asked to treat them as the SCP behavior. It is interesting that business sector is expected by nearly all consumers to take the leading role in the SCP development by incorporating environmental-awareness rising to product campaigns. Two histograms as shown in Figure 2 and 3 present consumers' performances in between resource efficiency and impact reduction for bottled water, respectively.

1. **Resource Efficiency:** Drinking up a whole bottle of water is considered best effective to resource efficiency target; otherwise, consumers tend to choose a smaller pack size of 330-350 milliliter that fits to demand, so does taking the leftover for further use. Consumers also like to optimize all product benefits and minimize resources used with the reuse. Additional are preparing personal flask when away from home and avoiding the use of bottled water for coffee, tea and cooking. Selling post-used bottles to junk shop is the preferable way for handling the wastes bottles, rather than recycling approach. According to consumers' feedback, a change to tap water is neither performed nor considered valuable for increasing efficiency in bottled-water consumption.
2. **Impact Reduction:** Thai consumers are willing to accompany the post-used bottle until finding a litterbin but hesitate to recycle the waste bottles for decreasing impact generation. In their opinion, changing to ordering glass bottles helps in decreasing the impacts from PET-bottled water as little as choosing refillable jug when eating out. Consumers prefer using personal flask for sake of decreasing the volume of waste bottles

In most cases, the post-used bottle are sorted for recycle bin rather than disposed in the environment inappropriately. Additional addressed is that the inadequacy of recycle bin for plastics waste, compared to consumers' need, becomes a significant burden to sort out the waste bottles. Among the concerns to waste-PET bottles, a large number of door-to-door collectors represent the key role of junk dealer in the logistic flow of recycling waste bottles.

In view of health concerns, most consumers do not avoid using the bottle that has been opened and exposed to direct sunlight contact. Nor is the reuse without proper cleaning that can cause the health risk. On the other, performing a mouth-to-bottle, without a straw or pouring into a glass is least considered related to health risk. Notwithstanding, PET refillable bottles could be safely reused, if the bottles derive from the good manufacturing procedures and the appropriate cleaning prior refilling. In brief, the

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Figure 2. Consumer behavior of resource efficiency in consuming PET-bottled water and disposing of the post-used bottles to fulfill the SCP

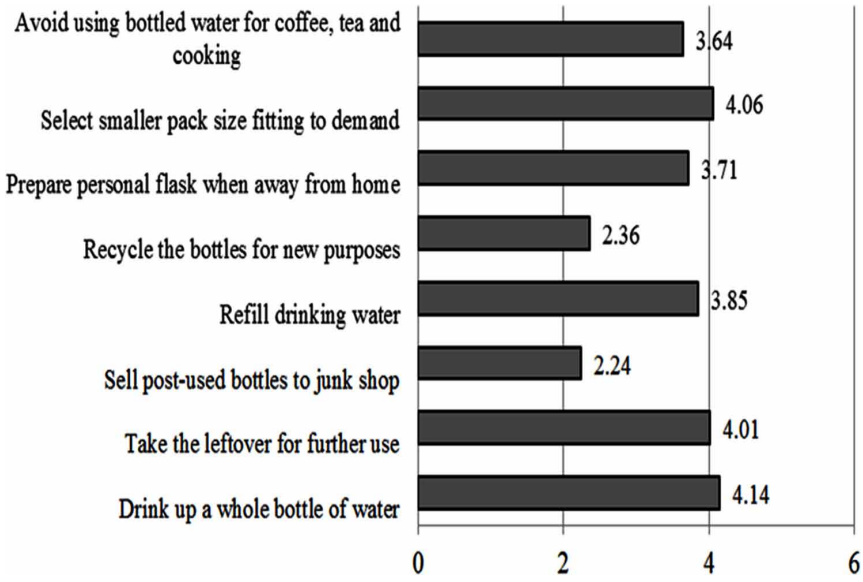

Figure 3. Consumer behavior of impact reduction in consuming PET-bottled water and disposing of the post-used bottles to fulfill the SCP

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consumption pattern of PET-bottled drinking water is somewhat away from impact reduction implication due to the speeding up of lifestyles together with increasingly disposable products for consumerism.

SOLUTIONS AND RECOMMENDATIONS

The conflict agenda of water resource; agriculture and fishery sectors against industries, habitants against businesses, and within the community, is heavily increasing, nationwide. Towards the undercurrents in the LCM of bottled water, a paradigm shift to the holistic view and sustainable actions is truly required so as to bring the implementable solutions to and from all concerns. As a production and consumption pattern is actually related to sustainability objectives, the increasing demand for bottled water shows what social gains for better living is what the world has lost. We must accept that without environmental awareness, the SCP will not advance the larger development in industry practice and consumer behavior. This is important to the SCP implementation, which several variables are associated, which public participation and regulatory policies have not been fully developed.

Under the leadership of the government, its role remains an option to foster a consumption and production pattern away from or toward sustainability. The tasks shall be responded by many governmental entities like the Department of Industrial Works, the Department of Industrial Promotion, the Department of Environmental Quality Promotion, the Department of Health, the Department of Mineral Resources and the Metropolitan, or Provincial, Waterworks Authority. Business would go beyond a product value chain to sustainability objectives in order to reach a viable solution that helps in reducing environmental disruption and compromising economic and social value at the same time. These concerns can be fixed by a removal of unsustainable goods and service from the market. The eco-tax or a refund fee shall be rewarded to those who produce and consume sustainable products and services or eco-products. If putting harm to environmental quality, the polluter could be charged a fee towards funding environmental rehabilitation, and finally edited out of the market – Polluter Pay Principle (PPP). Any related governmental entities could put a driving force to the SCP by either shaping the business practice to influence consumer behavior, or formulating solution taken by each stakeholder. In such case, they should separately set minimum recycling standards and indicate material combinations with recycled PET for the new packaging those covering nonfood-contact products.

Environmental themes in advertising and marketing processes should be employed for raising awareness of sustainable practices. Both business and consumers should be alert to the duties and responsibilities when there is no legislation, nor strict enforcement of disposing of waste bottles. Technological knowledge about recovery of waste-to-energy device should be widely disseminated to communities. Coupled with marketing-based instruments, public policies that support cleaner technologies for a value chain of bottled water could be established. The waterworks authority shall also be due on the establishment of tap-water supply throughout nation. There has to be a thematic agenda inspiring people for the quality of tap water that is appropriate for drinking. The consideration shall also direct to the role of recycling agents and retailers in responsibility for the logistics of waste bottles. These should be well organized in order to prevent the reverse channel from inappropriate approach at landfills and dumping areas.

Finally, environmental education has to be driven so that a positive change in production and consumption pattern of products and services like PET-bottled water can translate to larger sustainability gains. This is concurrent to the agreements across the globe adopted from the 2015 Paris Climate Conference

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(COP21) that sustainable lifestyle in the SCP approach is an important role in addressing climate change (United Nations Framework Convention on Climate Change [UNFCCC], 2015).

FUTURE RESEARCH DIRECTIONS

The content in this chapter is by no means exhaustive, but enables a potential for the methods and data-sets of sustainability framework. More extension could be observed in new areas of study and possible pathways that are branched in various directions. The approaches to soft drinks, energy drinks and health drinks could be developed to identify the differences of causes, effects and solutions on the SCP target themselves. There should be opportunities for future studies about the SCP approach that provide greater interdisciplinary expectations, especially externality cost analysis and a power of eco-journalism to public participation in SCP development. In addition, the improvement of assessment on a linkage between globalization and sustainability from a multi-disciplinary perspective could be set for reframing current public awareness of mitigation and adaptation manners towards climate agenda.

CONCLUSION

PET bottles are potential to the impact categories of global warming, eco-toxicity and human toxicity, especially waste-bottles management that causes a profound impact to the planet. The SCP of PET-bottled water is accounted by the businesses and consumers, with emphasis on efficiency in water and plastics resource use. Contributions to impact prevention and reduction are the contrary. The advance in plastics recycling technology is required, so does consumer behavior in recycling waste bottles. Due to the most practice in bottling the water by open-loop system, the LCM of PET-bottled water can be direct and indirect burden to sustainability target in water resource management, both at present and in future. In general, particular information about demand and supply of fresh water resource varies geographically and culturally. The undercurrents of bottled water are in evidence when the production and consumption pattern are radically addressed through the bottling system and consumer behavior towards the level of environmental awareness. A rapid growth of bottled-water business in Thailand that are captured by many thousands bottlers becomes the interplay of social, economic and environmental development. The concerns are in need to reconsider the impact on water supply, use and management. Businesses and consumer are challenging for greater efficiency in water resource consumption and the improvement of plastics recycling. Shortly, this chapter is particularly timely as water resource and waste plastics are shifting from one of environmental issues to what those are much more concerned to sustainability success.

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KEY TERMS AND DEFINITIONS

Bottled Water: A disposable product that serves one-way usage and appears in the form of PET bottle with the filled water for drinking.

Bottling System: An input-output approach for filling drinking water in the bottle. The system consumes the input of several resources, such as plastic bottles, purified and disinfected water together with electricity and fuel energy in order to deliver the output of bottled water and environmental impact profile.

Bottom-up Participation: Role of business and consumer in environmental protection and prevention from the interactive processes between production and consumption.

PET Bottles: A plastic container appears in bottle body which is made of polyethylene terephthalate polymer.

Sustainability in Bottled Water Production and Consumption: An integration of sustainable consumption and production approach into the whole product life cycle of bottled water.

Sustainable Consumption and Production Pattern: The ways of producing and consuming products and services with environmental awareness of improving efficiency in resource consumption and reducing potential impact generation.

Undercurrents of Bottled Water: Environmental impact profile occurs from PET-bottled water directly and indirectly, both at present and in future, in many categories, such as global warming, ecotoxicity and human-toxicity.

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ENDNOTES

1. The Marrakech Process is a global process driven by the United Nations Environmental Programme (UNEP, 2015) and the United Nations Department of Economic and Social Affairs (UN DESA) to support the elaboration of a 10-Year Framework of Programs (10YFP) on SCP according to Johannesburg Plan of Action in the World Summit on Sustainable Development (WSSD).
2. ISO 14040 (2006) is the leading standard to describe the principles and framework for life cycle assessment (LCA) that can be followed by the steps of environmental management - life cycle assessment - principles and framework.
3. ISO 14044 (2006) is the international standard to specify requirements and provide guidelines for life cycle assessment (LCA), with the following steps; environmental management - life cycle assessment - requirements and guidelines.
4. SimaPro 7.1 is the software developed by PRé Consultants as the tool for a product life cycle assessment through the phase of LCI. The software provides several literature-based inventory data covering the compilation and quantification of inputs and outputs for a given product system throughout its life cycle, plus various impact assessment methods, e.g. Eco-indicator, CML (Center of Environmental Science of Leiden University). The software and the literature LCIs used in this chapter are supported by the National Metal and Materials Technology Center (Thailand) for academic purpose only.
5. GWP is the abbreviation of global warming potentials. Due to the International Panel on Climate Change (IPCC), CO_2 emission is normalized as an equivalent weight of carbon dioxide for the relationship between greenhouse gases (GHGs) emission and the 100-year time horizon Global Warming Potentials (GWP).

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Chapter 19
Water Quality Impacts of Abattoir Activities in Southern Africa

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ABSTRACT

The meat processing produces solid, liquid and gaseous wastes from stockyards, abattoirs and packing plants contain blood, fats, protein, gut contents, heavy metals, antibodies, hormones and other substances. Solid and liquid wastes can lead to an impairment or disruption of water eco-functionality and a preponderance of disease-causing organisms. In developing nations, many abattoirs dispose of their waste directly into streams or rivers and also use water from the same source to wash slaughtered meat. Most solid, liquid and gaseous wastes are released into the immediate environs of the abattoir. This chapter is a literature review of the impact of untreated slaughterhouse wastewater on water quality in selected areas of Southern Africa. The review shows that abattoir activities significantly reduced the physical, chemical and microbiological quality of water bodies. Although an improvement of the water quality was observed downstream, this was a result of self-purification and dilution effects.

INTRODUCTION

The killing of cattle, sheep, pigs, goats, poultry and other equine animals to supply meat for human consumption is a common practice in Southern Africa. Abattoir waste contains high levels of organic matter due to presence of manure, blood, fats, grease, hair, grit or sediments and undigested feeds. Blood and fats contribute mostly to organic load; blood is also a major contributor of nitrogen content in the effluent. It can also contain high level of salts, phosphate, nitrates, trace or heavy metals, bacteria, viruses and other microorganisms (Muhirwa et al., 2010; Kosamu, Mawenda & Mapoma, 2011). Abattoir effluent affects water, land or air quality if proper disposal practices are not followed. Improper waste disposal reduces oxygen in water, thereby endangering aquatic life. It can lead to animal diseases being transmitted to

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humans through contact with animal faeces. Pollution of the environment in the vicinity of the abattoir as well as reduced quality of health of residents in the local area result in elevation of excessive coughing, typhoid fever, diarrhoea, and malaria and muscle pains (Benker-Coker & Ojior, 1995). Noise pollution is also associated with abattoir activities (WHO, 2011). Respiratory and mucous membrane effects are common in areas close to intensive swine operation (Itodo, Awulu & Harrison, 1999). Thus, surface and ground water quality in vicinity of the abattoirs can be adversely affected by effluents.

BACKGROUND

Meat processing, slaughtering and processing remain critical in ensuring that consumers receive a hygienically safe product. Production processes for meat products have been shown to have a significant impact on the environment, accounting for between 15% and 24% of greenhouse gas emissions (Mittal, 2006). Abattoirs are an important industry in Africa's domestic meat supply and export industry, as well as employment opportunities to many communities. Abattoir effluent is known to degrade the quality of receiving water bodies. Waste from abattoirs changes the microbiological and physico-chemical water quality parameters such as pH, temperature, electrical conductivity, salinity, turbidity, total dissolved solids (TDS), total suspended solids (TSS), dissolved oxygen (DO) and coliforms (GDARD, 2009). The effluent characteristics of the abattoir are nutrients and biologically active constituents which pose a considerable challenge for water resources management particularly the delivery of essential water, sanitation services and environmental protection. Nitrates are very high in the abattoir wastewater especially at the evisceration and slaughter step where the urine and undigested stomach content concentrated in nitrate was mixed in wastewater streams (Mittal, 2004). This is because wastewater streams for these processes consist of mixed intestinal contents and blood with a high content of nitrates. This chapter focuses on the environmental effects of meat processing in general. In particular, it highlights how meat processing contributes to changes in water quality.

Water Quality

Water quality describes the physical, chemical, biological and aesthetic properties of water which determine its fitness for a variety of uses and for protecting the health and integrity of aquatic ecosystems. The quality of any body of surface or ground water is a function of either or both natural influences and human activities. Levels of water quality are assessed in terms of: physical characteristics e.g. color, temperature, taste, turbidity, hardness and smell or odor which are determined by senses of touch, sight, smell and taste; chemical characteristics such as conductivity, dissolved salts and oxygen demand; and biological e.g. amount of micro-organisms present such as bacteria, protozoa and algae parameters (WHO, 2011).The definition of water quality takes into account the fact that even when water is polluted say with sewage, depending on the level of the contaminant, it can be used for other purposes such as agriculture.

Environmental Pollutants from Abattoirs

An abattoir is loosely defined as any registered facility that is responsible for the conversion of animals to meat via a slaughtering process. This includes livestock, poultry and special classes of animals, e.g. crocodiles and game (GDARD, 2009). The slaughtering process remains critical in ensuring that consumers receive a hygienically safe product.

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Effluent Salinity

Skin preservation by dry salting is a common procedure at small abattoirs that are remote from tanning operations and often export their hides and skins for tanning. After salting, often in converted cement truck mixers, the hides are hung to dry for a minimum of 5 days. During this period, the salt draws the moisture out of the hide, together with the protein-filled fluids contained in the attached flesh. The effluent from drying sheds is therefore highly saline and has a very high biochemical oxygen demand (BOD). It also contains high levels of fluoride, since the salt used contains up to 1 percent sodium fluoride as a bactericide.

Wastewater

Wastewater produced in animal slaughter areas typically has a high BOD. It is also very saline and has high levels of nutrients, suspended solids and bacterial contamination.

Solid Waste

Sources of solid wastes generated at abattoirs include: manure generated in animal holding areas; slaughterhouse and processing areas; sludge generated in waste treatment ponds; and unwanted carcasses, hide or skins, paper, cardboard, plastics, feathers and pieces, and unwanted carcasses and carcass parts (Mittal, 2004).

Odors

Potential sources of odors in abattoir operations include stale materials and fugitive emissions from cookers. Odors in animal holding pens are produced by manure and urine. Abattoirs odors come from solid wastes such as paunch contents and blood residues. Anaerobic waste treatment ponds may produce gases such as methane, ammonia and hydrogen sulphide, which give rise to objectionable odors (GDARD, 2009). Odor control may be a significant issue, particularly when the abattoir is located near residential areas or in a hot environment.

Dust

Potential sources of dust emissions at an abattoir are: paddocks, sale-yards and holding pens; and materials burned at an abattoir (GDARD, 2009).

Greenhouse Gases

Animals produce methane gas (a greenhouse gas) during the process of digestion which is released to the atmosphere during processes such as defecation. Little can be done to prevent or reduce the amount of methane produced. However, by varying the food types and quality, methane generation may be reduced. Chlorofluorohydrocarbons (CFCs) may be used in refrigeration and freezer plants. These are ozone depleting gases and their production and use are subject to national and international regulation

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(McLaughlin & Mineau, 1995). Ozone depleting gases used in refrigeration units should be replaced in existing abattoirs and new abattoirs must install refrigeration units that do not utilize such substances (Quinn & McFarlane, 1989).

Noise

In abattoirs noise can be generated by several sources, including: animals, especially when in concentrated groups; processing activities within the slaughterhouse; plant machinery; and plant and service vehicles (Muhirwa et al., 2010).

EFFECTS OF ABATTOIRS ON WATER QUALITY

The people and environment in Southern Africa are highly vulnerable to pollution from abattoirs. Availability of safe water in the region is worsened by poor sanitation and improper disposal of animal waste. The majority of the people living along and down river courses depend on untreated stream water supply for domestic purposes and sometimes for drinking. While rivers and streams serve as major sources of reliable domestic water supply, most abattoirs are located close to such water sources. Nevertheless, abattoirs discharge untreated wastewater into water bodies because they normally face difficulties in meeting costs of treating wastes such as fats, oils, greases and suspended solids (Chukwu, 2008). Thus, there are high chances of people drinking unclean water contaminated with bacteria or pathogens that could impact on public health. The following are case studies findings on the physico-chemical and microbiological impacts of abattoir activities on water quality in selected countries. Table 1 shows findings of a study conducted to assess the water quality of abattoirs in Ghana.

Generally the influent met the recommended standard for treated water quality except for fecal and total coliform counts of 36 and 84 CFU, respectively, instead of 0 CFU recommended by the World Health Organization (WHO, 2011). The effluent was highly polluted and did not meet the set standards for effluent discharges into the environment. Its extremely high levels of BOD (3300 mg/L) and low dissolved oxygen (0 mg/L) are strong indications of high organic pollution in the effluent. Effluent fecal coliforms level of 450,000/100 ml and total coliforms of 550,000/100 ml were recorded. Excessive turbidity, or cloudiness, in drinking water is aesthetically unappealing, and may also represent a health concern. Turbidity can provide food and shelter for pathogens. If not removed, turbidity can promote

Table 1. Effects of Tamale abattoirs on water quality in Ghana

Parameter	Influent	Effluent	WHO Standard
DO (mg/l)	4.6	0	5
BOD (mg/l)	2.2	3,300	20
TSS (mg/l)	4	2,567	30
Turbidity (NTU)	4.8	>1,000	5
Fecal coliforms (CFU/100 ml)	36	450,000	0
Total coliforms (CFU/100 ml)	84	550,000	0

(Weobong & Adinyira, 2011, p. 388).

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regrowth of pathogens in the distribution system, leading to waterborne disease outbreaks, which have caused significant cases of gastroenteritis throughout the United States and the world. Although turbidity is not a direct indicator of health risk, numerous studies show a strong relationship between removal of turbidity and removal of protozoa. Residents of the community where the abattoir is located complained about bad odor, pollution of their water source (dam) from the effluents and the outbreak of maggots, flies and diseases such as malaria, typhoid, dysentery and diarrhea (Weobong & Adinyira, 2011).

Table 2 shows the results of a study conducted in Malawi and Nigeria. The first sampling point was located 10 m upstream with respect to abattoir discharge point. It served as reference point. A second sampling point was located at abattoir effluent discharge point. The third sampling point located 10 m downstream from effluent discharge. The physico-chemical parameters tested were: pH, biochemical oxygen demand (BOD), dissolved oxygen (DO), suspended solids (SS) and electrical conductivity (EC).

From Table 2, it is clear that at a point upstream, the BOD value was 257.3 mg/l, and the concentration went higher to 612.3 mg/l at discharge point. This was because of the effluent discharged by the abattoir on the stream at this point and therefore not completely mixed. At the sampling point downstream, the mean value of BOD was reduced to 487.0 mg/l. This can partially be attributed to dilution due to mixing and partially as a result of settling along the stream course and dilution.

Because oxygen from the atmosphere is dissolved in the water, (Verheignjen, Weiersna, Hulshoff & de Wit, 1996). It is one of the most significant tests for measuring the quality of water. The standard for sustaining aquatic life is stipulated to be 5 mg/l. Concentration below 2 mg/l adversely affects aquatic and biological life hence lead to death of fish. The low DO concentration at discharge point was be due to high organic load as shown by BOD and suspended solid values (Table 2).

The concentration of suspended solids show the highest value of 477.3 mg/l at discharge point hence exceeded the WHO (2011) recommended maximum limit of 30 mg/l. This was due to lack of proper sedimentation facility to separate the solid waste from liquid waste before the effluent is discharged. High

Table 2. Effects of meat processing on water quality on Mchesa stream in Malawi and Ogbogoro stream in Nigeria

Parameter	Upstream	Discharge Point	Downstream	WHO Standards
BOD (mg/l)	257.3	612.3	487	20
COD (mg/l)	42.87	42.08	42.57	1000
DO (mg/l)	3.8	1.8	2.4	5
SS (mg/l)	286.0	477.3	272.0	30
EC	99.3	128.3	177.7	400
pH	7.4	7.7	7.5	6.5-9.5
Total alkalinity (mg/l)	2.55	2.37	2.25	NA
Nitrate (mg/l)	0.39	0.83	0.62	10
Phosphate (mg/l)	0.05	0.07	0.06	NA
Turbidity (NTU)	0.46	0.77	0.56	5
Odor	Odorless	Offensive	Offensive	Inoffensive

(Kosamu et al., 2011).

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concentrations of suspended solids can also cause problems to aquatic life such as by reducing water clarity and clogging fish gills (GDARD, 2009). The changes downstream can be attributed partially to dilution and partially to settling.

Electrical conductivity (EC) is used to indicate the dissolved solids in water because the concentration of ionic species determines the conduction of current in an electrolyte. The high values of electrical conductivity downstream therefore suggest that has a considerable loading of dissolved salts (WHO, 2011).

The mean values of pH obtained ranged from 7.4 to 7.7. These pH values were normal to unpolluted freshwater. Water having a pH range of 6.5 -8.5 will generally support a good number of aquatic species. Thus, the values obtained were also within the recommended ranges (6.5-9.5) as stipulated by WHO (2011).

Table 3 shows findings of a study conducted to determine the bacteriological characteristics of abattoir effluents from 6 abattoirs discharged into water bodies in Nigeria. The concentrations of total coliform (TC), fecal coliform (FC), F. streptococcus, and E. coli were determined from upstream water servicing the abattoir and water bodies receiving abattoir effluents downstream. Total coliform bacteria concentration in the abattoir wastewater discharged exceeded the recommended limit for the discharge of effluents into water bodies.

The receiving water bodies were used for drinking, bathing, washing, watering of animals, watering of crops, and other domestic purpose downstream. Total coliforms and fecal coliforms or E. coli are generally not harmful themselves. While total coliforms are common in the environment, fecal coliforms or E. coli are usually associated with sewage or animal wastes. The presence of these bacteria in drinking water is a result of a problem with water treatment or the pipes which distribute the water, and indicates that the water may be contaminated with organisms that can cause disease. Symptoms may include diarrhea, cramps, nausea, and possibly jaundice, and any associated headaches and fatigue (Benker-Coker & Ojior, 1995).

F. Streptococci are common bacteria that live in the human body, including the nose, skin, and genital tract. These bacteria can damage, and destroy red blood cells. Drinking water which meets the WHO standard is usually not associated with a health risk from disease-causing bacteria and is considered safe.

Twelve wells were sampled and assessed of their physico-chemical and bacteriological parameters in Nigeria (Adeyemo, Ayodeji & Aiki-Raji, 2002). Four wells were sited within the ground of the Bodija abattoir, four were about 50 m – 80 m upstream of the abattoir and four were 500 m – 100 m downstream of the abattoir in a residential area (Table 4).

Table 3. Mean wasterwater values of bacteriological characteristics upstream and downstream of Kuje, Gwagwalada, Kubwa, Deidei, Karu abattoirs in Nigeria

Parameter	Upstream Station	Downstream Station	Discharge Limit into Surface Water
TC ($x10^2$)	38	6100	4.0
FC ($x10^2$)	2.5	230	0
F. streptococcus ($x10^2$)	3.3	7	120
E. coli ($x10^2$)	2.7	24	0

(Chukwu, Adeoye & Chidiebere, 2011, p. 104; Agwa, Sito & Ogugbue, 2013, p. 882).

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Table 4. Mean values of physical, chemical and bacteriological characteristics of the well water used by butchers in Bodija Abattoir Ibadan, Nigeria

Parameter	Upstream Stations	At Discharge Point	Downstream Stations	WHO Limits
Coliform count ($x10^4$)	5.6	6.9	0	0
F. streptococcus ($x10^4$)	4.3	8.8	0	0
Bacteria count ($x10^4$)	11	15.4	2	0
pH	6.57	6.41	6.75	7.0-8.5
Temperature (^oC)	27.8	26.1	25.8	----
Sodium (mg/l)	35	40	46.30	---
Potassium (mg/l)	73.80	127.01	125.00	---
Calcium (mg/l)	81.30	143.00	131.30	75-200
Magnesium(mg/l)	13.70	27.00	12.30	30
Zinc (mg/l)	0.002	0.06	0.007	5-15
Iron (mg/l)	0.44	3.00	0.82	0.10-1.00
Copper (mg/l)	0.30	0.39	0.32	0.05-1.50
Manganese (mg/l)	1.18	2.19	2.19	0.05-0.50
Lead (mg/l)	0.02	0.09	0.01	0.01
Total dissolved solids	950.00	2,100.05	750.00	500-1500
Total hardness (mg/l)	133.25	371.25	151.00	100-500
Total chloride (mg/l)	134.75	312.05	94.85	250
Clarity	Clear	Clear	Clear	Clear
Odor	Odorless	Odorless	Odorless	Odorless
Taste	Tasteless	Tasteless	Tasteless	Tasteless

(Adeyemo et al., 2002, p. 52).

From Table 4 it is clear that most parameters at discharge points and downstream stations met the WHO standards. However, microbiological, total solids, manganese, lead and total chloride were outside the recommended limits.

Total dissolved solids in water supplies originate from natural sources, sewage, urban and agricultural runoff, and industrial wastewater. Salts used for treating animal hide can also contribute to the TDS loading of water supplies. Ingestion of TDS in drinking water appears to be associated with various health effects such as incidence of cancer, coronary heart disease and arteriosclerotic heart disease.

Manganese occurs naturally in air, soils, surface water and groundwater sources. However, human activities are also responsible for much of the manganese contamination in water in some areas. Manganese is an essential nutrient for the proper functioning of humans and animals, as it is required for the functioning of many cellular enzymes. Although manganese is an essential nutrient at low doses, chronic exposure to high doses may be harmful. The health effects from over-exposure of manganese are dependent on the route of exposure, the chemical form, the age at exposure, and an individual's nutritional status. The nervous system is the primary target organ with neurological effects generally observed (WHO, 2011).

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Chlorine is generally found only in industrial settings. It enters the body breathed in with contaminated air or when consumed with contaminated food or water. It does not remain in the body, due to its reactivity. Most direct releases of chlorine to the environment are to air and to surface water. Exposure to chlorine effect on human health depends on the amount of chlorine that is present, the length and frequency of exposure. Breathing small amounts of chlorine for short periods of time adversely affects the human respiratory system. Effects differ from coughing and chest pain, to water retention in the lungs. Chlorine irritates the skin, the eyes, and the respiratory system. These effects are not likely to occur at levels of chlorine that are normally found in the environment.

Lead is a useful and common metal but can be a very dangerous poison, particularly for children, when it is accidentally inhaled or ingested. In children, lead is most damaging when they are six years and younger. High levels of lead are life threatening and can cause seizures, unconsciousness, and death. Even at low levels, lead can be harmful and be associated with learning disabilities resulting in a decreased intelligence, attention deficit disorder, behavior issues, nervous system damage, speech and language impairment, decreased muscle growth, decreased bone growth and kidney damage. High levels of lead in adults can cause increased chance of illness during pregnancy, harm to a fetus, including brain damage or death, fertility problems in both men and women, high blood pressure, digestive issues, nerve disorders, memory and concentration problems and muscle and joint pain (WHO, 2011).

Thus, the discharge of abattoir waste negatively imparts on the chemical and microbiological quality of the stream especially at discharge points and downstream stations. The spatial distribution of the physico-chemical parameters along the stream showed relatively higher values at the effluent discharge point with increased attenuation in the levels of the parameters downstream indicating the capacity of the stream for self-purification. Nevertheless, the organoleptic assessment showed that the samples from all the wells were clear, without odor and taste. It is vital to have adequate treatment of waste before discharge and waste management practices that ensure waste reduction, re-use and recycling, should be encouraged by environmental regulatory bodies in order to protect the water resources from negative impacts of abattoir wastes. Therefore, the discharge of untreated abattoir waste into rivers and streams can have adverse environmental consequences on water quality (Agwa et al., 2013).

CONCLUSION

While the slaughtering of animals results in meat supply and useful by-products like leather and skin, livestock waste spills can introduce enteric pathogens and excess nutrients into surface waters and can also contaminate ground waters. These leachates consist largely of solids, microbial organisms and in special situations chemicals and shallow wells like hand-dug wells are more dangerously polluted. Abattoir operations produce a characteristic highly organic waste with relatively high levels of suspended solid, liquid and fat. The solid waste includes condemned meat, undigested ingesta, bones, horns, hairs and aborted fetuses. The liquid waste is usually composed of dissolved solids, blood, gut contents, urine and water. As population grows and urbanization increases, more water is required and greater demand is made on ground and surface sources and an even greater amount of organic and inorganic wastes are speared back into water sources so that less potable water becomes available. Water is regarded as being polluted when it is unfit for its intended use.

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In developing countries abattoirs are known to pollute the environment either directly or indirectly from their various processes. Wastewater from an abattoir is a particularly concentrated source of oxygen consuming waste. In most countries, abattoir operations are generally unregulated. Moreover, abattoirs are usually located near water bodies in order to gain unhampered access to water for processing. Abattoirs generally use large quantity of water for washing meat and cleaning process areas. The disposal of effluent into rivers and streams is a common practice.

This study has shown that the operations of abattoirs have some negative impacts on water quality in Southern Africa. The water used by the abattoir for its operations (influent) is generally of good physical, chemical and microbiological quality. If proper abattoir management practices are not followed, animal waste can be washed into unprotected water bodies. Abattoirs however pose the following contamination risks to water resources:

- Nutrients from animal manure and process wastewater leading to eutrophication in wetlands and waterways, and toxic concentrations of nitrogen compounds;
- Depletion of oxygen levels in surface waters due to the breakdown of organic matter;
- Pathogens such as salmonella bacteria from any diseased stock held at the site;
- Increased salinity derived from waste stabilization pond effluent evaporation;
- Increased turbidity due to solids transfer to waterways and wetlands; and
- Alkalinity and surfactants derived from equipment cleaning.

Even though there are a number of state of the art abattoirs around the world, waste management practices in such facilities remain incompetent in resolving the environmental and human contamination risks and impacts. In the context of Southern Africa, emergency response and remediation are not always readily available to address contamination and pollution considerations, which renders humans and the environment more vulnerable and mean the risk of environmental and human adverse impact is potentially more serious.

Based on current knowledge, no South African abattoirs operate on a closed water circuit, as in general, it is prohibitively costly to treat waste water to a water quality standard fit for recycling and/or re-use. Thus, most abattoirs discharge (after appropriate pre-treatment) to municipal sewers.

Many of these small abattoirs relied on denaturing as a sole option for the disposal of condemned products and blood. With the increase in slaughtering and structural changes to these abattoirs over the past ten years, by-product treatment, in any form, was not included as a prerequisite.

Discharge costs due to the high organic loads in the untreated abattoir waste water are relatively high. Abattoirs normally also have difficulty in meeting municipal by- law quality standards for fats, oils, greases and suspended solids. A degree of on-site pre-treatment is thus necessary. However, to minimize waste volumes, water conservation and optimum water housekeeping are essential. In addition to good abattoir housekeeping, abattoir waste management should be progressively implemented commencing with low-cost, low-technology practices and thereafter progressing to more sophisticated technologies.

Therefore, the importance of adopting appropriate abattoir wastewater treatment measures to prevent the chances of contaminating water bodies and ground water is recommended. Determination of specific pathogenic microorganisms in abattoir wastewater and their health impacts is also recommended. It is therefore instructive to treat the abattoir wastes appropriately and properly dispose them to avert environmental disasters. Furthermore, legislation on abattoir operations and management can reduce the negative impacts and enhance sustainability in the industry.

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KEY TERMS AND DEFINITIONS

Abattoir: An abattoir or slaughterhouse is a place where animals are slaughtered for meat.

Dissolved Oxygen: The measure of the degree of pollution by organic matter, the destruction of organic substance as well as self-purification of the water bodies.

PH: Refers to hydrogen ion concentration, and is the indicator of acidity or alkalinity of water. It is a measure of the effective concentration (activity) of hydrogen ions in water.

Pollution: The change in the physical, chemical, radiological or biological quality of the resource (air, land or water) caused by people or due to human activities that is liable to cause hazards to human health, harm to ecological systems, damage to structures or amenity and is injurious to existing, intended or potential uses of the resource.

Water Quality: Describes the physical, chemical, biological and aesthetic properties of water, which determine its fitness for a variety of uses and for protecting the health and integrity of aquatic ecosystems. Water quality is the degree of usefulness of water for a particular purpose. It is a measure of the amount and types of substances contained in water with respect to what it is intended to be used for.

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Chapter 20
Green Manufacturing: The Need of the Hour for Developing Nations – A Case Study

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ABSTRACT

The manufacturing sector has greater responsibility for conducting and operating its business. The primary objective of every unit is to maximize profits. The manufacturing sector is the key driver of energy consumption and if an automobile consumes high fuel or if the resources are under-utilized, it is definitely the fault of the manufacturer. If we seriously need a solution to these problems, we need to change the way we design, manufacture, and sell the products. The manufacturing sector must use energy and resources efficiently. 'Green Manufacturing' or sustainable industrial activity is the need of the hour and the Government of India requires the manufacturing sector to play a bigger role in the country's economy. This paper focuses on the initiative taken by the industries to make the environment eco-friendly. The paper further will emphasize upon a case study of Hero MotoCop.

MEANING AND IMPORTANCE OF 'GREEN'

The term Green here refers to the ecological sustainability and encompasses elements like energy usage, efficiency and waste management and recycling. Green initiative aims to minimize the impact of human activities on the environment.

There are various factors which call for concerns for Green. They are:

1. **Rising emissions:** Greenhouse gas emissions have been increased rapidly in the recent past and are continuously accelerating. It is revealed by the scientists that it will increase by double by 2050. This means that there would be an exceptional negative change in the global eco-system, sea-level, crop production and relative activities.

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2. **Fast depletion of scarce natural resources:** With growing population, the need for industrialization will increase and also the consumption of natural resources will rise. This will result in the imbalance between the demand and supply of products, rise in the price of goods and services. This problem could be solved by optimal utilization of natural resources and their alternate uses.
3. **Growing waste generation and pollution:** Rapid industrialization and urbanization has led to increase in industrial waste and chemical compositions. This results in environment pollution which can be dangerous to health of human beings.
4. **Growing Technological waste:** Another problem which is encountered by the nation is e-waste. With growing demand of technologies and gadgets, the problem of e-waste has emerged which again is a major source of environment pollution.

The above factors have persuaded the manufacturers to adopt Green manufacturing. A number of companies have started adopting Green initiatives as an integral part of their operations. These initiatives are driven by five factors:

- Rising energy and input costs
- Growing consumer pull for Green products
- Increasing regulatory pressures as policy makers introduce new and stricter environmental and waste management laws.
- Technological advances which open up new attractive business opportunities
- The need to enhance competitive differentiation, particularly for first movers or those who are able to break the compromise between short–term higher costs and numerous benefits (example: brand premium, new customer segments). (Bhattacharya, Jain & Choudhary 2011)

Why Green Manufacturing?

The manufacturing companies produce goods which are not eco-friendly. So, they should focus on three major areas:

1. **Green energy:** Green energy basically includes the renewable energy sources like biomass, wind, solar, CNG etc. The manufacturing units should use these green energy sources to produce goods which are not only eco-friendly but also benefits the society as a whole.
2. **Green products:** Green products are the products which can be recycled, low in carbon, organic and are natural. These products are gaining popularity but are little costly. However, if the consumers demand these products and if these products are marketed well, the cost of developing these products will gradually decrease.
3. **Green processes in business operations:** The third and the last area on which the manufacturing units should focus is the business operations. This includes the use of appropriate technology which may increase the efficiency and decrease the cost.

Green Manufacturing: The Need of the Hour for Developing Nations

Green manufacturing has the potential to achieve sustainable development and eradicate poverty on an unprecedented scale. A green manufacturing economy substitute‘s clean energy and low carbon tech-

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nologies for fossil fuels, which addresses climate change, creates jobs, and reduces import dependencies. Adopting new technologies promote energy, resource efficiency and provide growth opportunities in new directions. If a developing economy moves towards green manufacturing, it will require the initiatives of leaders, civil society and leading businesses. It will require a sustained effort on the part of policy makers and their constituents to rethink and redefine traditional measures of wealth, prosperity and wellbeing. A developing economy can however, develop better opportunities for the people by adopting the concept of 'Green'. It can be self-reliant and thus can minimize its dependency on other countries for importing goods. Not only this, the countries can develop their quality 'green' goods and play the role of exporters. Thus, a developing economy need to move ahead and think in a different way to promote green manufacturing so as to preserve the environment, maximize their profits, play active role as exporters and provide better living to its citizens.

India's Green Challenge

The rapid industrial, economic and demographic growth in India has resulted in high Greenhouse gas (GHG) emissions, rising demand of scarce resources and has generated wastes particularly in urban areas. Today, India is the fourth–largest economy and the fifth–largest GHG emitter in the world. During the 18 year period between 1990 and 2008, India's CO2 emissions increased more than 150 percent, placing it just behind China. Rapid urbanization and industrialization generate massive amounts of waste. For example, India generates close to 4 million tonnes of hazardous waste from industrial and biomedical sources. Apart from hazardous industrial waste and effluents which cause water and land pollution, e–waste is also becoming a major area of concern for India. Estimates suggest that only 3 percent of e–waste makes it to authorized recycling facilities, with the rest either going into landfills or being processed at informal recycling yards. (Digalwar Abhijeet, Tagalpallewar Ashok & Sunnapwar Vivek, (2013). The Indian e–waste market is expected to nearly double from 450 KT per annum currently to about 800 KT per annum by 2020.

Green Business: An Integral Part

Green business is an important strategy to build a green brand that customers can trust. Though, developing such a brand is not an easy task and requires an integrated promotion campaign which consistently communicates the company's Green positioning and policies. Standard setting and labeling can be powerful tools used by companies to build the credibility as well as to help consumers make informed decisions. A survey conducted by CII-Ascon for the April-June quarter (2014) indicates positive growth in important sectors like consumer durables including the vehicle industry and white goods industry, which recorded a growth of 5-10 percent, leading to improvement in the overall industry growth. The CII-Ascon survey found that sub-sectors such as tablets, LEDs and LCDs, smartphones have achieved phenomenal growth of over 20 percent. The passenger car segment also for the first time in last two years has grown between 5 and 10 percent. Thus, it can be interpreted that, if, the companies adopt green business, it will benefit not only the business but the entire eco-system.

The success of companies adopting Green depends on the economic assessment which includes two basic elements, costs and profits. The companies then select their quantitative and qualitative Green initiatives- price strategy, cost strategy, employee recruitment strategy etc.

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Making Sense of Green: Hero MotoCorp

Environmental sustainability lies at the core of manufacturing practices of Hero MotoCorp and the company have been continuously introducing new steps in this regards. The company has proactively restricted the use of mercury and cadmium in painting and rubber compounding processes. All plastic parts come in a moulded form, which facilitates easy recyclability at the end of a vehicle's life cycle at the Hero MotoCorp. The company also installed a waste heat recovery system to utilize waste heat from its gas generator. This enables to save 4,000 Standard Cubic Metre (SCM) of natural gas and thereby, prevent 2,600 tonnes of CO2 emissions. The company also installed a vapour absorption machine, which enables to reduce 400 TR (340 KW) of electrical energy, thereby saving 524 tonnes of CO2 emissions annually. It also recycled paint sludge from its paint processes, which is 5-10 percent of the total volumes of paint sludge generated.

The products of the company once used to rely on asbestos based parts. However, they have now been replaced with non-asbestos based parts, which include brake liners, gaskets and other assembly parts. Similarly, lead was replaced by lead-free materials. Hazardous chemicals like hexavalent chromium were substituted in the plating process. The Green Vendor Development Programme is a landmark initiative that disseminates and embeds green practices among suppliers of the Hero MotoCorp. Around 130 suppliers are part of the Green Vendor Development Programme.

The Green Vendor Development Programme of Hero MotoCorp is the supply chain initiative drive taken to extend the corporate environment responsibility down the supply chain. As the production at Hero MotoCorp is increasing, the manufacturing activities at the vendor's are also increasing in the same proportion. This gives rise to the load on the environment. In order to improve the vendor environmental performance, Hero MotoCorp has developed exclusive vendor development program, which is a collaborative effort between the Hero MotoCorp Environmental group and the materials department, in order to influence the vendors to adopt pre-specified environmental requirements and undertake environmental initiatives.

In addition to the above steps taken, the concept of Hybrid Scooters was also unveiled in the 2012 Auto Expo in Delhi by the Hero MotoCorp. The concept of Series Hybrid is fuel productive and eco-friendly. The Hybrid Scooter launched by HeroCorp runs primarily on battery in urban conditions and will use range extender gasoline engine for long runs.

There are other areas in which the company is taking initiative to make the environment eco-friendly.

1. **Green Roof:** Hero's green roof, covering about 45000 sq meters, helps to conserve energy by moderating the temperature on the roof and within surrounding areas. The green roof can restore aesthetic and ecological value of open urban spaces. It addition to this, it protects conventional roofing systems by doubling the service life of the underlying waterproof membrane.
2. **Sewage Treatment Plant:** Hero ensures that sewage is biologically treated to attain efficacy. This treatment plant is designed to accommodate up to 6 hours of holding and ensuring effluent is 100% treated and recycled into soft water that is used in cooling towers.
3. **Effluent Treatment Plant:** To prevent water pollution, Hero has also invested in an Effluent Treatment Plant which is capable of treating waste water that contains degreasing chemicals, acidic/alkaline nature, plating waste, heavy metals and waste oil that is generated out of processes. The output parameter is maintained strictly with norms to ensure that 100% treated water is recycled back into the process while the sludge is safely disposed of at a secured landfill.

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4. **Waste Food Recycling:** Hero ensures hygienic disposal of municipal waste through its organic waste converter, which in turn generates manure. This waste goes through 15 minutes of treatment and is then homogenized and odor free.
5. **Paint Conservation:** Along with preventing water pollution, Hero MotorCorp does its very best to prevent releasing pollutants in the air as well. On an annual average, the company recycles about 120 tons of paint sludge and additives and turns it into paint primer. It also has a Solvent Recovery Machine that helps to prevent 59 Kl of volatile organic compounds from getting released into the air on a yearly basis, thus ensuring cleaner air.
6. **Energy Conservation:** In January 2011, Hero initiated the Heat Recovery from Incineration project which has helped to save 1,258 tons of Co2 emissions and 16, 22, 400 units per annum. This process includes the recovery of waste heat from the incinerator through heat recovery coil. The waste heat is used for heating process water in engine component washing.

In October 2011, Hero introduced its Solar Power Project – 100 KW which has helped to save 1, 56, 000 units per annum, 121 tons of Co2 emissions and 37.96 tons on furnace oil. This is done through the solar energy that is captured by the photovoltaic cells during the day. This electrical energy is then connected to the main grid, to ensure optimum energy conservation.

In June 2012, Hero replaced its 400 ton air conditioner with a VAM chiller to reduce Co2 production and energy consumption. This machine produces chilled water by using heat from power generator sets or through heat sources such as oil, gas, hot water and steam.

Apart from these, Hero MotorCorp has also initiated other energy saving processes like:

- Substituting furnace oil with natural gas
- Replacing aluminum alloy fans by FRP fans of cooling towers
- Replacing copper ballast with electronic ballast in all lighting tasks
- Introducing power saving circuits in all machine panels of engine plants
- Installing power correction panels for loads running on state electricity for cost saving.

7. **Oil Conservation:** Hero MotorCorp has also initiated oil conservation through the installation of Chip Wringer which is capable of recovering neat cutting oil from chips that are generated from m/c operation. This has led to oil recovery of about 56 liters/ day per plant. The company also uses on line hydraulic oil filtration system on presses which has helped in saving 1200 liters/ year.
8. **Water Conservation:** Perhaps one of the biggest initiatives taken by Hero has worked consistently hard in conserving water through Water Management, Rain Water Harvesting and ETP Recycling Plant.
9. **Water Management:** Hero provides training and awareness on how to develop water balance. It also includes reducing water consumption at the source and recycling it back to process applications and other beneficial applications like cooling towers and irrigation after treatment. Water management also entails recharging rain water and regular monitoring to sustain savings.
10. **Rain Water Harvesting:** Hero has also introduced a rain water harvesting scheme that includes the collection and de-silting of rain water. The company has a catchment area in plants that measures about 2, 60, 000 square meters and has a potential recharge of about 1, 32, 600 cubic meters of rain water annually.
11. **ETP Recycling Plant:** This plant introduced by Hero has a capacity of recycling approximately 1400 Kld of treated effluent daily. It uses the modern technology of reverse osmosis and ultra

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filtration for purifying water. The recycled water is then supplied to the paint shop with desired parameters or used as Soft water/ DM as required.

12. **Green Supply Chain:** To complete the process of sustainable development, Hero MotorCorp has also included the company's supply chain in its green processes. It has put together a "Green Dealer Development Program" at the front end and a "Green Vendor Development Program" for the backend of the supply chain. Through these programs Hero makes it partners aware of the importance of caring for the environment. Dealers and vendors are also encouraged to manage their material resources, energy resources, industrial wastes, pollution and other effluents on the basis of a number of pre-determined parameters. Hero MotorCorp supports its partners in the Green Supply Chain venture by
    - Developing required competencies
    - Sharing knowledge
    - Providing technical support

Through its Green Supply Chain, Hero MotorCorp aims at generating sufficient momentum in the industry and looks forward to the day when the entire automotive industry runs on a seamless green chain.

CONCLUDING REMARKS

Green manufacturing is the core to manufacturing companies' competitive strategies. Though, the transformation journey to Green manufacturing has just started, yet the destination is far to reach. There are few early adopters like Hero MotoCorp to green manufacturing, yet other industries, manufacturers and the developing economies needs to develop comprehensive plans to address three basic areas — Green energy, Green products and Green processes. Hero MotoCorp has adopted numerous means and strategies to maintain and make the economy eco-friendly, but still it has to go a long way to make the economy a 'green' economy. The Government of these economies also has to play an effective role in this transformation with both stronger incentives on one hand and regulatory mechanisms on the other. Also, the industry associations can bring different stakeholders together and support the roll-out of a communication strategy. Thus, the chance for success is enormous for both manufacturing companies and the developing countries, what is required are the zeal to adopt 'Green Manufacturing'.

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KEY TERMS AND DEFINITIONS

Eco-Friendly: It is referring to goods and services, laws, guidelines and policies that impose reduced, minimal, or no harm upon ecosystems or the environment.

Environment: The sum of all surroundings of a living organism, including natural forces and other living things, which provide conditions for development and growth as well danger and damage.

Green Manufacturing: It is a process of reducing pollution and waste by minimizing natural resource use, recycling and reusing what was considered waste, and reducing emissions by the industries.

Manufacturing Sector: Collection of industries engaged in chemical, mechanical, or otherwise or physical transformation of materials, substances, or components into consumer or industrial goods.

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Chapter 21
Applications of Nanomaterials for Water Treatment:
A Future Avenue

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ABSTRACT

Development of new technologies, progressive urbanization, increasing consumerism and industrial boom in developing countries has led to elevated pollution of the environment. The spectrum of pollutants produced and released to the environment has increased in the last few decades including the agricultural, industrial, pharmaceutical and plastic industries. In the developed and underdeveloped countries where environmental pollution goes on increasing day by day, the concern of mankind to the threat of humanity increases which comes from anthropogenic degradation of the environment. An analytical chemist is always in search of cheaper, quicker, more sensitive, more reliable, precise methods of analysis. To achieve such a goal many properties of the materials are studied. Nanotechnology meets many of the conditions mentioned above and is very economic. So, analytical nanotechnology is an important tool for preconcentration and separation of pollutants at low levels.

INTRODUCTION

Rapid urbanization and industrialization of human civilization leads to the discharge of several hazardous contaminants and pollutants into aquatic streams, these effluents contains toxic wastes such as metals, organic impurities, etc., which directly produces a detrimental impact on the biotic resources (Mara 2003; Moore et al. 2003). The unmanageable discharge of pollutants and contaminants due to their severe toxicity and more carcinogenic nature as comparable to other water contaminants, metal ions can cause brutal health troubles for aquatic fauna as well as flora but it also troubles human health through the prevailing ecological food chain (Hutton et al. 2007). Thus, the instantaneous removal of these toxic pollutants from wastewater is a noticeable issue in the aerobic and aquatic world.

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The severity of pure drinking water scarcity has to be looked at from two aspects: First, quantity of available water and second, the quality of drinking water. With the rapid development of industries, such as batteries, metal plating facilities, mining operations, fertilizers industries, tanneries, and pesticides (Lvovich 1979).

As nanotechnology continues to proceed steadily, the primary focus of the research agenda has progressively advanced from the fundamental discovery and characterizations to look into the opportunities of presenting nanotechnology and the resultant nanomaterials as the major key to address the challenges of improving global sustainability, particularly in a wide spectrum of pivotal areas involving energy and environment (Seckler et al. 2003).

The properties of nanotechnology innovations are overpowering. Nanoscience and nanotechnology inspired images of "science fiction" with the word invoking visions of technologies wonders such as atoms and molecules joining to create materials with extraordinary physical and chemical properties which can mimic all of the things developed by nature in millions of years. This great deal of optimism and global enthusiasm about"small" encourages developing a lot of nanosensors which are used for detection of various pollutants. Nanotechnology is the creation and utilization of materials and devices at the levels of atoms, molecules, clusters supramolecular structures and exploitation of their unique properties at the nanoscale. It has introduced these novel Nanomaterials including Nanoparticles into our environment. Environmental protection, water pollution, food safety and human health are major issues which need to be addressed as soon as possible. Nanotechnology endeavored to provide" smatter" materials used in environmental sensing and remediation of water pollution problem as well as protecting human health from various toxic materials. The advent of nanotechnology has given immeasurable opportunities to purify water even at ionic state. The various nanostructures materials have been fabricated with features such as high aspect ratio, reactivity, and tunable pore volume, electrostatic, hydrophilic and hydrophobic interactions which are useful in adsorption, catalysis, sensing, and optoelectronics. Nanotechnology, which literally refers to the manipulations of materials and processes that are engineered to the molecular scale of 1–100 nm, is an emerging field that poses immense ability to hierarchically construct materials from the bottom up approach to significantly improve the performance as well as add new functionality to the existing products. The evolutions and advancements explored in this field have urged seawater desalination progress as a more economical and sustainable option (Shannon et al. 2008). In this context, the paradigm shift made by the new approaches and technological innovation based on the new frontier in enabling nanoscience and nanotechnology, although not one size fits all, has advocated the progress of maintaining the sustainability in terms of reduced membrane materials, chemical and energy usage that eventually leads to minimized sources of environmental issues (Cloete 2010). Nanomaterials are the drivers of the nanotechnology revolution and a key bottleneck to the applications of nanotechnology to solve this world water crisis. Nanomaterials have a number of key physicochemical properties that make them particularly attractive as separation media for water purification. On a mass basis, they have much large surface areas than bulk particles. Nanomaterials can also be functionalized with various chemical groups to increase their affinity toward a given compound. They can also serve as high capacity/ selectivity and recyclable legends for toxic metal ions, radionuclides, organic and inorganic solutes/ anions in aqueous solutions. Nanomaterials also provide unprecedented opportunities to develop more efficient water-purification catalysts due to their large surface areas and their size and shape-dependent optical, electronic and catalytic properties.

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Water pollutants have huge impacts on the entire living systems including terrestrial, aquatic, and aerial flora and fauna. In addition to conventional priority, and newly emerging micro/nano-pollutants, increasing global warming and consequent climate changes are posing major threats to the freshwater availability. Global warming and climate change are constantly increasing the salinity level of both land and sea water, dwindling the availability of existing fresh water for household, agriculture and industry. This has made it urgent to invent an appropriate water treatment technology that not only removes macro-, micro- and nano-pollutants but also desalinates water to a significant extension. Continuing population growth and urbanization as well as rapid industrialization are constantly putting pressure on global water demand and resulting in an alarming scenario where accessible freshwater supply is no longer matching the patterns of these developments. Desalination has long served as a feasible option to provide safe drinking water in many deserted areas, coastal regions or remote locations (Crittenden et al. 2005). Water, being a universal solvent dissolves all kinds of contaminants like metal ions, inorganic anions, organic dyes, pesticides and insecticides, radioactive elements, *etc.* Therefore, great challenges lie in the removal of contaminants from drinking water at ultra-trace levels at an affordable cost.A common problem in developing countries in drinking water that is contaminated with bacteria and viruses, which are the main cause of water-borane diseases (Patzke et al. 2002). Due to change in climatic conditions, growing pollution, water will become an even scarer, especially in developing countries. Moreover, in these countries, available water is often unsafe to drink. The interesting facts are shown in Table 1.

This chapter mainly concerned with providing a review of the interests of scientists and researchers in the application of nanomaterials in the improvement of water treatment, and application of nanotech in water treatments has several advantages than the traditional water treatments and this review also identifying the grand challenges and directions for future avenues in the field of Nanotechnology applications in water treatment.

2. NANOPARTICLES IN WATER TREATMENT

Nanoparticles have two key properties that make them particularly attractive as sorbents. First, on a mass basis, they have much larger surface areas than bulk particles. Second, they can also be functionalized with various chemical groups to increase their affinity towards target compounds.

Table 1. The interesting facts are shown in Table 1

Figures	Facts
3.4 millions	In developing countries people dies from water-related diseases every year
63 millions	In developing countries like Bangladesh, India and Nepal people suffers from arsenic pollution
6Km	Women's from Asia and Asian continent walk to fetch water
80%	Water-related deaths in children between age 0-14 years
40%	Water-related deaths are due to diarrhoea

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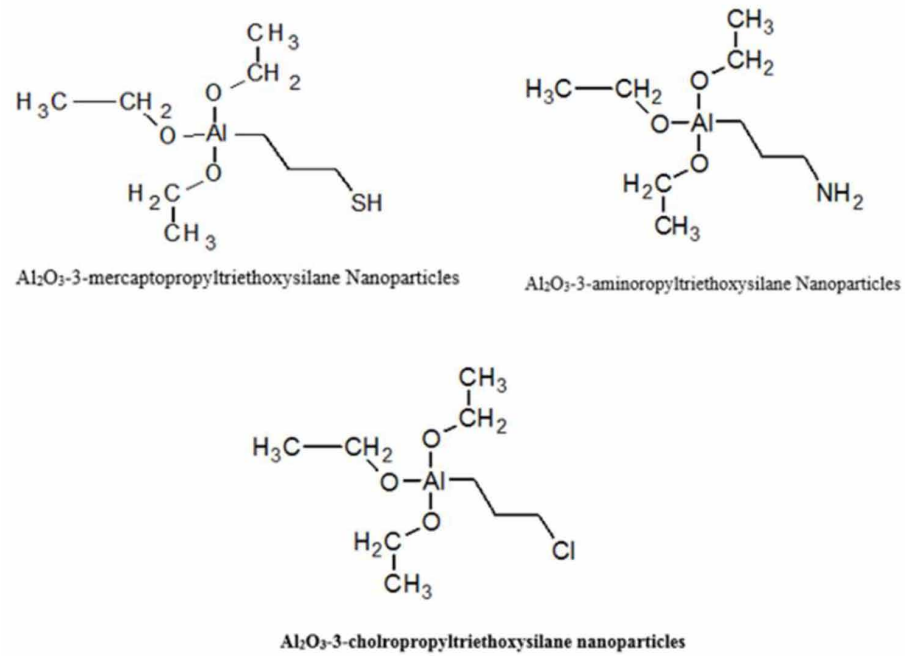
Applications of nanoparticles as adsorbents for high efficient removal of heavy metal ions from wastewater must satisfy the following criterions:

1. The nanosorbents themselves should be nontoxic
2. The sorbents must show relatively high sorption capacities and selectivity even to the low
3. The concentration of pollutants.
4. The adsorbed pollutant could be removed from the surface of the nanoadsorbent easily,
5. The sorbents could be infinitely recycled
6. The process should be reversible so that we can get our adsorbent back; the Nanoparticles
7. Studied in the removal of heavy metal ions from wastewater should show high adsorption
8. Capacity.

2.1 Alumina Nanoparticles for Water Remediation

Alumina is a traditional adsorbent for pollutants and Nanoparticles of alumina is anticipated to be more active than alumina in bulk state. Nanosized Al_2O_3 can be prepared by sol-gel method and has been employed as solid phase extraction materials for separation/ preconcentration of trace pollutants. Physical /Chemical modification of Al_2O_3 with various functional groups containing some donors atoms such as nitrogen, oxygen, and phosphorus have improved their separation/preconcentration toward emerging trace pollutants. Chitosan-grafted polyacrylamide nano-alumina Nanoparticles had been applied for the removal of arsenic from drinking water. Sorption of As(V) on aluminosilicate treated with iron nanocomposites and also alumina-silica nanocomposites had been applied for the adsorption of cadmium, lead from waste water (Medina et al. 2010). Figure 1 shows the structures of some alumina samples.

Figure 1. The structures of some alumina samples



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2.2 Silica Nanoparticles for Water Remediation

Silica nanoparticles is a promising material as a solid phase extractant because of its large surface area, high adsorption capacity, low-temperature modification, less degree of unsaturation and low electrophilicity (Kaur et al. 2009). The sequence of reactivity is expressed as follows:

$Zr(OR)_4$, $Al(OR)_4$> $Ti(OR)_4$> $Sn(OR)_4$>> $Si(OR)_4$

Some pollutants are poorly adsorbed on nanoparticles. To overcome this problem, physical or chemical modification of the surface of these nanoparticles with certain functional groups containing some donor atoms such as oxygen, nitrogen, sulfur and phosphorus are necessary. The most often used method is to load a kind of specific chelating reagent by the physical or chemical procedure. The formal method is simple but the loaded reagent is prone to leaking out from the sorbent, while the chemically bonded material is more stable and can be used repeatedly. The modification of nanometer sized materials is usually required in order to prevent a conglomeration of particles and to improve its consistency in relation to other materials. Also, the modification of nanometer-sized material can improve the selectivity of nanometer–sized materials toward pollutants. Selectivity of suitable specific functional groups towards metal ions depends on certain factors such as (1) size of the modifiers (2) activity of loaded group and also (3) on the basis of the concept of hard-soft acids and bases. Chemisorption of nanoparticles provides immobility, mechanical stability, and water insolubility, thereby increases the efficiency, sensitivity and selectivity.

Chemical modification is a process that leads to change in chemical characteristics of the surface of nanoparticles. By the modification, the adsorption properties are significantly affected. Chemisorption of chelating molecules on nanoparticle surface provides immobility, mechanical stability, and water insolubility, thereby increases the efficiency, sensitivity and selectivity of nanoparticles for the analytical application. Chemical modification of nanoparticles by silylation procedure using different silylating agents such as 3-aminopropyltriethoxysilane, 3-chloropropyltriethoxysilane and 3-mercaptopropyltriethoxysilane provides immobility, mechanical stability and water insolubility, Figure 2. 1-(2-pydriylazo)-2-naphthol-modified SiO_2 nanoparticles have been used for the preconcentration of some toxic heavy metal ions such as Cd(II),Zn(II), Mn(II), Ni(II), Sb(III), Pb(II) and also ferbam pesticides from various samples (Kaur and Gupta 2010). Resacetophenone-modified silica nanoparticles have also been used for the preconcentration of Pb(II) and Cd(II) from water samples.

2.3 Titania Nanoparticles for Water Remediation

Tiny particles of titanium dioxide are found as key ingredients in wall paints, sunscreens, and toothpaste; they act as reflectors of light or as abrasives. However, with decreasing particle size and a corresponding change in their surface-to-volume ratio, their properties change so that crystalline titanium dioxide nanoparticles acquire catalytic ability; activated by the UV component in sunlight, they break down toxins or catalyze other relevant reactions. Titanium oxide photocatalysts have been widely studied for solar energy conversion and environmental applications in the past several decades because of their high chemical stability, good photoactivity, relatively low cost and nontoxicity. However, the photocatalytic capability of TiO2 is limited to only ultraviolet light; to overcome this problem both chemical and physical modifi cation approaches were developed to extend the absorption band-edge of TiO2 into

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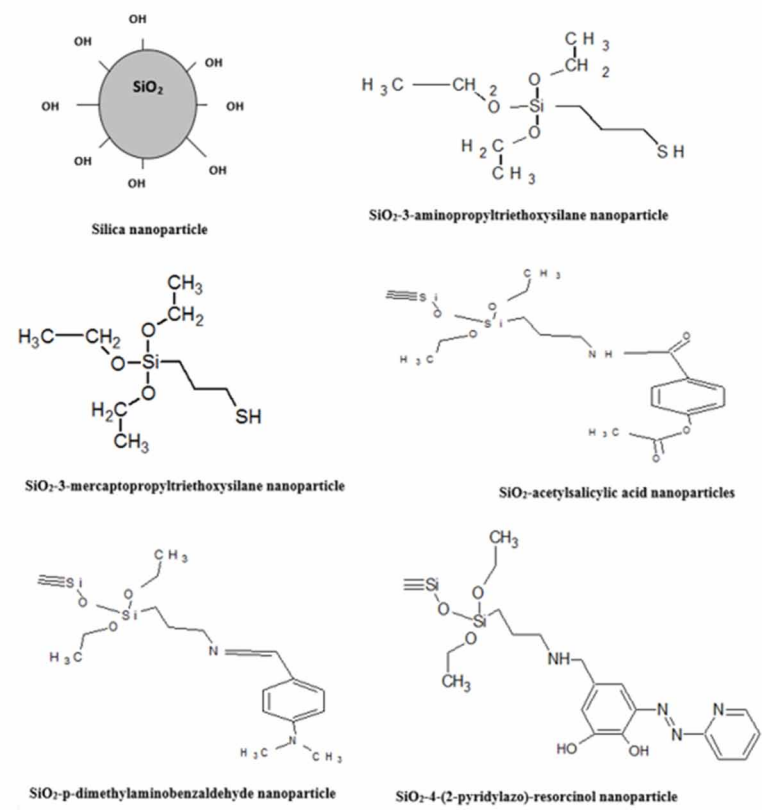
Figure 2. Chemical modification of silica nanoparticles with various silanes and ligands



visible region. In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts, an energetic light source, and an oxidizing agent such as oxygen or air. Only photons with energies greater than the bandgap energy (ΔE) can result in the excitation of the valence band (VB) electrons which then promote the possible reactions. The absorption of photons with energy lower than ΔE or longer wavelength usually causes energy dissipation in the form of heat.

TiO_2 nanoparticles have emerged as promising photocatalysts for water purification, Figure 3. The removal of total organic carbon from waters contaminated with organic wastes was greatly enhanced by the addition of TiO_2 nanoparticles in the presence of ultraviolet light. It was successfully used to degrade organic compounds (e.g. chlorinated alkanes and benzenes, dioxins, furans) pentacholorophenol and aromatic chlorinated compounds had been photo-catalytically studied using titania Nanoparticles (Mills Hoffmann 1993). Separation and microcolumn preconcentration of traces of rare earth elements on nanoscale TiO_2 and their determination in geological samples (Jardim et al. 1997).

2.5 Nanoscale Zero-Valent Metals

Iron is one of the most abundant elements on earth. Elemental iron has been used as an ideal candidate for remediation because it is inexpensive, abundant easy to prepare and apply to a variety of systems, and devoid of any known toxicity induced by its usage. The concept of using metals, such as iron, as remediation agents are based on reduction–oxidation or "redox" reactions, in which a neutral electron

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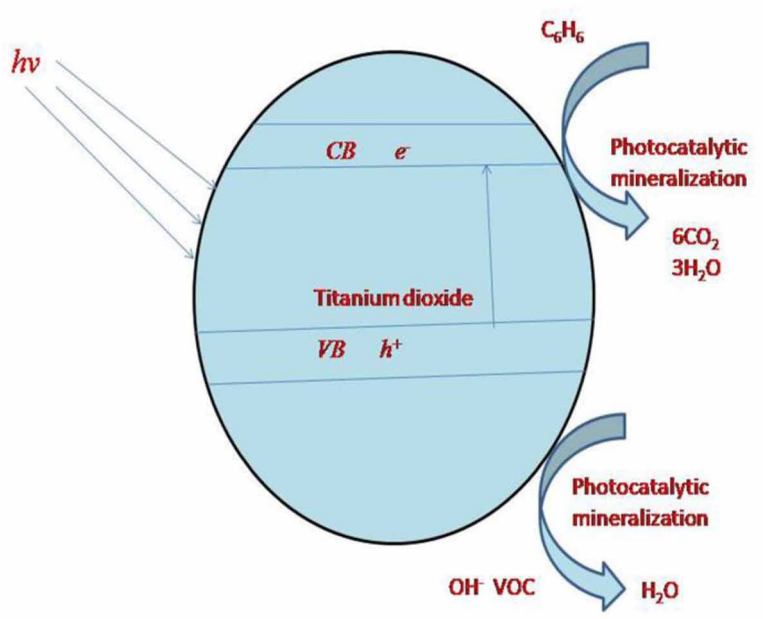
Figure 3. Photocatalytic studies by titania nanoparticles



donor (a metal) chemically reduces an electron acceptor (a contaminant). Nanoscale iron particles have surface areas significantly greater than larger-sized powders or granular iron, which leads to enhanced reactivity for the redox process. As a result, iron nanoparticles have been extensively investigated for the decomposition of halogenated hydrocarbons to benign hydrocarbons and the remediation of many other contaminants including anions and heavy metals. Zero-valent iron nanoparticles are highly reactive and react rapidly with surrounding media in the subsurface (Zhang Elliot, 2006). A significant loss of reactivity can occur before the particles are able to reach the target contaminant. In addition, zero-valent iron nanoparticles tend to flocculate when added to water, resulting in a reduction in the effective surface area of the metal. Therefore, the effectiveness of a remediation depends on the accessibility of the contaminants to the nanoparticles; and the maximum efficiency of remediation will be achieved only if the metal nanoparticles can effectively migrate without oxidation to the contaminant or the water/contaminant interface. To overcome such difficulties, a commonly used strategy is to incorporate iron nanoparticles within support materials, such as polymers, porous carbon, and polyelectrolytes. Dissolved As(III) had been removed by iron Nanoparticles-embedded macrporous composites. Amine-functionalized Nanoparticles used for the rapid capture and removal of bacterial pathogens. Nanoscale zero-valent iron and bimetallic particles for a contaminated site for water remediation. Zerovalent iron Nanoparticles were applied for reductive decholrination of octacholorodibenzo-p-dioxin. Bentonite supported Fe/Pd Nanoparticles for the dechlorination of p-cholorophenol and also for PCB (Zhao et al. 2011), Figure 4.

3.Other Materials for Nanoremediation

Graphene is the allotrope of carbon. Especially, graphene–metal oxide composites have attracted extensive attention for their potential applications in environmental and energy-related areas. In this brief

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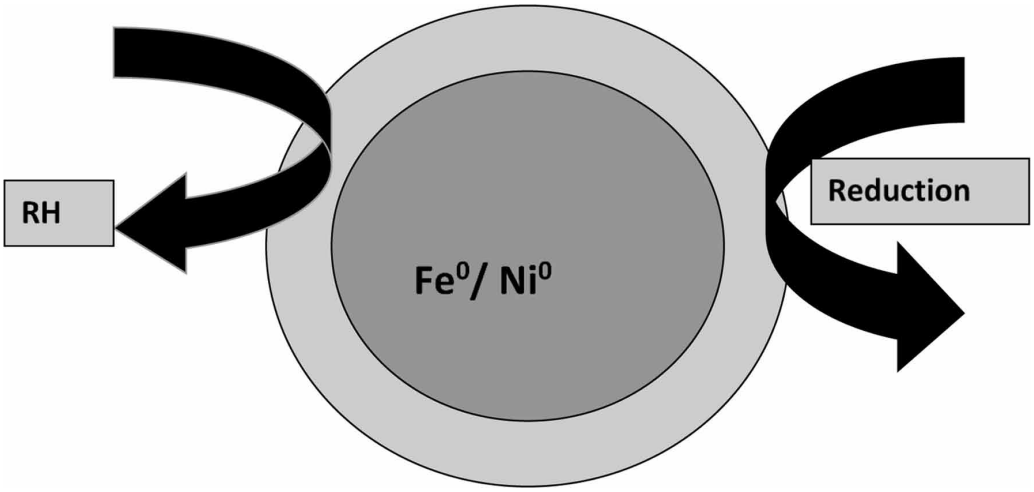
Figure 4. Dechlorination by Zerovalent iron Nanoparticles



review, we will summarize recent achievements of effective strategies for synthesizing high-quality graphene–metal oxide composites and their photocatalytic applications. Photo-catalytically degradation of volatile aromatic pollutant had done by TiO_2-graphene nanocomposites. Removal of Pb(II) ions from aqueous solutions on few-layered graphene oxide nanosheets (Zhao et al. 2011). Preconcentration of U(VI) ions on few-layered graphene oxide nanosheets from aqueous solutions. Folding/aggregation of graphene oxide and its application in Cu^{2+} removal. Adsorptive remediation of environmental pollutants using novel graphene-based Nanomaterials.Graphene-based PANI nanocomposites have also been used as sensing platforms due to their good electrocatalytic activity, high specific surface area, excellent reliability, and low-cost properties. These composites are successfully used for DNA, 4-aminophenol, dopamine, artesunate, hydrogen peroxide and hydrazine detection, as well as hydrogen (H_2), methane (CH_4) and ammonia (NH_3) gas sensing.

Innovative sensors with high sensitivity and selectivity, and fast response are in great need, and also we know the fast response is in great need. Biosensors and affinity sensor devices have been shown to have the ability to provide rapid, cost-effective, specific and reliable quantitative and qualitative analysis. To date, the developments in nanomaterials and biosensor fabrications technology are moving rapidly with new and novel nano biorecognition materials being developed which can be applied as the sensing receptors for mycotoxins analysis. Biosensors, as tools have proofed to be able to provide rapid, sensitive, robust and cost effective quantitative methods for on-site testing. Developing biosensor devices for different mycotoxins are attracting much research interest in recent years with a range of devices are being developed and reported in the scientific literature. However, with the advent of nanotechnology and its impact on developing ultrasensitive devices, mycotoxins analysis is benefiting also from the advances taking place in applying nanomaterials in sensors development (Saini and Kaur, 2012).

It was established that gold supported on various metal oxides is a useful candidate for alkenes hydrogenation. A few interesting revelations arose from this research. Thiol–modified gold-coated polystyrene particles had been used for adsorption of aromatic compounds. Dansyl-norvaline stereospecfic recognition had been done by albumin gold nanoparticles. Gold nanoparticles were also employed for an immunoassay for the detection of aflatoxin B1 (AFB1) in foods (Liu et al. 2003).

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Recently, MOFs, obtained by linking metal cations (or cationic metal clusters) with organic linkers, have attracted significant interest in the last years mainly due to the advantage of showing a large variety of structural types and chemical compositions, high surface area and permanent nanoscale porosity (Abhijith and Thakur 2012). MOFs have been widely studied as materials for catalysis gas storage and separation sensing and drug delivery and, more recently, the analytical applications of MOFs have emerged (Sumida et al. 2011). In this field, MOFs have shown to be promising materials as sorbents for sample preparation as chromatographic stationary phases, as well as for the development of improved detection systems and sensors. However, MOFs crystalline powders generally possess a random crystal size and shape, which makes troublesome their direct application and have led to engineer hybrid materials containing them, such as through supports, magnetic beads, beads coated with a MOF shell, or MOF crystals entrapped porous monolith. Porous materials are defined as solids containing empty voids which can host other molecules. The fundamental features of these materials are their porosity, the ratio between total occupied and empty space, the (average) size of the pores and the surface area (Meek et al. 2011). Typical surface area values for the porous materials applied in technological processes range between 2,000 and 8,000 $m^2\ g^{-1}$. The most important applications of such materials are the storage of small molecules and filtering .The metal organic frameworks are defined as a nanocomposite material which can be consisted of either inorganic or organic materials. MOFs have shown high potential in gas storage, separation, chemical sensing, drug delivery, and heterogeneous catalysis applications. In general, the flexible and highly porous structure of MOFs allows guest species such as metal ions to diffuse into their bulk structure. The shape and size of the pores lead to selectivity over the guests that may be adsorbed. These features make MOFs an ideal sorbent in solid phase extraction of heavy metals. However, there is little information about MOFs as an adsorbent.

Nanomaterials are well known to possess excellent electrical, optical, thermal, catalytic properties and strong mechanical strength, which offer great opportunities to construct nanomaterials-based sensors or devices for monitoring environmental contaminations in air, water, and soil. Various nanomaterials, such as carbon nanotubes, gold nanoparticles, silicon nanowires and quantum dots, have been extensively explored in detecting and measuring toxic metal ions, toxic gasses, pesticides, and hazardous industrial chemicals with high sensitivity, selectivity, and simplicity.

CNTs and graphene have been extensively studied for nanodevices or nanosensors (Bagheri et al. 2012). CNTs and graphene ideal candidates for environmental pollution detection, such as heavy metal ions (Hg^{2+}, Pb^{2+}, As^{3+}, Ag^{+}), organophosphate pesticides,toxic gasses,industrial wastewater. Kim *et al.* constructed a selective, sensitive, and fast single-walled carbon nanotube (SWCNT)- based field effect transistor nanosensor for Hg^{2+} ion detection (Kim et al. 2009; Zhang et al. 2010).

Metallic nanoparticles, especially gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) have received much attention due to their potential applications in chemical and biological sensors, medical diagnostics and therapeutics and biological imaging (Rosi et al. 2006). AuNPs or AgNPs exhibit high extinction coefficients and strong size- and distance-dependent optical properties, and are considered as a new class of reporters and have been applied in colorimetric sensing (Lee et al. 2007). Mirkin's group developed a series of colorimetric sensors based on the color of the AuNPs or AgNPs from the red to blue, which allow in situ, real-time qualitative or semiquantitative detection without complicated analytical instruments (Mirkin et al. 1997). On this basis, Lu et al. developed colorimetric sensors for environmental monitoring, such as heavy metal ions ($Pb^{2+,}$ $Hg^{2+),}$ radioactive metal detection ($UO_2^{\ 2+}$) (Liu and Lu, 2003).

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Chen et al. synthesized b-cyclodextrin (CD)-functionalized silver nanoparticles as probes for highly robust, quantitative, sensitive, and observable by the naked eye colorimetric detection of different isomers of aromatic compounds (Chen et al. 2010). He *et al.* developed an oligo-T-based gold nanoprobe for rapid and portable detection of mercury with the help of a power-free poly(dimethylsiloxane) (PDMS) microfluidic device (He et al. 2008).

Silicon-based nanomaterials are an important type of nanomaterial, which has been extensively studied due to their with single-molecule sensitivity. Therefore, metallic nanoparticles are also excellent candidate substrates for environmental monitoring by surface-enhanced Raman scattering techniques, such as phenol, pesticides, TNT and heavy metal ions.

Dasary *et al.* 2009, used a cysteine modified AuNPs-based miniaturized, inexpensive, ultrasensitive SERS probe for highly sensitive and selective screening of 2,4,6-trinitrotoluene (TNT) from aqueous solution, which can induce aplastic anemia and abnormal liver functions.

Other nanomaterials also have been used for environmental monitoring, such as Fe_3O_4, SiO_2, ZrO_2 *etc*. For example, Zuo et al. 2009, used a nanocomplex made of MWNTs and magnetic nanoparticles (MNPs, Fe3O4) for highly efficient catalytic oxidation of phenols and their removal from wastewater.

More importantly, several portable nanomaterials-based devices have been designed in this direction. The unique chemical and physical properties of nanomaterials provide a versatile toolbox for developing various detection techniques with high sensitivity, specificity, speed, simplicity and cost-effectiveness for environmental monitoring. However, there is still an urgent need to further improve the sensitivity, and probably more importantly, the operation convenience from a practical point of view. The possibility for mass production is also a critical point for widespread application of nanomaterials-based sensors. In this regard, the design simplicity and compatibility with industry standards should be considered. Overall, we expect that the exploration of new nanomaterials and/or elaborate nanostructures will become an innovative source for developing sensors for environmental monitoring, and such sensors may eventually find widespread applications with the efforts from both academics and industry.

CONCLUSION

Decontamination is the reduction or removal of chemical and biological agents by means of physical, chemical neutralization or detoxication techniques. Nanotechnology revolution will play an essential role in solving the problem of rising demands of clean water and decreasing of the available supplies of fresh water. Nanomaterials have a number of physicochemical properties that make them particularly attractive as separation media for water purification.Nanotechnology has shown huge potential in areas as diverse as drug development, water decontamination, information and communication technologies, and the production of stronger, lighter materials and human health care. Water and air are two vital components of life on earth; the existence of life on earth is made possible largely because of their importance to metabolic processes within the body. Clean and fresh water and air are essential for the existence of life. The recent development of nanotechnology has raised the possibility of environmental decontamination through several nanomaterials, processes, and tools. This chapter summarizes the expertise of various approaches of decontamination for the successful realization of remediation in the environment.

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Chapter 22
Determination of Rate of Medical Waste Generation Using RVM, MARS and MPMR

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ABSTRACT

The prediction of medical waste generation is an important task in hospital waste management. This article uses Relevance Vector Machine (RVM), Multivariate Adaptive Regression Spline (MARS) and Minimax Probability Machine Regression (MPMR) for prediction of rate of medical waste generation. Type of hospital, Capacity and Bed Occupancy has been used as inputs of RVM, MARS and MPMR. RVM is a probabilistic bayesian learning framework. MARS builds flexible model by using piecewise linear regressions. MPMR maximizes the minimum probability that future predicted outputs of the regression model will be within some bound of the true regression function. MARS, RVM and MPMR have been used as regression techniques. The results show that the developed RVM, MPMR and MARS give excellent models for determination of rate of medical waste generation.

INTRODUCTION

All over the world, wastes are generally interpreted as industrial or domestic. However, one kind of waste, on the rise, is bio-medical waste, disposed by hospitals. The number of hospitals is on the rise but these hospitals carry their share of potentially harmful baggage, that is, bio-medical wastes. These wastes, which can be municipal, pathological, sharps, etc, pose several threats such as environmental

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pollution, unfavourable smell. If they serve as breeding grounds for rodents, insects, they aid in affecting human and animal health by spreading diseases like typhoid, cholera, hepatitis and AIDS due to reuse of contaminated syringes, etc. The best possible method to tackle this is efficient and effective waste management. Unfortunately, collection, transport and disposal of waste have no proper strategy or planning behind its implementation. It urgently needs to that needs to be regulated by definitive rules (Askariana et al., 2004). Thus, the data that is needed primarily is the rate of waste generation. This depends upon several factors such as (i) number of bed/patient available at the hospital; (ii) type of specialization (type and range of care); and (iii) number, kind, and size of departments (Award et al., 2004). The objective of this paper is to predict the rate based on these factors as it will directly assist in planning an efficient waste management strategy. Artificial Neural Network (ANN) and Multiple Linear Regression (MLR) have been used for this purpose (Jahandideh et al., 2009). But they have shortcomings such as the low accuracy of MLR and the black box approach, over fitting issues, lack of generalization capability and slow convergence rate of ANN (Park & Rilett, 1999; Kecman, 2001).

This article adopts Relevance Vector Machine (RVM), Minimax Probability Machine Regression (MPMR) and Multivariate Adaptive Regression Spline (MARS) for determination of rate of medical waste generation. This article adopts the database collected from the work of Jahandideh et al., (2009). The dataset contains information about type of hospital, Capacity(C), Bed Occupancy (B_0) and Waste generation rates (kg/day) (w_t). RVM is based on Bayesian Estimation Theory. The distinctive advantage is that it gives rise to sparse regressors without affecting the performance (Tipping, 2000). RVM typically uses very less basis functions and it has proven its accuracy (Tipping, 2001). It has been used to solve different problems in engineering (Wang et al., 2012; Hsu et al., 2013; Cui et al., 2014). In MPMR, prediction is done while ensuring that the maximum probability of error is minimized (Lanckriet et al., 2002). This method has a plus point over ANN as control on future prediction data is possible (Lanckriet et al., 2002). MPMR has been used to solve different engineering problems (Sun et al., 2009; Yang et al., 2010; Zhou et al., 2013). GPR is a generic supervised learning method used to solve regression problems. This is developed based on Gaussian Processes. This is done by modelling the random processes as Gaussian processes. This method is versatile, practical, allows for generalization, and can specify very flexible non-linear regression too. This has been implemented for solving different problems in engineering (Heyns et al., 2012; Verrelst et al., 2013; Sun et al., 2014). A comparative study has been presented between the developed MARS, MPMR and RVM models.

DETAILS OF MARS

MARS uses basis functions to model the complex relationship between input(x) and output(y). The expression of MARS model is given below.

$$y = a_0 + \sum_{m=1}^{M} a_m B_m(x) \tag{1}$$

where a_0 is coefficient, $B_m(x)$ is basis function, a_m is coefficient of $B_m(x)$ and M is the number of basis functions. In this study, $x=[C, B_0, x_3, x_4, x_5, x_6]$ and $y=[w_t]$. Table 1 shows the value x_3, x_4, x_5 and x_6 for the different hospitals.

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Table 1. Input variables for different types of hospital (Jahandideh et al., 2009)

Type of Hospital	x_3	x_4	x_5	x_6
Private	1	0	0	0
Governmental	0	1	0	0
Educational	0	0	1	0
Non-educational, but university-related hospital	0	0	0	1

MARS adopts two-sided truncated power functions as basis function. The expression of two-sided truncated power function given below:

$$b_q^-\left(x-t\right)=\left[-\left(x-t\right)\right]_+^q=\begin{cases}\left(t-x\right)^q & \text{if } x>t\\ 0 & \text{otherwise}\end{cases} \tag{2}$$

$$b_q^+\left(x-t\right)=\left[+\left(x-t\right)\right]_+^q=\begin{cases}\left(x-t\right)^q & \text{if } x>t\\ 0 & \text{otherwise}\end{cases} \tag{3}$$

where q is power, t is the knot location and $b_q^-\left(x-t\right)$ and $b_q^+\left(x-t\right)$ are the spline functions.

A two-step procedure is used to develop the MARS model. In 1st step, basis functions are added to define equation (1). This step is called forward step. Overfitting can occur due to large number of basis functions. In 2nd step, basis functions are deleted based on Generalised Cross-Validation (GCV) (Craven & Wahba, 1979). This step is called backward step. The value of GCV is determined from the following equation.

$$GCV=\frac{\frac{1}{N}\sum_{i=1}^{N}\left[y_i-f(x_1)\right]^2}{\left[1-\frac{C\left(B\right)}{N}\right]^2} \tag{4}$$

where N is the number of data and C(B) is a complexity penalty that increases with the number of BF in the model and which is defined as:

$$C(B)=(B+1)+dB \tag{5}$$

where d is a penalty for each basis function (BF) included into the model.

In MARS, Analysis of Variance (ANOVA) is possible (Friedman, 1990). The expression of ANOVA for the MARS is given below:

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$$f(x) = \beta_0 + \sum_{B=1} f_i(x_i) + \sum_{B=2} f_{ij}(x_i, x_j) + \sum_{B=3} f_{ijk}(x_i, x_j, x_k) + \ldots \quad (6)$$

$\sum_{B=1} f_i x_i$ is over all basis functions that involve only a single variable.
$\sum_{B=2} f_{ij}(x_i, x_j)$ is over all basis functions that involve exactly two variables.
$\sum_{B=3} f_{ijk}(x_i, x_j, x_k)$ represents (if present) the contributions from three variable interactions and so on.

The total datasets have been divided into the following two groups:

- **Training Dataset:** This is used to develop the MARS. In this article, 35 datasets out of 50 have been adopted as training dataset.
- **Testing Dataset:** This is used to verify the developed MARS. This article uses the remaining 15 datasets as testing dataset.

The datasets are scaled between 0 and 1. The programming of MARS has been done by using MATLAB.

DETAILS OF RVM

RVM is a sparse Bayesian approach. In RVM, Gaussian prior is introduced on each parameter. RVM uses the following equation for prediction of output(y).

$$y = \Phi w + \varepsilon \quad (7)$$

where w is weight vector, $\Phi=[\varphi(x_1),\ldots,\varphi(x_N)]^T$ is design matrix, ε is noise and it follows mean-zero Gaussian distribution with variance σ2. The expression of $\phi(x_n)$ is given below:

$$\varphi(x_n) = \left[K(x_n, x_1), K(x_n, x_2), \ldots, K(x_n, x_M)\right] \quad (8)$$

where $K(x_n,x_i)$ is a kernel function.

The likelihood of the training dataset is given below:

$$p\left(y \mid w, \sigma^2\right) = \left(2\pi\sigma^2\right)^{-N/2} \exp\left\{-\frac{1}{2\sigma^2}\left\|y - \Phi w\right\|^2\right\} \quad (9)$$

The value of w and σ^2 has been determined by maximizing the above expression (9). To avoid over-fitting, w is set as a zero-mean Gaussian prior distribution with variance α-1:

$$p\left(w/\alpha\right) = \prod_{i=0}^{n} \mathrm{N}\left(w_i/0, \alpha_i^{-1}\right) = \prod_{i=0}^{n} \frac{\alpha_i}{\sqrt{2\pi}} \exp\left(-\frac{\left(w_i\alpha_i\right)^2}{2\pi}\right) \quad (10)$$

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where $\alpha=[\alpha_1,\alpha_2,\ldots,\alpha_n]$.

The posterior distribution of weight is given below:

$$p\left(w/y,\alpha,\sigma^2\right)=\left(2\pi\right)^{-(n+1)/2}\left|\sum\right|^{-1/2}\exp\left[-\frac{1}{2}\left(w-\mu\right)'\Sigma^{-1}\left(w-\mu\right)\right] \tag{11}$$

where μ is mean and $\sum$ is variance.

The marginal likelihood is given below:

$$\begin{aligned} &p\left(y/\alpha,\sigma^2\right)= \\ &\int p\left(y/w,\sigma^2\right)p\left(w/\alpha\right)dw=\left(2\pi\right)^{\frac{-n}{2}}\left|\sigma^2 I+\Phi A^{-1}\Phi'\right|^{\frac{-1}{1}}\times\exp\left[-\frac{1}{2}y'\left(\sigma^2 I+\Phi A^{-1}\Phi'\right)^{-1}y\right] \end{aligned} \tag{12}$$

Hyperparameter estimation is typically carried out with an iterative formula such as a gradient ascent on the objective function (Tipping, 2000). Predictions for a new data are then made according to integration of the weights to obtain the marginal likelihood for the hyperparameters.

RVM adopts the same training dataset, testing dataset, inputs, output and normalization technique as used by the MARS model. Radial basis function has been adopted as kernel function. The expression of radial basis functions is given below:

$$K\left(x_k,x\right)=\exp\left\{-\frac{\left(x_k-x\right)^T\left(x_k-x\right)}{2\sigma^2}\right\} \tag{13}$$

where σ is the width of radial basis function.

The program of RVM has been done by using MATLAB.

DETAILS OF MPMR

MPMR is developed by using kernel formulation on Minimax Probability Machine Classification (MPMC) (Lanckriet et al., 2002).

In MPMR, the relation between input(x) and output(y) is given below:

$$y=\sum_{i=1}^{N}\beta_i K(x_i,x)+b \tag{14}$$

where N is number of datasets, $K(x_i,x)$ is kernel function, βi and b are outputs the MPMR.

The datasets are divided into two classes (u_i and v_i).

$$u_i=(y_i+\varepsilon,\ x_{i1},\ x_{i2},\ \ldots,\ x_{in}) \tag{15}$$

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$$v_i = (y_i\text{-}\varepsilon, x_{i1}, x_{i2}, \ldots, x_{in}) \quad (16)$$

The classification between these two classes is regression surface.

MPMR adopts the same training datasets, testing dataset, inputs, output normalization technique, and kernel function as used by the RVM model. The program of MPMR has been constructed by using MATLAB.

RESULTS AND DISCUSSION

For MARS, ten basis functions have been added in forward step. In backward step, three basis functions have been deleted. So, the final MARS model contains seven basis functions. The expression of final MARS model is given below (by putting $y=w_t$, $a_0=0.047$ and $M=7$ in equation 1):

$$w_t = 0.047 + \sum_{m=1}^{7} a_m B_m(x) \quad (17)$$

Table 2 shows the details of a_m and $B_m(x)$.

The performance of training and testing datasets has been determined by using the above equation (Sun et al., 2014). Coefficient of Correlation(R) has been adopted to assess the performance of MPMR model. For a good model, the value of R should be close to one. The performance of training and testing datasets has been depicted in figure 1 and 2 respectively.

It is observed in figures 1 and 2 that the value of R is close to one for training as well as testing datasets. Therefore, the developed MARS proves his capability for prediction of wt. ANOVA decomposition has been done on the developed MARS. Table 3 shows the result of ANOVA decomposition.

The value of GCV is maximum C and B_0. So, C and B_0 have maximum effect on the predicted w_t. For developing RVM, the design value of σ has been determined by trial and error approach. The developed RVM gives best performance at σ=0.7. The performance of training and testing dataset has been illustrated in figure 1 and 2 respectively. It is clear from figures 1 and 2 that the value of R is close 1. The developed RVM presents the following equation for prediction of w_t.

Table 2. Details of $B_m(x)$ and a_m

$B_m(x)$	Equation	a_m
$B_1(x)$	max(0, C - 0.132)	-0.036
$B_2(x)$	$B_1(x)$max(0, B - 0.347)	4.109
$B_3(x)$	max(0, 0.038 – C)	-2.188
$B_4(x)$	max(0, C – 0.038) max(0, x_6 – 0)	0.231
$B_5(x)$	max(0, 0.277 – B)	-0.176
$B_6(x)$	max(0, 0.132 – C) max(0, 1 – x_6)	0.5
$B_7(x)$	max(0, 0.038 – C)	1.57

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Figure 1. Performance of training dataset

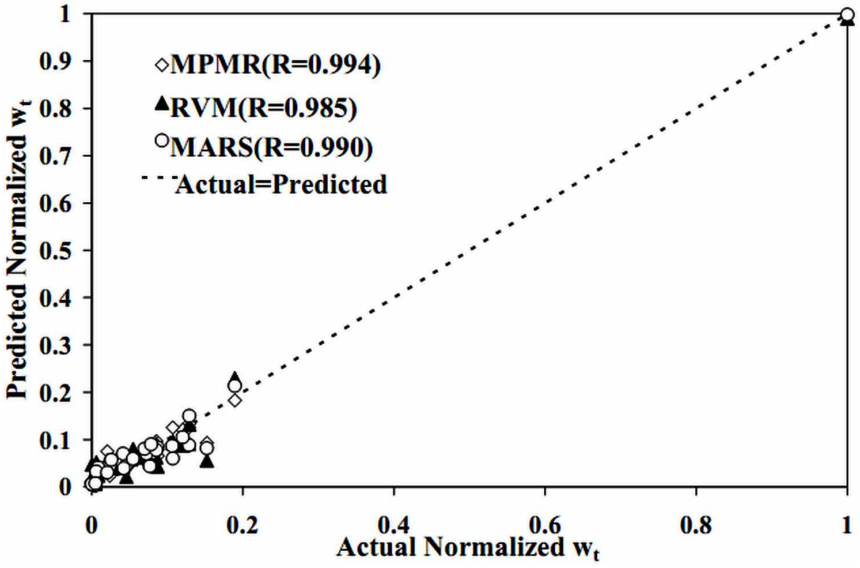

Figure 2. Performance of testing dataset

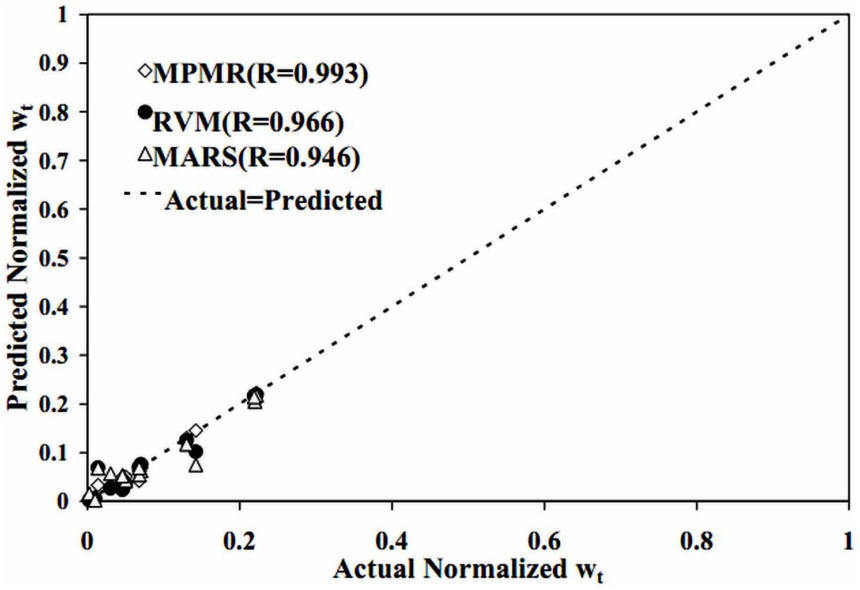

Table 3. Result of ANOVA decomposition

Function	GCV	STD	Basis Function	Variable
1	0.003	0.031	2	C
2	0.002	0.015	1	B_0
3	0.058	0.167	1	C, B_0
4	0.003	0.027	3	C,x_6

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$$w_t = \sum_{i=1}^{35} w_i \exp\left[\frac{-(x_i - x)(x_i - x)^T}{0.98}\right] \tag{18}$$

where the value of w has been given in figure 3.

This article adopts trial and error approach for determination of design values of ε and σ for developing the MPMR model. The developed MPMR gives best performance at ε=0.009 and σ=0.8. Figures 1 and 2 illustrate the performance of training and testing respectively. As shown in figures 1 and 2 that the value of R is close to one for the MPMR model. The performance of MPMR, MARS and RVM is comparable. MARS uses basis function for final prediction. However, RVM and MPMR adopt kernel function for developing model. There is a control over future prediction in the MPMR model. Whereas, the developed RVM and MARS have no control over future prediction. There are some statistical parameters mean (μ), and standard deviation (σ), other than the coefficient of correlation value, which have been used to justify the performance of the prediction techniques. The ratio of the predicted capacity (C_p) to the measured capacity (C_a) is the important parameter in evaluating the developed models (Farsakh & Titi, 2004; Das & Basudhar, 2006). The mean (μ), and standard deviation (σ) values of C_p/C_a explains the precision and accuracy of the developed predictive models.

From the above table 4, it was clearly depicted that the developed models mean and standard deviation values are nearby 1 and 0. Hence we can justify that the developed model performs well. Also with other distribution techniques have been adopted to determine the performance of the predictive techniques. The cumulative distribution values and probability density values of C_p/C_a have been determined and it's been plotted. The following figures will clearly project the performances of the developed models (see Figures 4, 5, and 6).

Figure 3. Values of w for the RVM model

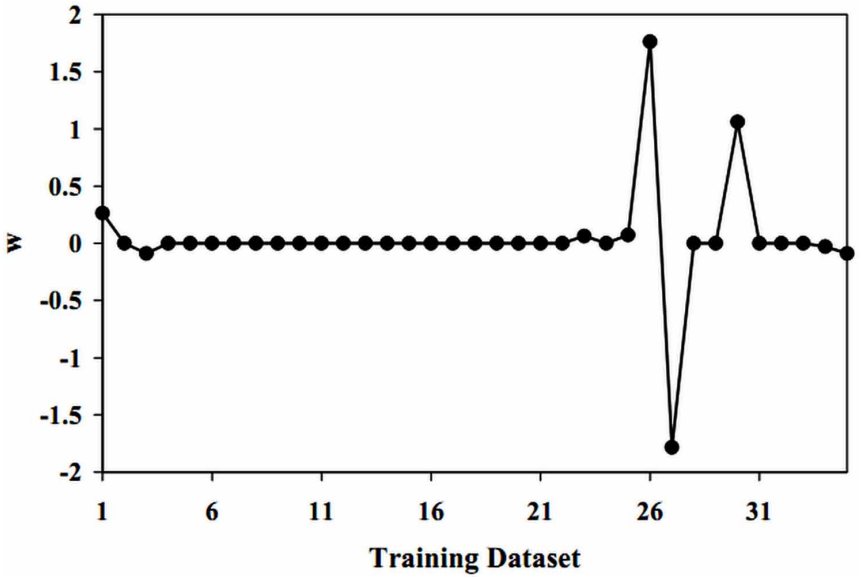

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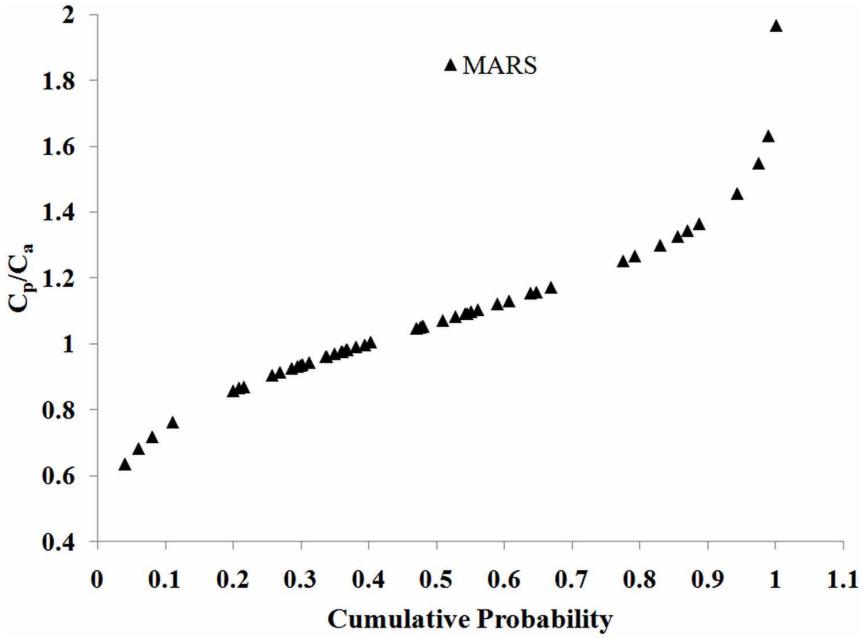
Table 4. Statistical criteria for the developed models

	MPMR	RVM	MARS
Mean (μ)	1.0371	1.0536	1.0648
Standard Deviation (σ)	0.176	0.3169	0.247

Figure 4. Cumulative probability plots of C_p/C_a for MARS model



These figures show that the maximum values have been lie on and nearby 1. These also refer the performance of the developed models. The following figure depicts the normal distributions of the developed models (see Figure 7, 8 and 9).

These figures exposed that the maximum values are closely packed on and nearby the peak 1. This also can be justified for the performance of the developed models.

In this chapter, the capacity of beds has been determined by using various techniques like MARS, RVM and MPMR. Different statistical criteria like Root Mean Square Error (RMSE), Mean Absolute Error (MAE), Coefficient of Efficiency (E), Root mean square error to observation's standard deviation ratio (RSR), Normalized Mean Biased Error (NMBE) and Performance Index (ρ) have been used to compare the developed model. The above mentioned statistical criteria have been determined by using the following equations.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(h_i - t_t\right)^2}{n}} \tag{19}$$

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Figure 5. Cumulative probability plots of C_p/C_a for RVM model

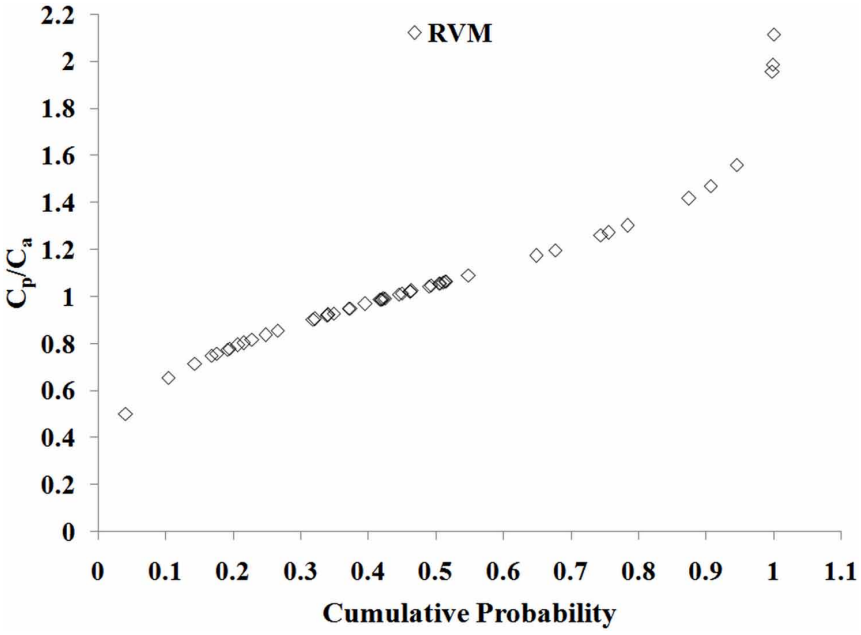

Figure 6. Cumulative probability plots of C_p/C_a for MPMR model

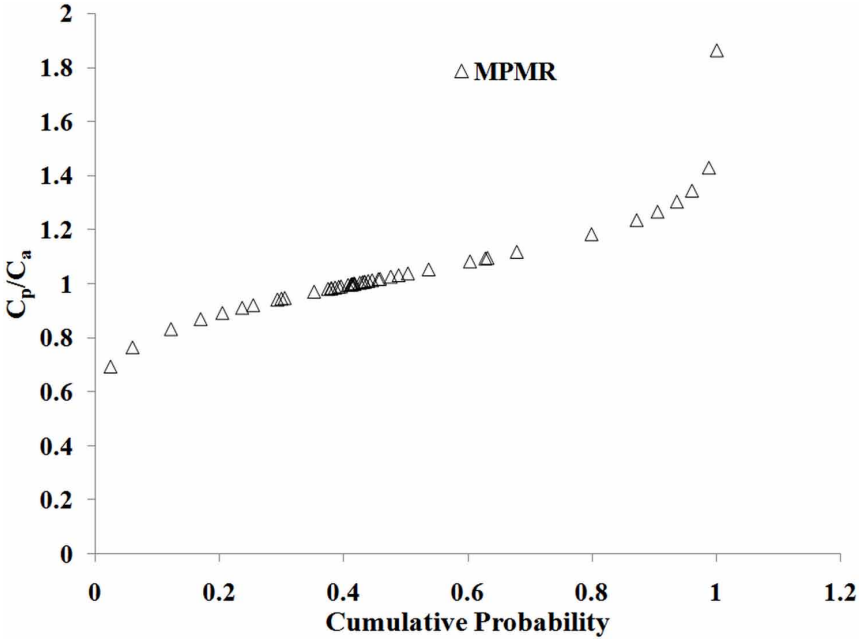

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Figure 7. Normal distribution of C_p/C_a for MARS model

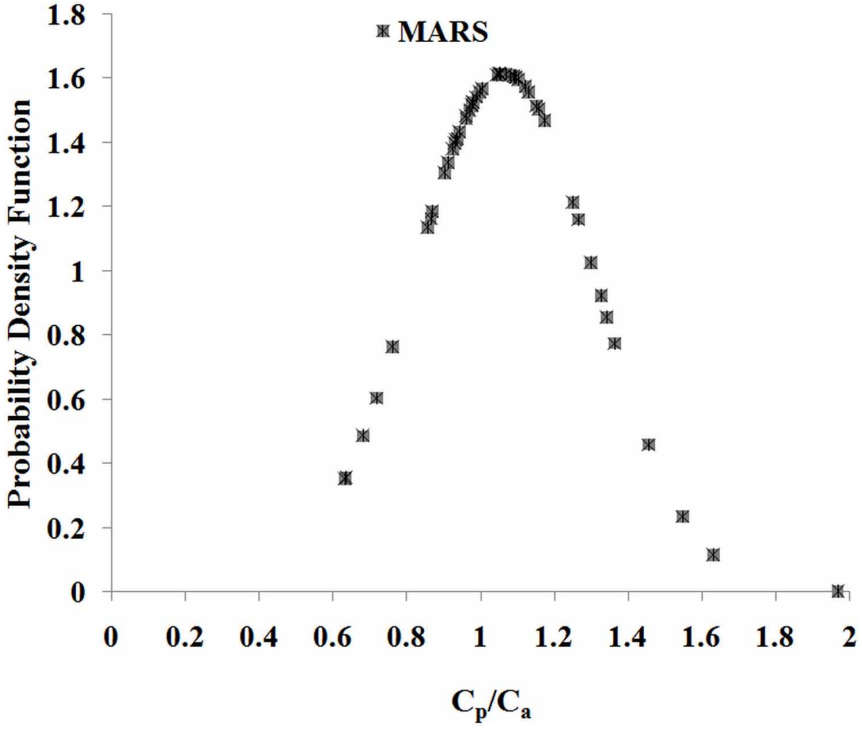

Figure 8. Normal distribution of C_p/C_a for RVM model

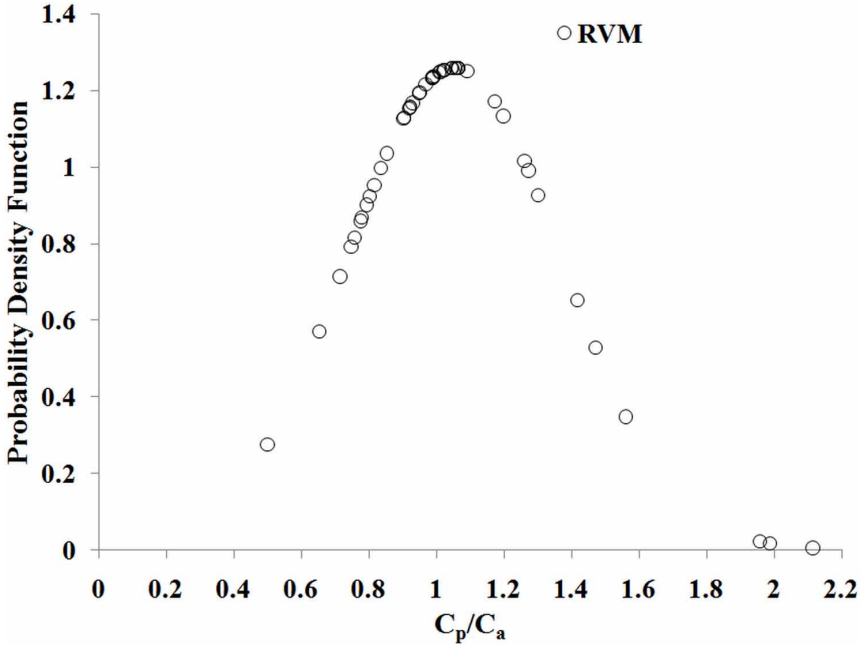

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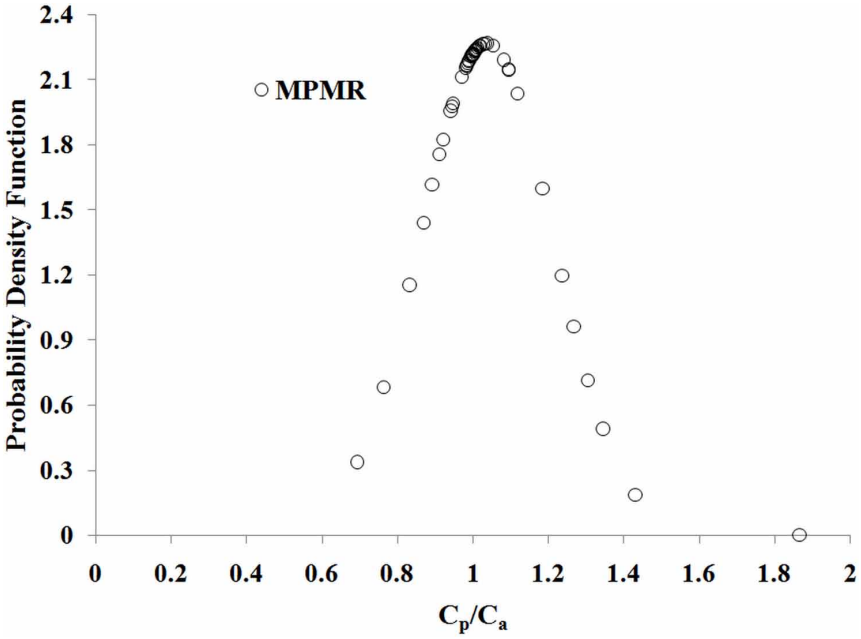
Figure 9. Normal distribution of C_p/C_a for MPMR model



$$MAE = \frac{\sum_{i=1}^{n} |h_i - t_i|}{n} \tag{20}$$

$$E = 1 - \frac{\sum_{i=1}^{N} \left(h_i - t_i\right)^2}{\sum_{i=1}^{N} \left(hi - \bar{h}_i\right)^2} \tag{21}$$

$$RSR = \frac{RMSE}{\sqrt{\frac{1}{N}\sum_{i=1}^{N} \left(hi - \bar{h}_i\right)^2}} \tag{22}$$

$$NMBE = \frac{\sum_{i=1}^{n} \left(t_i - h_i\right)}{\bar{h}_i \left(n - p\right)} \tag{23}$$

$$\rho = \frac{RMSE}{\bar{h}_i} \frac{1}{R+1} \tag{24}$$

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Table 5. Statistical criteria's for the developed models

	MPMR		RVM		MARS	
	Training	**Testing**	**Training**	**Testing**	**Training**	**Testing**
RMSE	10.02467	5.03506	16.37498	11.92397	13.28719	14.80699
MAE	5.94222	2.33106	11.69365	7.56408	9.61780	9.93414
E	0.98946	0.98753	0.97188	0.93005	0.98149	0.89213
RSR	0.00105	0.00248	-45.60998	0.00587	0.00139	0.06754
NMBE (%)	0.84955	-0.00623	-0.46869	-3.26163	0.90300	-1.77127
ρ	0.06563	0.28911	0.10769	0.29308	0.08717	0.29609

where h_i and t_i are the actual and predicted values for the i^{th} output, $\bar{h}_i$ and $\bar{t}_i$ are the average of the measured and predicted outputs, n is the total number of data and p is the number of predictor variables.

By using the above equations the values have been determined and it is tabulated in the following table 5.

CONCLUSION

This chapter examines the capability of MARS, MPMR and RVM for prediction of rate of medical waste generation based on type of hospital, capacity and bed occupancy. The developed MARS, MPMR and RVM give encouraging performance. The developed equations can be used practically. The result of ANOVA decomposition shows that C and B0 have maximum impact on the predicted w_t. The developed RVM only produces sparse solution. This article gives robust models based on MARS, RVM and MPMR for prediction of rate of medical waste generation.

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KEY TERMS AND DEFINITIONS

Artificial Neural Network: Artificial Neural Network is a structure framed with densely interconnected with artificial neurons that performs the parallel computations for data processing and knowledge representations.

Medical Waste: Medical waste is all waste materials generated at health care facilities, such as hospitals, clinics, physician's offices, dental practices, blood banks, and veterinary hospitals/clinics, as well as medical research facilities and laboratories.

Minimax Probability Machine Regression: It is the method used for maximizing the minimum probability of future predictions being within some bound of the true regression function.

Multivariate Adaptive Regression Spline: MARS is a nonparametric regression modeling technique based on split and conquer approach in which the training dataset are segregated into separate piecewise linear segments (splines) of differing gradients.

Prediction: The action of forecasting or estimating something is called as prediction.

Relevance Vector Machine: Relevance Vector Machine (RVM) uses Bayesian inference to get the solutions for classification and regression problems. It has same functional form of SVM, but provides the probabilistic classification.

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Chapter 23
Decision Insights for Shipbreaking using Environmental Impact Assessment:
Review and Perspectives

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ABSTRACT

This article describes how the shipbreaking industry has been under the microscope, more often in recent years, with scrutiny from governments, international agencies and environmental activists, on issues pertaining to sustainability in general and environmental impact in particular. Several cases of vessels-to-be-dismantled, by and large in yards located in South Asia, have been discussed in literature, with concerns on the modus operandi of dismantling end-of-life ships, and the mode of disposal of hazardous residual wastes. In this article, the authors review extant methodologies, and examine the decision alternatives available to shipbreakers, recyclers and waste material handlers to minimize damage to the environment. Impact assessment results using Open-LCA has been presented to demonstrate the relative impact loadings on various environmental parameters, from the path functions adopted. The results of the environmental impact assessment provide decision insights on various alternatives that may be appropriated in order to mitigate environmental damage. The article concludes with discussion, perspectives and future research directions to improve decision making for sustainable shipbreaking.

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1. INTRODUCTION

Shipbreaking is the process of dismantling a vessel, generally after its service period, for disposal, recycling or recovery of its structural components (Demaria, 2010; Patel et al., 2012). Over the last few decades, shipbreaking has grown into a multibillion dollar industry primarily located in India, Bangladesh, China, Pakistan and Turkey (Neşer et al., 2008; Sawyer, 2001). The industry is a major feeder of raw materials to the steel and construction industries (Sujauddin et al., 2015; Singh & Kaushik, 2002) in these countries and has flourished, thanks to the abundant labor resources available for shipbreaking at relatively cheaper rates (Rousmaniere & Raj, 2007). The regulatory framework (Bhattacharjee, 2009; Puthucherril, 2010; Alam & Faruque, 2014) and geographical advantages (Sibilia, 2015; Chang et al., 2010) have also contributed towards the growth of the shipbreaking industry in these locations. However, there has been increasing concern on the sustainability (Kusumaningdyah et al., 2013; Khan et al., 2012) of shipbreaking industry, particularly in view of the practices (Dodds, 2007; Hossain & Islam, 2006) that were prevalent in yards located in the subcontinent, comprising of the nation states of India, Bangladesh and Pakistan. This article examines the sustainability issues associated with shipbreaking activity, and draws insights to mitigate environmental impact using Life Cycle Assessment tool.

The desiderata of sustainable development envisioned by Brundtland Commission (1985) has been widely acknowledged and conceptualized as the sustainability pillars of (a) Economic Benefit, (b) Environmental Protection, and (c) Social Justice. The post-Brundtland world (Sneddon et al., 2006) has evolved on the tenets of sustainability and branched into field-specific discourses such as in operations (Kliendorfer et al., 2005; Gimenez et al., 2012; Tang & Zhou, 2012), manufacturing (Jayal et al., 2010; Garetti & Taisch, 2012) and supply chain management (Seuring & Müller, 2008; Carter & Rogers, 2008; Carter & Easton, 2011; Pagell & Wu, 2009; Gold et al., 2010). Over the years, there have been several research studies on environmental and social impact due to shipbreaking activities, capturing both qualitative and quantitative aspects. Considerable research in the past has been fixated on the environmental issues (Reddy et al., 2003, 2004a, 2004b, 2005a, 2005b; Hossain & Islam, 2006; Hossain et al., 2010; Asolekar, 2006, 2012) due to ship scrap wastes, while some researchers (Anderson, 2001; Deshpande et al., 2012; Neşer et al., 2008) have focused on worker safety aspects and human impact due to shipbreaking. Case studies of vessels-to-be-dismantled such as the French Aircraft Carrier 'Le Clemenceau' (Thomas, 2007) and Cruise liner 'Blue Lady' (Pelsy, 2008) have been deliberated in literature. Some researchers (Mikelis, 2008; Knapp et al., 2008) have undertaken statistical and econometric analyses of shipbreaking industry whereas others (Carvalho et al., 2011) have demonstrated methodologies for environmental impact modeling. However, we observe a lacuna in literature on insights to determine cause-effect relations on environmental impact parameters during shipbreaking, recycling and disposal. These insights would be useful to mitigate specific and measurable environmental impacts based on standard parameters.

The motivation for this study stems from the need to address and contain issues (Smith, 2003) related to environmental impact due to shipbreaking and waste disposal post-dismantling that affects the local population and their livelihoods in the form of health problems, resource degradation, lower agricultural produce and deterioration in fishing catchment areas (Abdullah et al., 2013; Pasha et al., 2012) among others. Shama (2005) had proposed the use of Life Cycle Assessment to determine the environmental performance of ships, and since then, several studies (Kameyama et al., 2005; Zuin et al., 2009; Tincelin et al., 2010; Chatzinikolaou & Ventikos, 2013) have been conducted along those lines. However, the employment of this technique is constrained in practice by the necessary inventory control documentation

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required. With the adoption of Hong Kong Convention (Nassar & Moursy, 2016) and book keeping of the Inventory of Hazardous Materials (IHM) on board in the form of 'Green Passport', we demonstrate in this research the decision insights available to mitigate environmental impact post-dismantling.

2. SHIPBREAKING SCENARIO

The shipbreaking business got an impetus post the Lehmann crisis (Ahn et al., 2011), with global ship-scrap tonnage volumes swelling up to decade high levels (MEPC, 2012). This trigger that boosted the shipbreaking activity was understandable, given the concerns about the world economy slipping into a recessionary phase, plunging spot rates and declining shipping indices such as Baltic Dry Index (Gemen & Smith, 2012), HARPEX (Balliauw, 2015) and BDTI (Kavussanos & Dimitrakopoulos, 2011). Foreseeing excess supply of ships and lackluster business for the next couple of years, several ship owners took their ships to the shores, for scrapping well ahead of its service life; sometimes cutting into as much as a third of the vessel's intended design life. A majority of these vessels found their graveyards along the beaches of South Asia, principally in Bangladesh, India, Pakistan, and to a lesser extent in China (Mikelis, 2013). The location of the major shipbreaking yards and their salient characteristics are depicted in Figure 1 and Table 1 respectively. The data for ship demolition gross tonnage over the years was collated from a combination of registers such as Clarkson Research, Lloyd's IHS Fairplay and BIMCO bulletins, and trends of ship demolition market from 1980-2011 are represented in Figure 2. More recent trends of country-wise ship demolition from 2011-2015 is presented in Figure 3.

It may be noted that the type of vessels demolished and the method of shipbreaking varies at different locations. For example, a great majority of the large vessels such as bulkers, general cargo vessels, oil tankers, chemical tankers, gas tankers and large passenger vessels run up on the intertidal zones of Alang, Gadani and Chittagong where beaching method is practiced (Lloyd's Register, 2011). The beaching method in open mudflat areas is a source of severe coastal pollution, combined with dangerous working conditions for the workers (NGO Shipbreaking Platform, 2016), although more profitable for the ship owners, and cash-buyers, who often recourse to re-register waste laden end-of-life vessels with flags of convenience, to circumvent stringent norms. Vessels that are dismantled in controlled conditions such as in dry-docks at locations in Western Europe, United States and to some extent in China, represent

Figure 1. Major shipbreaking locations around the world

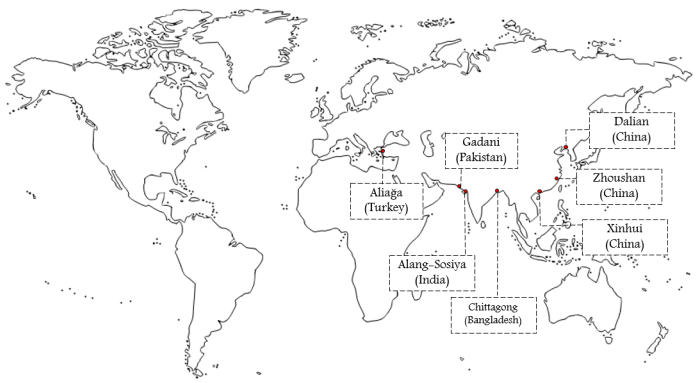

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Figure 2. Shipbreaking (in terms of GT) trends from 1980-2011 based on location of demolition (Source: Shipbuilding Statistics, Shipbuilders' Association of Japan (2013))

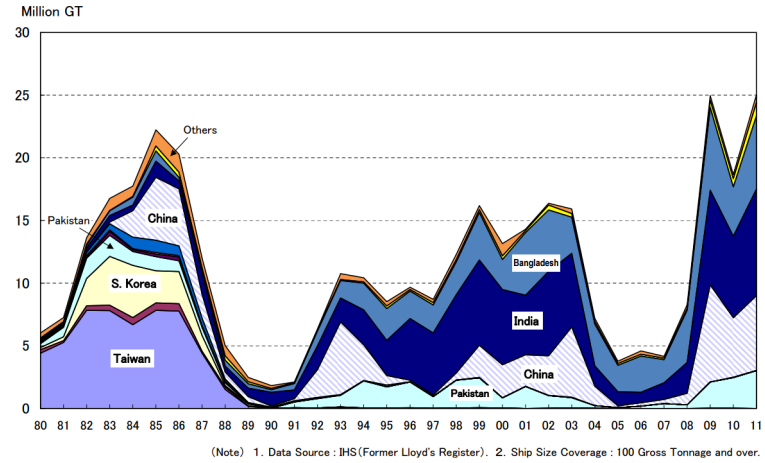

Figure 3. Country-wise ship demolition trends from 2011-2015

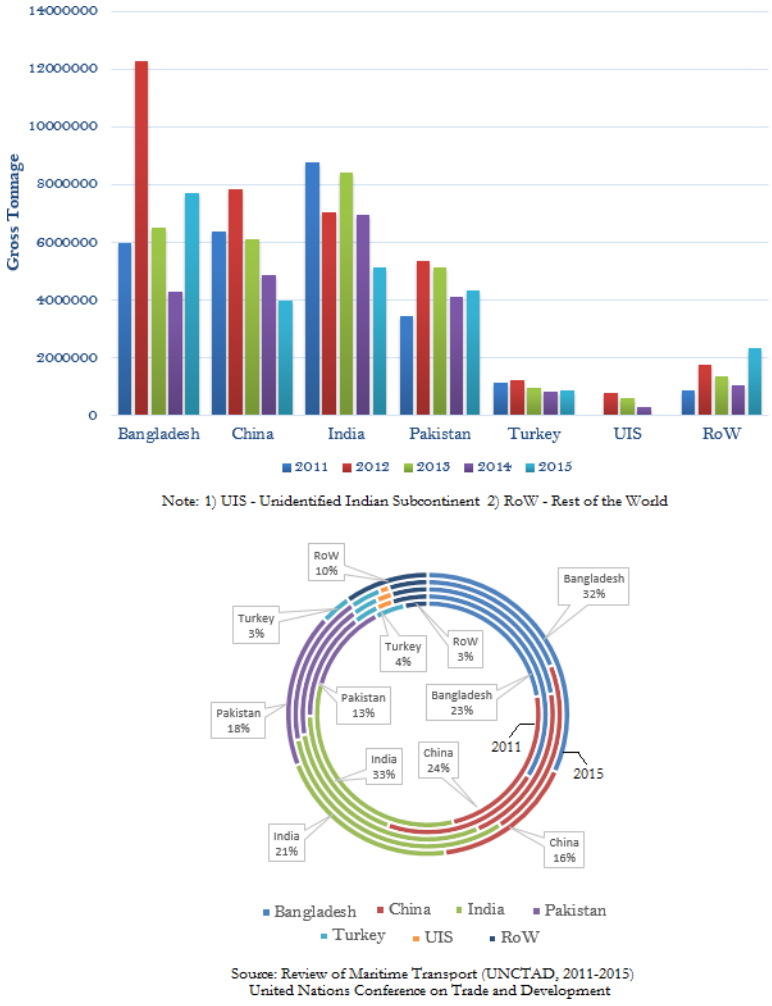

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Table 1. Salient Characteristics of Shipbreaking Facilities around the world

Shipbreaking Facility (Location)	Shipbreaking Method and Unique Characteristics	Business Practices and Areas of Concern
Bangladesh	Beaching method is practiced for shipbreaking over the 15 km long intertidal mudflats in Sitakund region along the coastline just outside the major port city of Chittagong in Bangladesh. Dismantling happens in open beaches using winches and cutting equipment, predominantly in leased government owned land with little regulation.	Dangerous working condition due to lack of proper Personal Protection Equipment (PPE) for workers, medical facilities, low pay, long working hours, exploitation of underage or child laborers. No strict law enforcement, hazardous waste dumping and absence of downstream waste management facilities are major points of concern.
India	Alang-Sosiya Ship Recycling Yard, 50 km away from the port city of Bhavnagar (Gujarat) was the largest shipbreaking facility in the world particularly during the last decade, employing the beaching technique. Of the 170 shipbreaking plots leased-out, about 50 are active and 4 are compliant with IMO's Hong Kong Convention [certified by Class NK], with cemented secondary cutting zones, installed drainage systems & improved hazardous waste storage facilities.	Environmental concerns related to continued operations in unprotected tidal waters at some shipbreaking plots at Alang. No proper disposal site for some end components of disassembled ship such as PCBs, re-sale of asbestos containing materials in second hand market, inadequate environmental impact assessment regarding pollution by toxic paints, slag, debris, oil spill etc. at the intertidal zone, and air pollution due to release of toxic fumes.
Pakistan	Beaching is practiced at Gadani, in Balochistan Province, about 50 km west of Pakistan's largest port city of Karachi. There are about 40 companies operating in 130 shipbreaking plots. Shipbreaking is labor intensive with large migrant workforce from the North-Western Frontier Province of Khyber Pakhtunkhwa. The yards operate directly on the beach without any impermeable and drained working sites to protect land & sea from pollution.	Shipbreaking is unregulated and there is no proper legal regime in place. The hazardous working conditions came to light recently with the campaigns of international and local NGOs to provide better working conditions and environmental protection. The shipbreaking sites at Gadani do not have any hazardous waste management system, resulting in wastes, asbestos & chemicals being dumped at site.
China	Shipbreaking in China is mainly done at 3 locations: Dalian in the north, and Xinhui & Zhoushan in the south. The quay-side method of breaking the vessel from the superstructure to the keel using cranes is practiced in some locations; slipways & dry-docking is also being practiced in China. Beaching is banned in China with efforts to upgrade & modernize facilities for environmental protection as per IMO's Hong Kong Convention.	China subsidizes demolition of Chinese flagged vessels retaining domestic end-of-life vessels for its own dismantling industries. Banning beaching, facility upgrade and compliance with Hong Kong Convention has made China preferred destination for European Owners. Concerns include absence of independent trade unions, minimal protective gear for workers, lack of fully safe asbestos removal & hazardous waste tracking downstream.
Turkey	Shipbreaking is practiced at Aliaga in Turkey using the Landing Method, wherein the bow of the vessel is grounded on the shore while the stern is afloat, and cut blocks lifted up stepwise using cranes and moved to a controlled working area for further disassembly. Aliaga is 50 km north of Izmir on the Aegean coast, and shipbreaking activity is carried out mostly by migrant workers from Tokat and Sivas area in Eastern Turkey.	Although shipbreaking yards in Turkey are in better standing than their South Asian counterparts, the working conditions and environmental standards lag OECD criteria. In recent years, Turkish yards have opened doors to cooperate with European governments, research experts & consultants to dismantle obsolete naval vessels; concerns still persist on downstream management of heavy metals, paints and PCBs.
Rest of the World	Shipbreaking facilities such as dry-docks & slipways are available in OECD countries such as USA, UK, Belgium, Denmark, South Korea and Sweden. Dismantling at these locations are done under controlled and safe environment, nonetheless not viable at large scale due to high cost factor.	Small and medium size commercial vessels and naval ships are dismantled in these locations in North America & Western Europe. The quality of service is generally considered high in OECD countries, with proper worker safety and downstream waste management systems in place.

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only a minority of the global shipbreaking activity (UNCTAD, 2015). The European Regulation on Ship Recycling (European Parliament, 2013), which entered into force in 2013, requires all ships (not only EU-flagged vessels) entering EU ports to have an Inventory of Hazardous Material (IHM) on board, enabling tracking vessels of European origin, and effectively prohibiting and preventing trans-boundary movement of hazardous wastes including end-of-life ships. The regulation also mandates EU flagged vessels to be dismantled only at locations in the European Commission approved list of global recycling facilities.

Turkey and China are two other notable shipbreaking locations. The landing method is generally practiced at Aliaga, Turkey, which accounts for less than 5 per cent of the global shipbreaking. China, has maintained its foothold at about one-fifth of the global shipbreaking, and is attracting new customers using a combination of policies, domestic subsidies and investments in modern, environment friendly, ship dismantling & recycling facilities. The method of ship dismantling in China include slip-way, dry-docking and quay side method.

3. METHODOLOGY

In this research, we use life cycle assessment (LCA) method to study the environmental impact during ship dismantling and subsequent waste treatment. It may be noted that the total impact of the vessel during its lifecycle will be dependent on the original design and components of the vessel, its operation and maintenance during service, and method of shipbreaking and waste treatment adopted. In this study, we will be focusing on the final phase post-decommissioning of the vessel, i.e. the impact due to breaking, disposal or recycling of the vessel.

The environmental impact due to method of decommissioning, and the consequent effects can be assessed by using an appropriate LCA tool. In this study, we adopt CML 2001 impact assessment criteria developed by the Centre of Environmental Science, Leiden University, which has been applied in similar contexts (Shen et al., 2010; El-Houjeiri et al., 2013) to assess the impact of end-of-life products. The analysis is performed using Open-LCA 1.3.0, an open-source software for Impact Assessment created by GreenDelta. The inventory of materials is sourced from the 'Green Passport' of the vessel (ship or boat), and the requisite path functions representing the material treatment processes post decommissioning is coded using the *Ecoinvent* database inbuilt in the software. Based on the LCA model, the effects observed from analysis results is interpreted. Further, the effects on multiple parameters such as acidification potential, climate change, eutrophication potential, freshwater aquatic eco-toxicity, freshwater sediment eco-toxicity, human toxicity, ionizing radiation, land use competition, photochemical oxidation, marine aquatic eco-toxicity, marine sediment eco-toxicity, stratospheric ozone depletion, terrestrial eco-toxicity etc. are deliberated. In conclusion, using LCA, we consider and evaluate the alternatives for mitigating the environmental impact on specified standard criteria, and in effect alleviate the carbon footprint associated with the shipbreaking and recycling processes.

4. CASE ILLUSTRATION

This section illustrates a case of applying LCA tool to model and assess the environmental impacts from breaking a vessel. There have been few case studies (Thomas, 2007; Pelsy, 2008) in the past illustrat-

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ing the visible impacts of shipbreaking, such as decrease in agricultural produce, reduction in fishing catchment in the region, and occupational diseases affecting workers involved in shipbreaking activity. However, the latent effects of shipbreaking which are explicit only in medium or long term can be significant, as exemplified in this case.

The case is of a Ro-Ro Lo-Lo (Roll on / Roll off & Lift on/ Lift off) Semi-Submersible Heavy Lift Container Carrier Vessel. The vessel is over 20 years old and is lined up for decommissioning and subsequent disassembly. The location of last port of call is Alang, Gujarat (India), one of the largest shipbreaking and recycling yards in the world. In order to ascertain the impact, the system, material and energy inflows and outflows from the system boundaries are to be defined. The boundaries of our system, in this context is defined as the region in Bhavnagar, Gujarat, within 100 km radius of Alang-Sosiya yard wherein there is maximum concentrated impact due to the shipbreaking activity. The material and energy flows are collated from the vessel data (effectively, the *Green Passport*), inclusive of inventory of all structural, piping, outfit, and other components. This serves as the input data to the LCA model, the major part of which is mass-component, with a minor component representing energy transactions. The inventory of material is sourced from 52 functional group categories of the vessel with subcategories, the total of which amounts to 6700 Tonne of lightship with over ten thousand parts at component level.

It must be critically noted that the model inflows may include traces, heavy elements such as zinc, cobalt, chromium, traces of asbestos etc. that may be part of the vessel in small quantities but can cause significant impact on certain impact categories. The mass-energy factors such as transport fuel burnt, routing and logistical distances covered, amount of heavy fuel, plastic wastes, landfill disposal quantity, amount of incinerated wastes etc. also need to be represented in the model. In this case, we compare 2 product systems representing decision alternatives: (a) Ship Recycling where over 90% of the vessel is recycled, and (b) Ship Scrapping where over 50% of the vessel components are disposed, and not reused. The 5-step LCA model preparation for each of the product systems is enumerated below:

1. Defining boundary condition for product system
2. Defining flows: Material & Energy Movement in/out of the system
3. Defining Processes: Combination of flow relations within the system
4. Defining Product Systems: Combination of 2 or more Processes
5. Inputting Specific Data relating to Product Systems

The processes within alternative product systems defined, namely ‘ship recycling’ and ‘ship scrapping’ could be inherently different. This is because, despite the basic flows such as steel smelting and transport being similar in alternative product systems, the process paths and distribution may vary. For example, in ship recycling more than 90% ideally is recycled and fed back into the steel rolling and reusage; unlike in ship scrapping wherein sometimes about 50% of the material may be disposed away in landfills. The processes within a product system is therefore defined by the path it ensues, and hence to be defined by the system modeler to be as close to reality. The complexity of the processes varies according to the flows within the systems and the inter-linkages between them. Figure 4 show part of the processes within the ‘Ship Recycling’ product system. Note that there are sub-processes as well, some of which may be defined within the open source database.

The data is inputted from the *Green Passport* of the vessel to model the ‘Ship Recycling’ and ‘Ship Scrapping’ Product Systems. Note that in this case, 50-60% of the decommissioned vessel was retrieved for reuse during Ship Scrapping’. About 40-50% of outfit and structural & paneling material such as glass-

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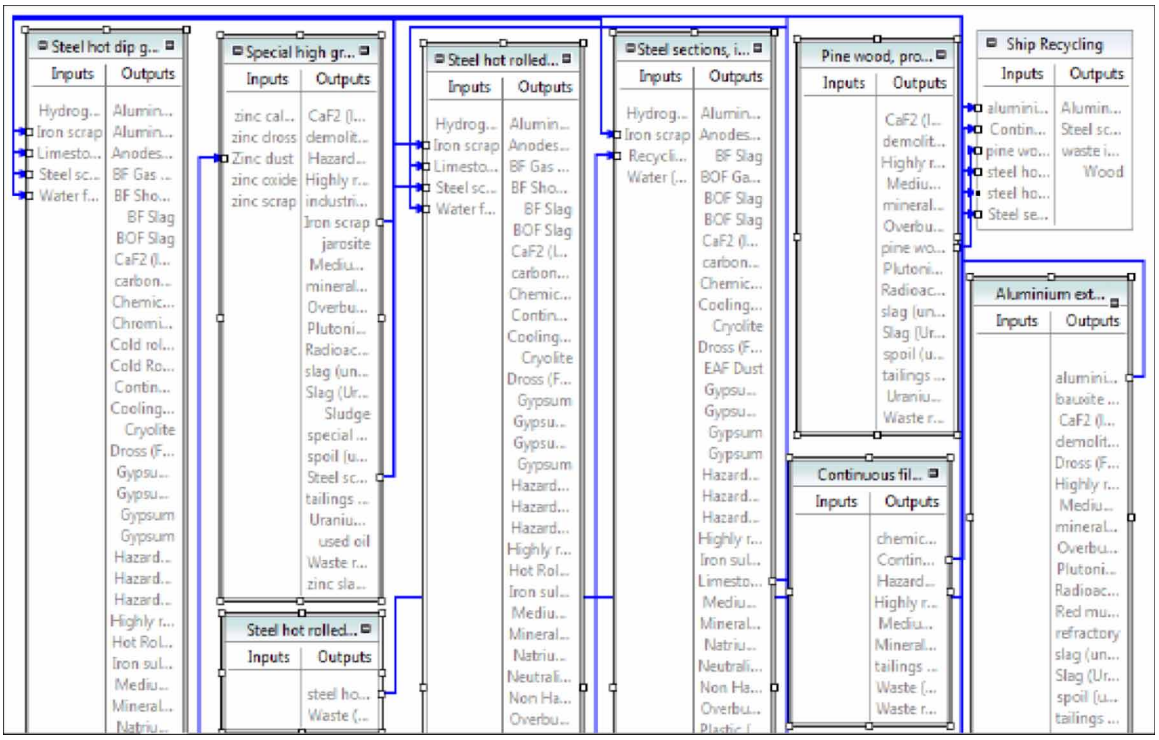
Figure 4. Processes defined by paths in a product system (ship recycling)



wool /filament was disposed during disassembly, in addition to heavy elements that otherwise seep into the environment during the disassembly process. In contrast, for the 'Ship Recycling' Product System, over 90% of the materials enter the closed-loop of the supply chain and are remanufactured, recycled or reused. Figures 5 & 6 depict representative summaries of Data input/output for Ship Recycling & Ship Scrapping Product Systems respectively. The product systems are analyzed based on CML 2001 criteria. The parameters for impact comparison based on the two product systems are listed in Table 2 with their definitions.

5. RESULTS

In this section, we describe the results of LCA analysis of the two product systems, namely, 'Ship Scrapping' & Ship Recycling'. For the purpose of comparative representation of results we present the relative impact of 2 product systems, in addition to absolute impact of ship scrapping product system, which the LCA analysis demonstrates to cause higher environmental impact. Figure 7 depicts the comparative analysis of impact due to steel. Note that steel is the principal category of the vessel by weight including significant of structural components such as hot rolled steel plates, steel piping and outfit components.

It may be observed from Figure 7 that there is significant difference in impact based on post treatment of steel, based on recycling or scrapping methods; photochemical oxidation causing the highest impact in recycling but considerably lesser than the alternative of scrapping. Steel being major component of ships, accounting for over 80% weight of small-to-medium sized ships and as much as 95% for very

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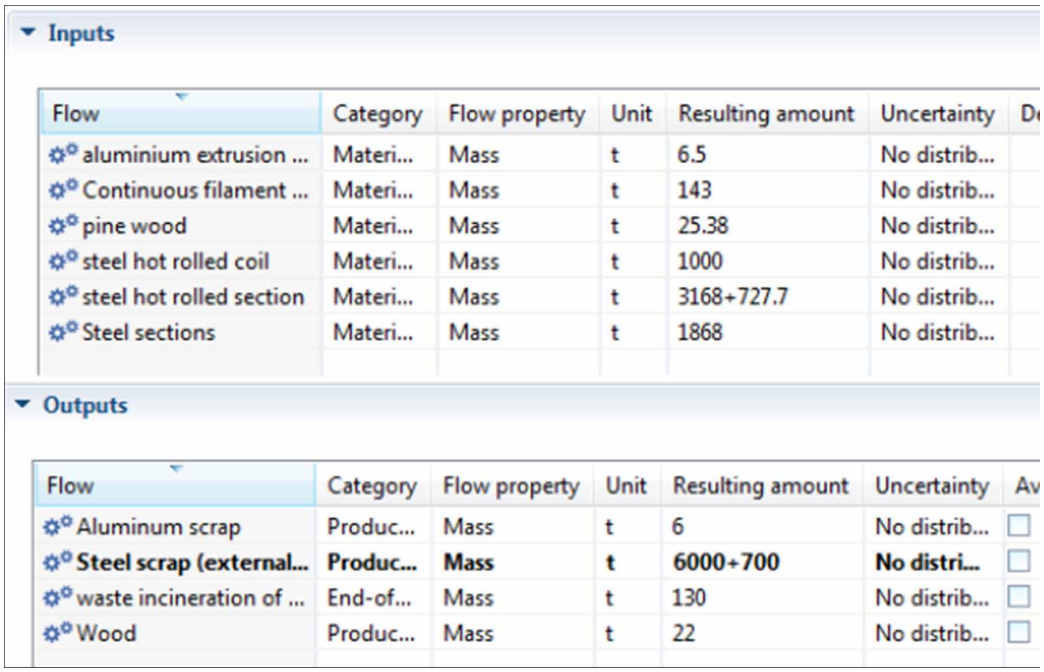
Figure 5. Summary of data input/output summary for ship recycling



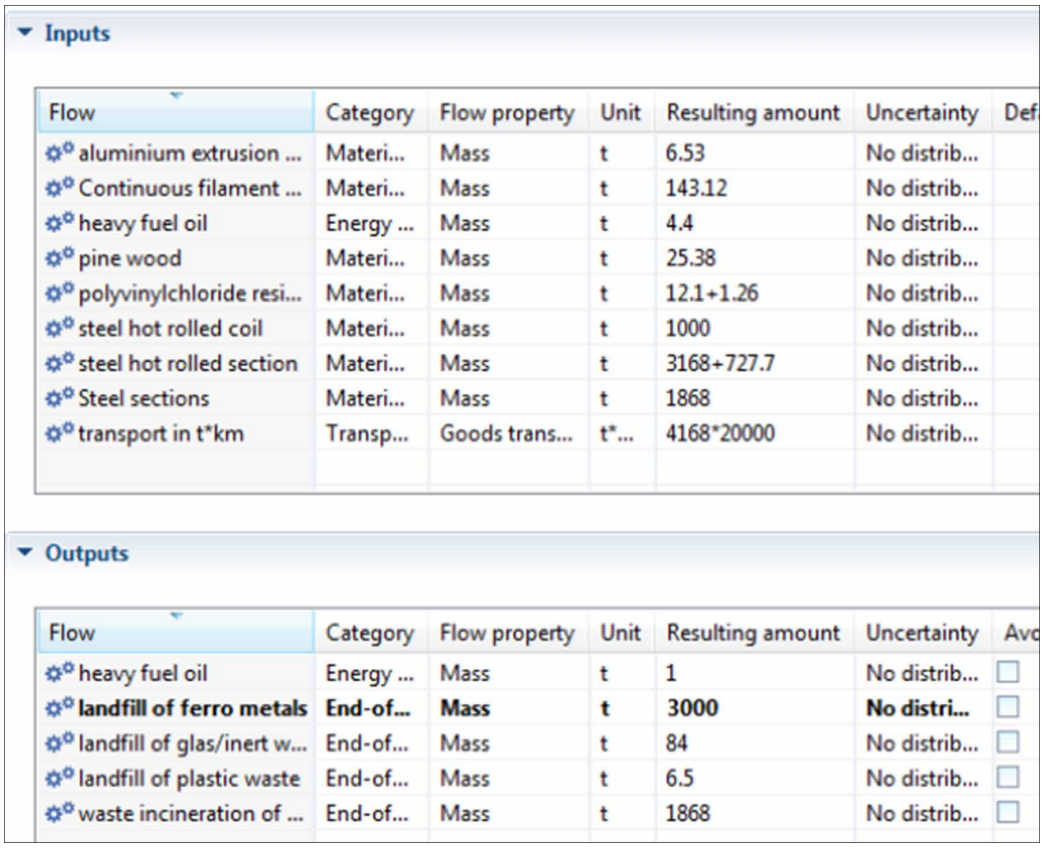
Inputs

Flow	Category	Flow property	Unit	Resulting amount	Uncertainty	D
aluminium extrusion ...	Materi...	Mass	t	6.5	No distrib...	
Continuous filament ...	Materi...	Mass	t	143	No distrib...	
pine wood	Materi...	Mass	t	25.38	No distrib...	
steel hot rolled coil	Materi...	Mass	t	1000	No distrib...	
steel hot rolled section	Materi...	Mass	t	3168+727.7	No distrib...	
Steel sections	Materi...	Mass	t	1868	No distrib...	

Outputs

Flow	Category	Flow property	Unit	Resulting amount	Uncertainty	Av
Aluminum scrap	Produc...	Mass	t	6	No distrib...	☐
Steel scrap (external...	**Produc...**	**Mass**	**t**	**6000+700**	**No distri...**	☐
waste incineration of ...	End-of...	Mass	t	130	No distrib...	☐
Wood	Produc...	Mass	t	22	No distrib...	☐

Figure 6. Data of input/output summary for ship scrapping



Inputs

Flow	Category	Flow property	Unit	Resulting amount	Uncertainty	Def
aluminium extrusion ...	Materi...	Mass	t	6.53	No distrib...	
Continuous filament ...	Materi...	Mass	t	143.12	No distrib...	
heavy fuel oil	Energy ...	Mass	t	4.4	No distrib...	
pine wood	Materi...	Mass	t	25.38	No distrib...	
polyvinylchloride resi...	Materi...	Mass	t	12.1+1.26	No distrib...	
steel hot rolled coil	Materi...	Mass	t	1000	No distrib...	
steel hot rolled section	Materi...	Mass	t	3168+727.7	No distrib...	
Steel sections	Materi...	Mass	t	1868	No distrib...	
transport in t*km	Transp...	Goods trans...	t*...	4168*20000	No distrib...	

Outputs

Flow	Category	Flow property	Unit	Resulting amount	Uncertainty	Avo
heavy fuel oil	Energy ...	Mass	t	1	No distrib...	☐
landfill of ferro metals	**End-of...**	**Mass**	**t**	**3000**	**No distri...**	☐
landfill of glas/inert w...	End-of...	Mass	t	84	No distrib...	☐
landfill of plastic waste	End-of...	Mass	t	6.5	No distrib...	☐
waste incineration of ...	End-of...	Mass	t	1868	No distrib...	☐

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Table 2. Impact parameters for product systems analysis based on CML 2001 criteria

Parameter	Description
Acidification Potential	It is an important environmental indicator that denotes the acidic latency of the atmosphere due to aggregating acid air emissions. It is expressed in SO_2 equivalents.
Climate Change	It refers to any significant change in the measures of climate lasting for an extended period of time. It includes major changes in temperature, precipitation, or wind patterns, among other effects.
Eutrophication Potential	It is defined as the potential of nutrients to cause over-fertilization of water and soil which in turn can result in increased growth of biomass.
Freshwater Aquatic Eco-Toxicity	It refers to the impact on fresh water ecosystems, as a result of emissions of toxic substances to air, water and soil. Eco-Toxicity Potential (FAETP) is calculated with USES-LCA, describing fate, exposure and effects of toxic substances. Characterization factors are expressed as 1, 4-dichlorobenzene equivalents/ kg emission. This indicator applies at global/ continental/ regional and local scale.
Freshwater Sediment Eco-Toxicity	It is the impact on the sediments of freshwater or increase in the amount of toxic substances such as heavy metals (cadmium, for example) on freshwater sediments over a period of time.
Human Toxicity	It is the degree to which a chemical substance elicits a deleterious or adverse effect upon the biological system of human exposed to the substance over a designated time period. The human toxicity potential (HTP) reflects the potential harm of a unit of chemical released into the environment.
Ionizing Radiation	It is the radiation with enough energy so that during an interaction with an atom, it can remove tightly bound electrons from the orbit of an atom, causing the atom to become charged or ionized. Only the high frequency portion of the electromagnetic spectrum which includes X rays and gamma rays is ionizing.
Land use competition	It refers to the conflict over multiple forms of use for land resources especially over agricultural use. A comparison on this parameter for different product/eco-systems shows the amount of land lost from one system to another, particularly regarding agricultural usage.
Marine Aquatic Ecotoxicology	It refers to the impact of toxic substances emitted to marine aquatic ecosystems. The characterization factor involved is the potential of marine aquatic toxicity of each substance emitted to the air, water or/and soil. The unit of this factor is kg of 1, 4- DB equivalents per kg of emission.
Marine Sediments Eco-Toxicity	It refers to the accumulation of a variety of contaminants that demonstrate toxicity. Toxicity identification evaluation (TIE) methods provide tools for identifying the toxic chemicals causing sediment toxicity like arsenic and chromium.
Photochemical Oxidation	Photochemical oxidation (also known as summer smog) is the reaction of a chemical change in a substance which causes it to lose electrons which is initiated by light. An example of photochemical smog which is when hydrocarbons and NOx react under the influence of UV light.
Depletion of Abiotic Resources	This refers to the depletion of abiotic substances (any fundamental chemical element or compound in the environment like hydrogen, oxygen, carbon etc.) due to processes within a product system.
Stratospheric Ozone Depletion	The growing emissions of synthetic chlorofluorocarbon molecules cause a significant diminution in the ozone in stratosphere, resulting more solar ultraviolet-B radiation (290–320 nm wavelengths) reaching the surface, causing drastically severe problems such as the 'Antarctic ozone hole'. Stratospheric Ozone Depletion is primarily due to reactions of atomic Cl and Cl-O, the product of its reaction with ozone.
Terrestrial Eco-Toxicity	It is a parametric index in the subfield of ecotoxicology which is used to evaluate and quantify the effects of toxic substances on the diversity and function in soil-based plants and animals. The test measures the relevant parameters and meets environmental requirements, and also reveals toxic responses given variation in environmental conditions such as pH, solubility, exposure time, antagonism, and synergy.

large crude carriers (VLCC) and ultra large crude carriers (ULCC), is a component category that merits careful treatment to contain environmental impact. In recycling, although most of metallic components such as aluminium and other heavy elements are recovered, there is some impact due to disposal in shipbreaking vicinity or landfill occurs during scrapping particularly during beaching. Table 3, 4 and 5 presents the impact results of example case considered, emanating from to aluminium, glass fiber and plastic waste disposal respectively, in ship scrapping product system.

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Figure 7. Comparative analysis of impact due to steel

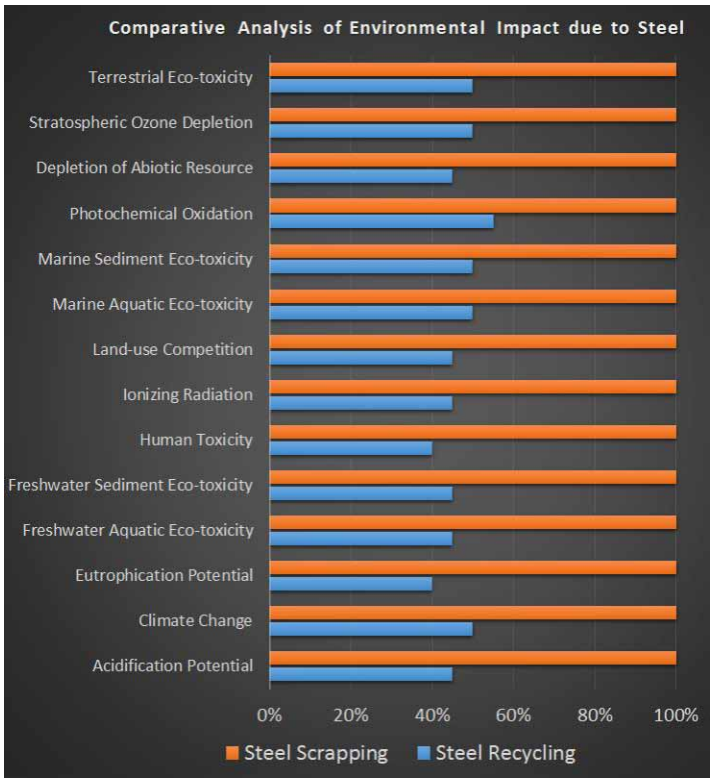

Table 3. Impact due to aluminium waste disposal during ship scrapping

Impact Category	Reference Unit	Result
Acidification Potential – generic	kg SO2-Eq	501732.4
Climate Change – GWP 500a	kg CO2-Eq	10825314.3
Eutrophication Potential – generic	kg PO4-Eq	992.6
Freshwater Aquatic Ecotoxicity – FAETP 500a	kg 1,4-DCB-Eq	398725.6
Freshwater Sediment Ecotoxicity- FSETP 500a	kg 1,4-DCB-Eq	1121207.5
Human Toxicity – HTP 500a	kg 1,4-DCB-Eq	768730815.1
Ionising Radiation	DALYs	0.3
Land Use	m2a	0.0
Marine Aquatic Ecotoxicity – MAETP 500a	kg 1,4-DCB-Eq	43292216.5
Marine Sediment Ecotoxicity – MSETP 500a	kg 1,4-DCB-Eq	66139579.1
Photochemical Oxidation (summer smog) – EBIR	kg formed ozone	7600.5
Resources – Depletion of Abiotic Resources	kg antimony-Eq	0.3
Stratospheric Ozone Depletion – ODP 40a	kg CFC-11-Eq	8.7
Terrestrial Ecotoxicity – TAETP 500a	kg 1,4-DCB-Eq	118696.6

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Table 4. Impact due to Glass Fiber waste disposal during ship scrapping

Impact Category	Reference Unit	Result
Acidification Potential – generic	kg SO2-Eq	0.0094
Climate Change – GWP 500a	kg CO2-Eq	85.6121
Eutrophication Potential – generic	kg PO4-Eq	0.0097
Freshwater Aquatic Ecotoxicity – FAETP 500a	kg 1,4-DCB-Eq	2.9813
Freshwater Sediment Ecotoxicity- FSETP 500a	kg 1,4-DCB-Eq	8.8045
Human Toxicity – HTP 500a	kg 1,4-DCB-Eq	142.1831
Ionising Radiation	DALYs	0.0000
Land Use	m2a	0.0000
Marine Aquatic Ecotoxicity – MAETP 500a	kg 1,4-DCB-Eq	24.0593
Marine Sediment Ecotoxicity – MSETP 500a	kg 1,4-DCB-Eq	23.9153
Photochemical Oxidation (summer smog) – EBIR	kg formed ozone	0.0293
Resources – Depletion of Abiotic Resources	kg antimony-Eq	0.0006
Stratospheric Ozone Depletion – ODP 40a	kg CFC-11-Eq	0.0000
Terrestrial Ecotoxicity – TAETP 500a	kg 1,4-DCB-Eq	0.0394

Table 5. Impact due to plastic waste disposal during ship scrapping

Impact Category	Reference Unit	Result
Acidification Potential – generic	kg SO2-Eq	18188.7
Climate Change – GWP 500a	kg CO2-Eq	2118650.9
Eutrophication Potential – generic	kg PO4-Eq	737.9
Freshwater Aquatic Ecotoxicity – FAETP 500a	kg 1,4-DCB-Eq	35617.9
Freshwater Sediment Ecotoxicity- FSETP 500a	kg 1,4-DCB-Eq	79214.5
Human Toxicity – HTP 500a	kg 1,4-DCB-Eq	469847.1
Ionising Radiation	DALYs	0.0
Land Use	m2a	0.0
Marine Aquatic Ecotoxicity – MAETP 500a	kg 1,4-DCB-Eq	726517.4
Marine Sediment Ecotoxicity – MSETP 500a	kg 1,4-DCB-Eq	628896.1
Photochemical Oxidation (summer smog) – EBIR	kg formed ozone	2820.4
Resources – Depletion of Abiotic Resources	kg antimony-Eq	3000.0
Stratospheric Ozone Depletion – ODP 40a	kg CFC-11-Eq	0.0
Terrestrial Ecotoxicity – TAETP 500a	kg 1,4-DCB-Eq	478.0

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It may be noted that in the ship-scrapping product system, most of the solid-material waste are considered to be disposed in landfill, whereas liquid wastes such as bilge oil are incinerated. For bio-degradable components such as wood, which has a sizeable quantity of almost 25 Tonne as part of the vessel considered in the case, which is mainly used for paneling and framing, the relative impact is not substantial vis-à-vis landfill or incineration methods. This is opposed to the relative impacts for other materials such as oil, glass fiber and plastic wastes for which there is significant difference in impact based on the post-process method of material treatment during shipbreaking. From Table 4, it may be observed that disposal of glass fiber contributes to the effect on impact parameters such as climate change, human toxicity, marine aquatic and sediment eco-toxicity; whereas Table 5 explains effect of plastic waste disposal on most of the 14 impact categories except Ionizing Radiation, Land Use and Stratospheric Ozone Depletion.

In order to view the big picture, and ascertain the total impact contribution from a holistic standpoint with regards to this case, we list the top 2 contributors for each of the 14 CML 2001 impact parameters. This is represented in Table 6, which shows that the principal impact causality is due to steel sections and glass fiber, and therefore, primarily the need to recycle them as opposed to disposal to mitigate the damage to environment. Glass fiber is the chief contributor for 7 listed parameters; climate change, fresh water eco-toxicities, depletion of abiotic resources etc. to name the significant few. Container Ocean Transport is a major contributor to acidification potential and photochemical oxidation. We can infer from the LCA results that at a generic level ship recycling product system causes lesser impact than ship scrapping eco-system. At a practical level, from LCA results, we can ascertain the contributors of significant impact on CML 2001 parameters and adopt material treatment methods post vessel-disassembly to mitigate environmental impact.

Table 6. Major contributors to overall impact

Parameter	1st Major Contributor	%	2nd Major Contributor	%
Acidification Potential	Container Ocean Transport	63.73	Hot Rolled Steel Section	27.72
Climate Change	Glass Fibre	71.94	Hot Rolled Steel Section	15.61
Eutrophication Potential	Hot Rolled Steel Section	42.21	Glass Fibre	24.22
Freshwater Aquatic Eco-toxicity	Glass Fibre	94.19	-	-
Freshwater Sediment Eco-toxicity	Glass Fibre	94.82	-	-
Human Toxicity	Glass Fibre	58.36	Aluminium	10.52
Ionising Radiation	Glass Fibre	79.49	Steel Sections	9.29
Land-Use Competition	-	-	-	-
Marine Aquatic Eco-toxicity	Hot Rolled Steel Section	51.75	Hot Rolled Steel Coil	12.70
Marine Sediment Eco-toxicity	Hot Rolled Steel Seciton	48.54	Hot Rolled Steel Coil	13.76
Photochemical Oxidation	Glass Fibre	52.90	Container Ocean Transport	36.24
Depletion of Abiotic Resources	Glass Fibre	97.33	-	-
Stratospheric Ozone Depletion	Glass Fibre	36.34	Steel Sections	28.77
Terrestrial Eco-toxicity	Hot Rolled Steel Section	70.94	Hot Rolled Steel Coil	13.88

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6. DISCUSSION, LIMITATIONS, MANAGERIAL IMPLICATIONS & FUTURE RESEARCH DIRECTIONS

The LCA methodology is a useful tool in analyzing the environmental impact based on specific parameters as discussed in the case article in the previous sections. To conduct LCA is a difficult challenge since the accuracy of the results depends on the quality of inputs vis-à-vis material and energy inflows and outflows across the system boundaries, the nuances in path functions adopted, interpretation of relative impacts etc. However, the mandating of the *Green Passport* for new vessels by IMO, with inventory of all components on board to be maintained since the vessel construction, has been beneficial for industry analysts and researchers to obtain data, which was earlier often not archived as a set, untraceable, and difficult to obtain from behind proprietary veils of vessel design data. It is now possible to conduct LCA of vessel much more easily given the record tracking that is enabled by maintenance of *Green Passport*. LCA also reveals specific cause-effect relationships, pin-pointing the root cause of higher values on certain impact categories that may be otherwise be counterintuitive. For example, recent research (Rahman et al., 2016) in the context of ship recycling in Bangladesh showed that certain impacts on parameters such as Human Toxicity may be more due to usage of certain cutting torches, fuel or gas during the shipbreaking process, than from the material release from the ship as widely believed. This emphasizes the need to allocate appropriate path functions in the LCA design in well-defined stages of dismantling processes, lest the objective to accurately identify causes of impact be lost in translation.

While acknowledging the progress made possible in conducting LCA for end-of-life-ships using *Green Passport*, there are limitations for the current studies. Future research should focus on bridging these gaps and filling some of the following specific lacunas. Firstly, the process of LCA is still a research-intensive process. To the best of our knowledge, there are no Decision Support Systems (DSS) for managers to practically employ LCA philosophies in ship recycling at a detailed level in work-related contexts. Data used to be an issue, but now and in future, handy managerial tools and software needs to be developed to incorporate LCA techniques into standard operating procedures of ship-recycling industry, much along the lines of an Engineer's Handbook for quick reference and application. In recent years, researchers (Hiremath et al., 2015, 2016) have developed emission factors classified based on 'ship type' and their inherent composition. Such efforts are a first towards understanding impacts from different types of ships such as general cargo ships, bulk carriers, container ships, oil tankers, chemical takers, reefer vessels, passenger vessel etc. However, more progress towards development of managerial tools is vital to integrate these contextual ship impact information directories, for practical decision-making.

Second, we draw the reader's attention towards use of inventory suites and databases. Several tools used for LCA are based on *Ecoinvent* database. Although, at the moment, this database serves not only as a useful tool but vital for conducting LCA analyses, it is important to note that it has been developed based on European contexts (Weidema, 2013), processes and ecosystems. For shipbreaking ecosystems largely based out of South Asia (India, Bangladesh and Pakistan) and China, the results drawn from information databases not reflective of local ecosystems need to be taken with a pinch of salt. Having said that, these databases are currently the best options available, but future research must focus on developing geography specific inventory suites and databases that reflect the true conditions accurately.

Third, the choice of impact assessment method (Bach & Finkbeiner; 2017) used for industry and context specific studies such as ship recycling merits serious deliberation. There are several methods that are extensively used in environmental impact assessment studies, such as CML 2001, IMPACT 2002+, IPCC 2013 100a etc., with varying criteria and impact assessment parameters. In this regard, it is

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important to note the accuracy and contextual relevance of results drawn in selecting and applying these tools (Kounina et al., 2013; Wathern, 2013; Kelly et al., 2013). From our review of assessment tools and observation of results in the context of ship recycling, it is inferred that some techniques fail to capture pertinent impact categories, parameters, and elemental processes involved vis-à-vis other methods. The objectives of the assessment, including but not limited to understanding of issues, disciplines, processes and stakeholders involved, scales of measurement and their comparisons, are points to be considered while selecting the method.

Fourth, we draw the readers' attention on the relatively lesser progress made in development and usage of SIA (Social Impact Assessment) method, an important pillar in the realm sustainable management (Hildebrandt & Sandham, 2014). Future research must focus on developing and integrating social indicators such as worker safety, training, job satisfaction, corruption, medical facilities etc., particularly in the community-driven ship recycling industries to develop a holistic sustainability framework.

Fifth, the mandate of Green Passport introduced through instruments envisaged by IMO creates a mechanism for identifying, tracking and documenting vessel details at firm level, industry level and port state (government) level. There are several benefits emanating out of the concept of Green Passport. In the short term, it delineates vessels, builders and scrappers that comply with the requirements, and works akin to a social security number for tracking real-time health status of the vessel. In the medium term, the Green Passport will aid in closing the supply chain loop of materials (Broadbent, 2016), tracking raw, processed or finished inventory that enters or leaves the system, and to enforce norms for implementing baseline environmental standards. In future, ship designers, naval architects and operators equipped with information on vessel's environmental impact throughout its life cycle are empowered to think along the lines to Design-for-Recycling (Sivaprasad & Nandakumar, 2013), an extension from the concept of Design-for-Manufacture (Kuo et al., 2001), encompassing considerations of the extended supply chain, and moving in the direction of broader sustainability targets.

In conclusion, through this research we may decisively infer that recycling of steel is superior with marked advantages than disposal of steel during scrapping. Recycled steel may substitute use of virgin steel for good, reducing the carbon footprint and contributing towards lesser impact on a multitude of environmental indicators. LCA also helps practitioners understand and use better options among disposal alternatives, and internalize procedures to be adopted for mitigating environmental impact. It also enables vessel designers, manufacturers and regulators to identify components associated with higher impact on important environmental parameters and substitute them with alternative materials, in order to minimize the carbon footprint during the vessel's lifecycle.

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Chapter 24
Advanced Nanomaterials for the Removal of Chemical Substances and Microbes From Contaminated and Waste Water

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ABSTRACT

The development of cost-effective, efficient and stable materials helps to provide the affordable solutions to get safe and fresh water to increasing population with health guidelines of emerging contaminants. Nanomaterials (NMs)-based techniques involve the design, synthesis, manipulation, characterization and exploitation of materials for adsorption and separation of target species from the contaminated and waste water. NMs show better adsorption capacity and catalytic for number chemical species and microbes because of their small size and large surface area that favors the purification and treatment of waste or contaminated environmental water. Here, we present the chemical properties, adsorption/removal mechanism and applications of advanced NMs such as magnetic nanoparticles (MNPs), carbon nanotubes (CNTs), graphene and graphene oxide (GO), titanium oxide (TiO_2), silica (SiO_2), silver (Ag), gold (Au) NPs and zeolites in effective and efficient removal of toxic metal ions, organic and inorganic chemical substances and disease-causing microbes from contaminated and wastewater.

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1. INTRODUCTION

Water is a most important resource for vitality for life on earth and sustaining human life. The major civilizations of the world originated nearby the water reservoirs or river due to the ample supply of water and fertile land. Water is a universal solvent that dissolves most of the organic and inorganic substances to meet the requirement of the life. Providing clean and safe water is a necessity and it is also challenging attempt to sustain the same level (LVovich 1979; Postel et al., 1996; World Health Organization 2013). About, millions of people die every year because of contaminated drinking water incorporated with water borne microorganism, toxic chemical substances and thousands of children die due to the water-related problems and diseases. At present, more than billions of people in the world lack to access the safe drinking water and a couple of decades the supply of safe water would suppose to be reduced one-third of the present scenario (Hutton et al., 2007; Mara 2003; Ashbolt 2004; Moore et al., 2003). The limited supply of fresh water to the increasing populations throughout the world is due to the drastic exploitation of water resources for domestic, industry and irrigation purposes in many parts of the world. The increased disposal of industrial, domestic and agricultural and mining wastages into surface and ground water bodies cause the contamination of several inorganic, organic and microbes (Ritter et al., 2002; Fawell et al., 2003). The inorganic species such as arsenic (As), mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr) and selenium (Se), etc.; organic substances such as pesticides, dyes and phenolic compounds etc.; and microbes such as bacteria and viruses could cause contamination of water (Cao et al., 2014; Yu et al., 2014; Walcarius et al., 2010). Today, the providing of safe and clean water to the fast-growing world population is on the high challenge and needs the plan to sustain the life for future generations.

There are several technologies have been developed for the removal of toxic chemical substances from environmental water samples, including chemical oxidation or reduction (Kohler et al., 2006; Theepharaksapan et al., 2011), chemical precipitation, coagulation or flocculation (Kim et al., 2002; RubI et al., 2009), UV or chlorination (Zhang et al., 2015), ozone treatment (Xiao et al., 2015), adsorption (Kojima et al., 2002), biological treatment (Rosal et al., 2010), reverse osmosis (Jian et al., 1999), membrane filtration (Amin et al., 2014) and ion exchange system (Velizarov et al., 2001). The use of conventional chemical oxidation or reduction through the activated sludge or carbon process unable to remove complex materials comprises of pharmaceuticals, surfactants, dyes various industrial additives. Activated sludge and biological trickling filters come under the biological treatment systems are also not efficient in removing the wide range of chemical substances and remain soluble in the effluent (Urase et al., 2005). Coagulation and flocculation process showed an ineffective in removing the variety of pharmaceutical drugs in different investigations (Vieno et al., 2006). The purification of water by chlorination is implemented to prevent the growth of bacteria and pathogens; however, this treatment causes the undesirable tastes and odors with different by-products (Becher, 1999). Ozone and UV treatment are used to stop the growth of microbes but these techniques are found to very expensive (Adams et al., 2002). Purification of water through the membrane filtration such as microfiltration, ultrafiltration, nano-filtration and reverse osmosis are found most effective and efficient techniques. All these filtration techniques are pressure driven process and removal of contaminants are dependent on the pore size of a semi-permeable membrane which is found specific for the removal specific particulates from water. Microfiltration, ultrafiltration, nano-filtration and reverse osmosis are cost-effective because these techniques require a more energy for the removal of contaminants (Walha et al., 2007; Saleh et al., 2016; Saleh et al., 2012).

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There is the need for the sustainable development of cost-effective, eco-friendly and stable materials that meets the challenges of providing the fresh water to the increasing world population. Nanotechnology has established an effective way for the removal of harmful toxic chemical substances and microbes from the wastewater or contaminated water (Bottero et al., 2006). In recent years, there have been increasing activities in design and development of nanomaterials (NMs) for versatile applications. It is still a challenging task to synthesize a novel NMs with unique physical, chemical and electrical properties suitable for biochemical probes, sensors, separating and pre-concentrating probes (Obare et al., 2004). NMs can be synthesized using various methods such as chemical, electrochemical, γ-radiation, photochemical, laser ablation, etc. NMs of these substances exhibit an excellent adsorption capacity and photochemical activity because of their high surface to volume ratio and unusual electronic properties (Rickerby et al., 2007). Currently, there are many NMs such as magnetic nanoparticles (MNPs), carbon nanotubes (CNTs), titanium oxide (TiO_2), mesoporous silica (SiO_2), graphene, zeolite, silver (Ag), gold (Au) and other oxide NPs are used for removing the toxic metal ions, organic substances and disease-causing microbes from waste and contaminated water.

2. ADVANCE OF NMS FOR REMOVAL OF CHEMICAL SUBSTANCES AND MICROBES FROM CONTAMINATED AND WASTE WATER

2.1. Magnetic Nanoparticles (MNPs)

Magnetic nanoparticles (MNPs) have many unique properties such as supra magnetic, high coactivity and high magnetic susceptibility that make them extraordinary for distinct function. There are various types of MNPs such as hematite (α-Fe_2O_3), maghemite (γ- Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO) used for variety applications. Among these Fe_3O_4 MNPs exhibit the most fascinating properties because the presence of non-equivalent iron such as Fe(II) and Fe(III) in the crystal structure (Yantasee et al., 2007; Domingo et al., 1994). The co-precipitation method is used for the synthesis of Fe_3O_4 MNPs in basic condition (Mascolo et al., 2013). MNPs have been used in medicinal applications, catalysis and now specifically used for water purification (Yallapu et al., 2011; Rossi et al., 2014; Ambashta et al., 2010). MNPs act as an efficient adsorbent with ionic exchange capacity for removal of heavy metals and organic substances assisted with magnetic separation property. The magnetic and surface properties of MNPs allow it for the selective adsorption of ions, molecules, macromolecules, cells, colloidal substances from sample solution. The zero-valent of MNPs make it for specific removal of metallic species such as Hg(II), As(III), Cd(II), Se(III), Cr(VI) and Pb(II) from drinking water and wastewater to show its potential for environmental applications (Ambashta et al., 2010; Xu et al., 2012; Singh et al., 2011). The oxidation of zero-valent iron produces ferrous iron to magnetite in presence of water and oxygen. The adsorption of different pollutants on the MNPs from water sample is demonstrated with Figure 1. The adsorption capacity of organic, inorganic and microbes on the surface of MNPs depends on the electrostatic force, van der Waals force and chemical binding. The adsorption and removal of contaminants from water sample is also dependent upon redox conditions and pH (Tang et al., 2013). Many carbonaceous NMs such as graphene, graphene oxide, CNTs, etc., are attached with MNPs for better adsorption and separation for the removal of contaminants (Yang et al., 2012).

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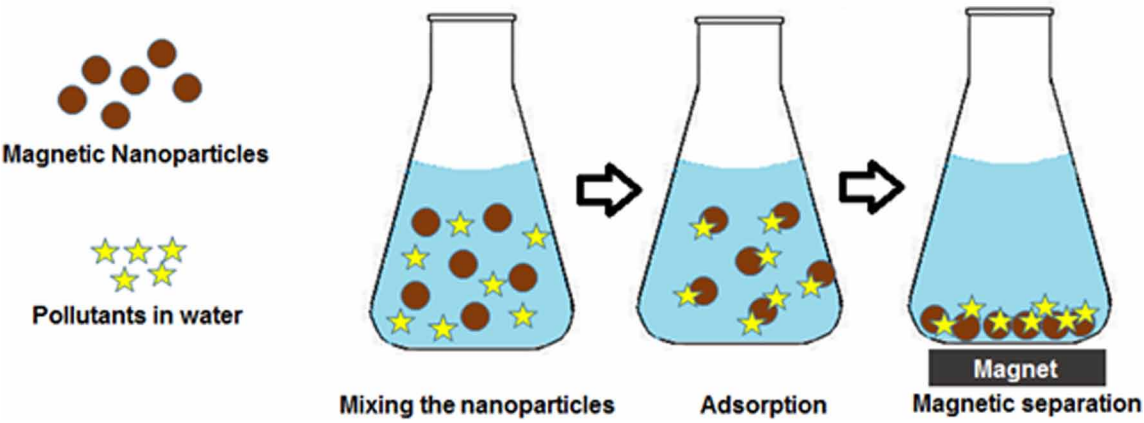
Figure 1. MNPs used for the separation of pollutants present in water by chemical adsorption and further removal of MNPs by magnetic separation



2.2. Carbon Nanotubes

Carbon nanotubes (CNTs) are fascinating a new material and have wide range of applications such as reinforcing materials in composites, chemical sensors and catalysts due to their large surface areas, hollow and layered structures and remarkable electrical conductivities (Peng et al., 2014; Saleh et al., 2011; Saleh et al., 2010). CNTs can act as potential solid phase separating probes for removal of metal ions, organic and organometallic compounds from variety of samples. CNTs can be divided into single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) according to the carbon atom layers in the wall of the nanotubes (Izakmehri et al., 2015; Tawabini et al., 2010). Recently, there is more increase in the applications of CNTs by surface modifications or making the composite materials with NPs. The carboxyl groups or hydroxyl groups can be introduced into CNTs by the treatment with H_2SO_4 and HNO_3. The presence of oxygenated functional groups or other modification helps in binding with a positive species. The removal of dyes using CNTs can be explained with hydrophobic interaction, π-π stacking interaction, covalent and electrostatic interactions. The high π electron density of sp^2 carbons on sidewalls of CNTs provides it high hydrophobic property. The π-π stacking interaction takes place between the bulk π system of CNTs and the C-C or benzene rings (Ai et al., 2011). This is very much similar to the interactions in graphene oxides. Also, the hydrogen bonds formations take place between the functional groups present on the surface of CNTs and the dyes. However, the heavy metals mainly get adsorbed by electrostatic interactions.

2.3. Graphene and Graphene Oxide

Graphene is a two-dimensional sp^2 carbon network with a honeycomb structure in the form of sheets with only one atomic thickness. It is supposed to be next-generation NMs that could be applied for nano-electronics, nano-composites, nano-sensors and nano-devices due to its high electron mobility, high thermal conductivity and mechanical strength. In addition, it has a high specific surface area of 2,630 m^2g^{-1}. Therefore, this superiority allows graphene to be used as a novel adsorbent for the removal of different types of pollutant from water (Liu et al., 2012). The graphite is used as a starting material for

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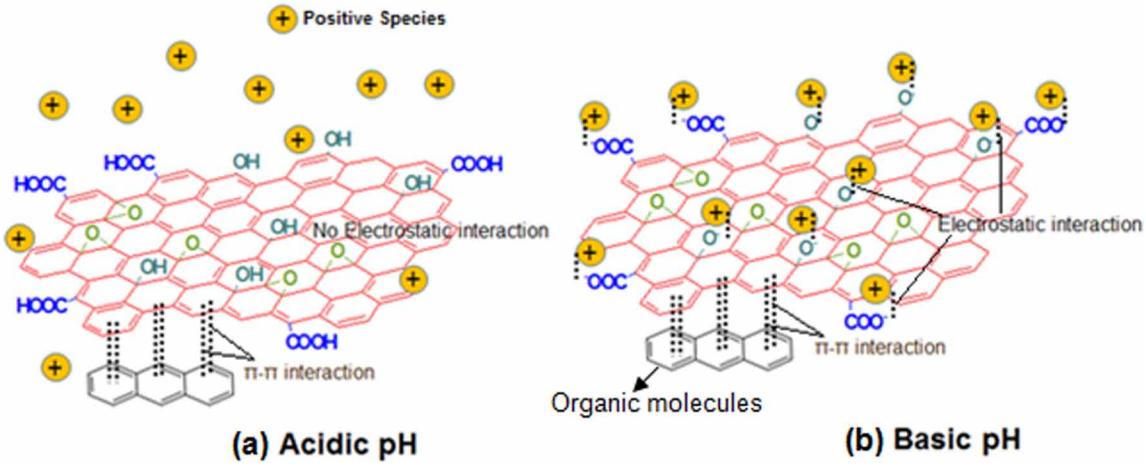
preparation of graphene in the presence of $NaNO_3$, H_2SO_4 and $KMnO_4$. The whole solution is stirred for 30 min followed by the addition of 30% H_2O_2 in warm water (Saleh et al., 2010). Graphene oxide (GO) is prepared from graphene by modification with different functional groups such as epoxy (C–O–C), hydroxyl (OH) and carboxyl (COOH) capping groups on the surface (Mkhoyan et al., 2009). Graphene and GO have shown many versatile applications in nanoelectronics (Westervelt, 2008), sensors (Ang et al., 2008), and structural composite materials (Liang et al., 2009). The large number of functional groups on GO makes it a smart material for removal of metal ions, biomolecules or cationic substances from sample solution through the electrostatic and coordination interactions. In solution phase, GO can act as a cation exchange resin because of the ionizable carboxyl groups, which allows surface complexation with metal ions or positively charged organic molecules (Dreyer et al., 2010; Zhang et al., 2010). Figure 2 demonstrates the π-π interaction between the sp^2 hybridized GO sheet and the organic molecules responsible for the interaction and separation of organic compounds (Ji et al., 2013). In addition, the removal of positive ions (metal ions) using GO is increased in basic pH due to the base abstracts the protons of the acidic group and hydroxyl groups present on the surface of GO. These take part in attraction with the positive ions and the GO resin by electrostatic interaction. Although the adsorption occurs due to the π-π interactions have no effect on the change of pH of sample solution. Yang and coworkers reported the use of as a GO separating probe for removal of Cu (II) from sample solution considering the electrostatic attraction between the GO and Cu (II) ions as driving force for the separation (Yang et al., 2010). Fan et al. gave a simple route for the fabrication of a magnetic beta-cyclodextrin/GO nanocomposite for fast removal of Cr (IV) from water. This material could be a good candidate for efficient separation of Cr (VI) from wastewater and also useful for purification of polluted water (Fan et al., 2012). There are several reports are available for separation of toxic metal ions, organic substances and microbe from water samples. The graphene/GO NPs composite material exhibits an efficient candidate for removal of heavy metals and organic substances in short period of time with good recovery percentage (Cao et al., 2014; Yang et al., 2010; Fan et al., 2012; Teymourian et al., 2013; Sun et al., 2014; Zhu et al., 2012; Sivashankar et al., 2014). Graphite can be also directly used for the removal of organic pollutant and desalination of water with 55% removal of efficiency (Zhou et al., 2015).

Figure 2. Schematic design showing the electrostatic interaction between GO and target positive chemical species from water and also π–π stacking in organic molecules in (a) acidic medium (b) basic medium



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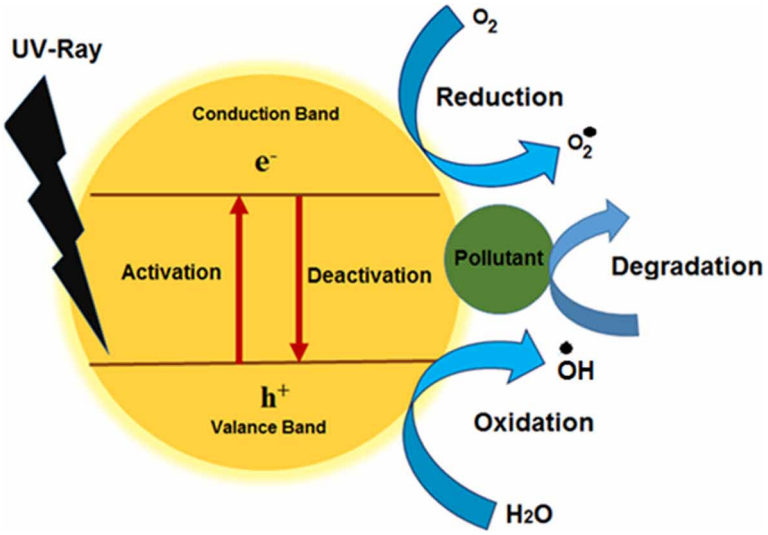
2.4. Titanium Oxide Nanoparticles

The surface properties of titanium oxide (TiO_2) NPs are better than that of bulk TiO_2, though it has been used for years in industries and water treatment and purification of water. TiO_2 NPs have better photo-catalytic, adsorption capacity and anti-microbial properties that have been used for removal of toxic substances and microbes from a water sample. The photo-catalytic activity of the TiO_2 NPs causes the removal of pollutants from waste water through the generation of reactive hydroxyl radicals upon the irradiation with UV light (Gupta et al., 2012; Saleh et al., 2011; Daels et al., 2015). Gupta et al. demonstrated the photo-catalytic activity of TiO_2NPs for the degradation of contaminates (Gupta et al., 2012). The interaction of TiO_2 NPs with a photon of light having a comparable band gap of energy results in the separation of conduction and valence bands given in Figure 3. These photo-catalytic reactions involved oxidation and reduction reactions by the photo generated electrons and holes. The hydroxyl radical is a strong oxidizing agent for the organic matters presents on the surface of TiO_2 which further undergo the degradation. This property of TiO_2 makes it an excellent catalytic material for the removal of toxic chemical substances from the environment by gaining solar light as an energy source (Mahlambi et al., 2015). Nabi et al. demonstrated the use of TiO_2 and iron doped-TiO_2 NPs for removal of As(III) and As(V) and iron-doped TiO_2 NPs are found to be better material for the removal of arsenic from contaminated water (Nabi et al., 2009).

2.5. Mesoporous Silica Nanoparticles

Silica (SiO_2) NPs have a high surface area with a number of pore sizes that make them highly reactive and useful for making effective adsorbents in water and wastewater treatment. The mesoporous SiO_2 NPs such as MCM-41 and SBA-15 having a uniform pore, high pore volume, surface area, high adsorption capacity with high hydrothermal and chemical stability (Adjdir et al., 2015; Gandhi et al., 2012). The mesoporous SiO_2 NPs is mainly functionalized with NPs or organic compounds with suitable functional

Figure 3. Mechanism for the photo-catalysis of organic pollutants on the surface TiO_2 NMs



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groups for better removal of pollutants from water. The amino-functionalized SiO_2 NPs showed an excellent capacity to separate a wide variety of harmful metal ions from water samples through the complexation between the amine group and metal ions. In addition, the regeneration of amino-functionalized adsorbents is found to be easy by proton displacement of the metal ion in acid washing. Chung et al. demonstrated the separation of Pb (II) and Cu(II) using multi-amine grafted mesoporous SiO_2 with MNPs (Chung et al., 2012). MNPs/SiO_2core-shell NPs can be easily dispersed in aqueous solutions due to the hydrophilic nature. In acidic condition, the presence of hydroxyl or silanol groups can be used for attachment and chemical modification to remove the target chemical species from the sample (Emadi et al., 2013). In addition, silica can be grafted with a variety of functional groups, leading to considerable enhancement of their surface properties. Fellenz et al. reported the synthesis and characterization of MNPs embedded with mesoporous MCM-41 (Fellenz et al., 2006). Jing-po et al. accounted the removal and detection of Hg(II) using core-shell structured nanocomposite of SiO_2 NPs (Jing-po et al., 2015).

2.6. Silver and Gold Nanoparticles

Silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) have received considerable attention for their potential application in catalysis, biological, medicine, pharmaceutical and environmental as adsorbents and disinfectants (Sondi et al., 2004; Agnihotri et al., 2014; Sumesh et al., 2011). The synthesis of these NPs was done by wet chemical methods using a reducing agent and stabilized with certain bulky groups to provide a stability in aqueous solution and also responsible for the interaction with target chemical substances for the separation from contaminated water samples. The colloidal AgNPs have been used as a disinfectant in hospitals and medical centers which are approved by the U.S. Environmental Protection Agency (U.S. EPA, 1993). This is also exploited as a supporting agent for several materials to prevent the microbial formation on the most of the surfaces. AgNPs have good potential antibacterial activities (U.S. EPA, 1993; Gunawan et al., 2011). AgNPs can penetrate into the bacterial membrane of *Escherichia coli* and other gram-negative bacteria. The bactericidal activity of NPs was found to increase with decreasing the size of NPs and also depends on particles shape (Sondi et al., 2004; Agnihotri et al., 2014; Sumesh et al., 2011; Gunawan et al., 2011; Shrivastava et al., 2007). In addition, the inhibition of nitrification in activated sewage sludge is also observed by AgNPs than by the equivalent amount of Ag (mgL^{-1}) as Ag(I) ion (Kaegi et al., 2011). Abbasi et al. reported the synthesis of AgNPs through a greener approach with a garlic extract as stabilizing and reducing agents. The synthesized NPs have demonstrated for the removal of phenanthrene, pyrene and anthracene with 85% removal capacity (Abbasi et al., 2014). Karimi et al. presented the use of activated carbon capped with AgNPs for the removal of methyl orange from water sample (Karimi et al., 2012).

AuNPs is also used as a scavenger for removal of mercury ions from polluted waters in the presence of sodium borohydride. The NPs capped with citrate ions act as a reducing agent to catalyze the Hg(II). The removal of mercury ions from waste water sample is means of amalgamation by mounting onto the colloidal NPs, which are then removed from the AuNPs solution (Ojea-Jimenez et al., 2012). Lee at al. showed the use of nano-composite film of AuNPs/BSA-decorated agarose gel membrane for removal of Hg(II) and Pb(II) from waste water (Lee at al. 2012). Ayati et al. exploited the use of AuNP/TiO_2 NPs for photo-catalytic oxidation of various toxic organic pollutants such as azo dyes and phenols under solar, visible and UV irradiation. The loading amount and particle size of AuNPs are the most important parameters to show the better catalytic activity of AuNP/TiO_2 (Ayati et al., 2014).

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2.7. Zeolites

Zeolites are named after two Greek words "zein" and "lithos" which mean "boiling stone" which was first used by a Swedish geologist, in 1756. Zeolites are micro-porous minerals which may be natural or synthetic. They are hydrated aluminosilicates having a general composition of $Al_xSi_yO_{2(x+y)}$ and are insoluble in water (Diale et al., 2011). The structure of zeolites is three-dimensional, micro porous, crystalline solids being used for water treatment because of their ion exchange properties and thermal stability. In addition, the surface modifications and pore size of zeolites make them attractive candidates for a variety of applications (Liu et al., 2013; Rahamani et al., 2006). They act as base exchangers in the removal of metal ions from contaminated water (Hui et al., 2005; Mehdizadeh et al., 2014; Dong et al; 2015).

3. REMOVAL OF INORGANIC CHEMICAL SUBSTANCES FROM WATER USING NMS

Trace metals are essential constituents of our body that are needed for proper physiological and chemical process. However, the excess intake of metals through the drinking water are harmful to humans including Hg, Pb, As, Cr, Se, and Cd. Chronic exposure to these toxic metals can have serious health consequences. Humans are exposed to metals through inhalation of air pollutants, consumption of contaminated drinking water, exposure to contaminated soils or industrial waste, or consumption of contaminated foods. Natural sources such as weathering, erosion of rocks or soils and volcanic emissions also contribute the metal pollution. There are serious effects of exposure of metals on human health including reduced growth, cancer, damage to nervous system and extreme cases death. Therefore, the removal of these toxic metals is important to prevent the entry of these chemical substances into the different compartments of the environment.

3.1. Removal of Arsenic

As is a toxic element with metalloid properties and it exists in soil, water, plants. Arsenic exists in both organic and inorganic compounds in the oxidation states, shown as –3, 0, +3 and +5. The compounds of As have wide application in agriculture as pesticides and semiconductors, transistors, metal adhesives, explosives and pharmaceutical products in various industries (Patel et al., 2005; WHO, 1999; Furst et al., 1983). In term of toxicity, As(III) is more toxic than As(V). The tolerance limit of arsenic is 10 μgL^{-1}. Hyper pigmentation, depigmentation, keratosis, peripheral vascular disorders are the most commonly reported symptoms of chronic exposures of arsenic (Bissen et al., 2000; Chen et al., 1995). Therefore, the separation of arsenic from contaminated water is required to provide the clean water to the world increasing the population.

Recently, there are several NMs have been reported for the removal of As(III) and As(V) from contaminated and waste water. For As removal, NMs exhibited a better response compared to existing conventional technologies. The different NMs are used for separation of As(III) and As(V) from contaminated water, given in Table 1. Martinson et al. synthesized CuO NPs of the surface area of 85 m^2g^{-1} with a diameter of 12–18 nm and employed as an adsorbent for removal of As(III) and As(V) from ground water in the pH range of 6-10. The maximum adsorption capacity of As(III) and As(V) is 26.9

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mgg^{-1} for and 22.6 mg/g, respectively (Martinson et al., 2009). Shipley et al. demonstrated the adsorption efficiency of As using MNPs at different NPs concentration, pH, ionic strength, and temperature (Shipley et al. 2009). Jegadeesan et al. synthesized nano-sized amorphous and crystalline TiO_2 and used for specific separation of As (III) and As(V) due to its size and crystalline property of NPs (Jegadeesan et al., 2010). Thanh et al. prepared a nano-composite of γ-Fe_2O_3 and α-MnO_2 through a ball-milled process and illustrated for removal of As(V) from water (Thanh et al., 2011). The adsorption of As(V) on the NMs was dependent on the pH of the sample using pseudo-second-order kinetic model. Selvakumar et al. synthesized a carbonized yeast cells on AgNPs for the removal of As(V) using yeast strain *Saccharomyces cerevisiae* (Selvakumar et al., 2011). Savina et al. synthesized nanocomposite gels of α-Fe_2O_3 and Fe_3O_4 NPs of pore size up to 100 µm through the polymerization. These nanocomposite materials showed an excellent capability for the removal of 3 mg of As(III) from sample solution (Savina et al., 2011). Similarly, nano p(4-vinylpyridine)-based hydrogels (Sahiner et al., 2011)[106], bi-metal doped nano multifunctional polymeric adsorbents (Kumar et al., 2011), nano-alumina dispersed in chitosan-grafted polyacrylamide (Saha et al., 2012), polysaccharide stabilized Fe-Mn oxide NPs (An et al., 2012) and mesoporous γ-Al_2O_3 NPs demonstrated for efficient removal of different species of As from water (Patra et al., 2012).

Table 1. Different NMs for removal of arsenic at specific particle size, surface area, pH, Adsorption capacity

NMs	Particle Size	Surface area (m^2g^{-1})	pH	Adsorption capacity (mgg^{-1})	Arsenic	Ref.
CuO	12-18 nm	85	–	26.9	As(III)	Martinson et al. 2009
Fe_3O_4	20 nm	60	8	–	As(III)+As(V)	Shipley et al. 2009
Nanocrystalline TiO_2		98	4.8	38.4	As(III)+As(V)	Jegadeesan et al., 2010
Perlite/γ-Fe_2O_3	14.9 µm	27.7	7.1	-	As(V)	Thanh, et al. 2011
Silver/yeast cells	19 nm	–	–	0.975	As(V)	Selvakumar et al., 2011
α-Fe_2O_3–Fe_3O_4–polymer	2 nm	50	–	2.7	As(III)	Savina et al., 2011
P(4-VP)-HCl NPs	20 nm	–	–	31.75	As(V)	Sahiner et al., 2011
Al-doped phenolic bead	0.80 µm	330	–	20	As(V)	Kumar et al., 2011
Al_2O_3 polymer bead	–	–	–	6.56	As(V)	Saha et al., 2012
CMC-Fe-Mn NPs	0.35 µm	~6	–	338	As(III)+As(V)	An et al., 2012
γ-Al_2O_3	3–6 nm	–	–	–	As(III)+As(V)	Patra et al., 2012

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3.2. Removal of Chromium

Cr is a transition metal with oxidation states of III and VI, where Cr(VI) is more toxic than Cr (III) due to its high solubility and mobility in biological systems. Cr(III) is an important element needed for proper functions of biological process in human (Agency for Toxic Substances and Disease Registry (ATSDR), 1993; Kotas et al., 2000; Nriagu et al., 1988). The main sources of Cr contamination are through industries like chrome plating, electroplating, pigment fabrication, water-cooling towers and sanitary landfill leaching (Sharma, 2003). The chronic exposure of Cr(VI) causes the chronic ulcer and damage of lining of nose, throat, lungs as well as the gastrointestinal tract (Basu et al., 1983). Thus, the separation of chromium from contaminated water is needed to assure the good public health.

For this, different NMs are showed effective results for the removal of chromium from contaminated water. Xiao et al. used a greener approach for the synthesis of FeNPs for highly effective removal of Cr(VI) from the water. They used fifteen plants extract for the plant-mediated synthesis of FeNPs and then used for removal of Cr(VI) (Xiao et al. 2016). Zhong et al. exploited the use of TiO_2 nanotubes (NTs) coupled with CuNPs for efficient photoelectron-catalytic removal of Cr(VI) (Zhong et al., 2016). Niu et al. reported the application MNPs for the removal Cr(VI) (20 mgL^{-1}) with 100% removal efficiency (Niu et al., 2005). Zhu et al. prepared magnetic graphene nano-composite through a thermal decomposition process to remove Cr(VI) ions from water. The synthesized NMs had double shell-structure where iron oxide as inner shell and amorphous Si-S-O compound as an outer shell. It showed the fast removal of Cr(VI) in few minutes (Zhu et al., 2012).

3.3. Removal of Mercury

Hg is a toxic persistent pollutant that affects the nervous system. There are three main species of mercury such as Hg(II), methyl mercury (MeHg) and dimethylmercury (Me_2Hg). MeHg is found to be more poisonous since it readily undergoes bio-magnifications in the food chain as well as it is found to be water soluble (US Environmental Protection Agency). Mercury has a wide range of industrial applications such as the production of batteries, cathode tubes, medical laboratory chemicals and electronic production of mercury vapor lamps and household cleaners, etc. There are several harmful effects of mercury such as cancer, damages the stomach and large intestine, brain and kidneys, lung and increase blood pressure and heart rate (Stern et al., 2001). Hence, the potential materials are needed for the effective removal of these toxic substances from contaminated water.

For this, Shen et al. synthesized Cys-Fe_3O_4 MNPs functionalized with cysteine using Fe (II) as a precursor by oxidation–precipitation method at room temperature. The MNPs were used for removal of Hg(II) from the water. It showed a fast removal with 95% removal efficiency (Shen et al., 2014). Parham et al. demonstrated the application of MNPs capped with 2-mercaptobenzothiazole as an efficient adsorbent. MNPs showed very high adsorption ability than non-magnetic NMs. It shows fast, simple and effective for treatment of Hg polluted water (Parham et al. 2012). Girginova et al. employed silica coated MNPs for removal of Hg(II) from water with 74% removal capacity (Girginova et al., 2011). Sumesh et al. synthesized mercaptosuccinic acid capped AgNPs supported on activated alumina for the removal of mercuric ions from contaminated water at room temperature (Sumesh et al., 2011).

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3.4. Removal of Cadmium

Cd is one of the most toxic metal presents in the form of Cd(II). It enters the environment through mining, smelting, oil and coal combustion. Gastrointestinal absorption of Cd(II) from food or water is the principal source of internally deposited Cd(II) in the human body. The excess intake of Cd(II) through the contaminated water may result in the damage of respiratory system, causing bronchial and pulmonary irritation (Seiler et al., 1988; Forstner et al., 1981). So, the separation of Cd(II) from contaminated water is highly demanded.

For this, Gupta et al. prepared Fe_3O_4 MNPs by aco-precipitation method using agricultural waste for the removal of cadmium ions (Gupta et al., 2012). Vukovic et al. prepared ethylene-diamine modified MWCNTs via chemical modification. The biocompatibility of the material is found to be goad and showed no cytotoxic effect (Vukovic et al., 2010). Skubal et al. synthesized colloids of anatase TiO_2 NPs through the controlled hydrolysis of $TiCl_4$ and surface modification with the bidented thiolactic acid. These nanocolloidsshowed10% removal of cadmium ions from water without undergoing reduction or modification in aerobic condition; however, the removal is increased up to 40% in anoxic condition without undergoing reduction or modification of the metal ion as before (Skubal et al., 2002).

3.5. Removal of Lead

Pb is a highly toxic metal and its compound is found in a variety of commercial products and industrial materials, including paints, storage batteries, insecticides, and ceramics. Presently, the important source of Pb in our environment is anthropogenic activities such as the burning of fossil fuels, mining, and various manufacturing processes. Pb may cause irreversible neurological damage as well as renal diseases, cardiovascular effects, reproductive toxicity, damage the kidney and brain when it is taken in large excess through the contaminated drinking water (Qi et al., 2004; WHO, 1989; Patel et al., 2006). As consequences, smart materials are needed to get rid of the Pb present in contaminated water sample.

Masoumi et al. used rice husk and poly methylmethacrylate-co-maleic anhydride for the removal of Pb(II) ions from water. The system can undergo adsorption and desorption in few cycles of removal process (Masoumi et al., 2016). Mostafa et al. exploited the use of $CoMo(CO_3^{2-})$ NMs for spontaneous and endothermic removal of Pb(II) ions (Mostafa et al., 2016). Awual et al. developed a ligand-based conjugate adsorbent for simultaneous removal and detection of Pb(II) from water samples. The organic ligand 4-dodecyl-6-[{4-(hexyloxy) phenyl}diazenyl] benzene-1,3-diol is immobilized onto mesoporous silica by a direct immobilization approach for removal detection and of lead. The detection of Pb(II) ion is based on charge transfer (π–π transition) transduction mechanism (Awual et al. 2014). Zhang et al. synthesized monodispersed and spherical $Fe_3O_4@SiO_2–NH_2$ core–shell NMs with uniform core-shell structure. The high loading of amino moieties on MNPs helped the material for easy removal of Pb(II) from water (Zhang et al., 2013).

3.6. Removal of Selenium

Se is present in the environment in the form of selenide, selenate, or selenite. A maximum acceptable concentration of Se in drinking water is 0.01 mgL^{-1} (U.S. Environmental Protection Agency, 1980). Se is an important element present in several enzymes needed for the proper function of thyroid gland. The excess intake of inorganic and organic Se through the contaminated drinking water may result in the

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symptoms such as fatigue, hair loss, and white blotchy nails (Schamberger et al., 1984; Merian, 1984). Hence, the appropriate elimination of this toxic chemical species is required with specific material to get the clean water.

Awual et al. described the use of organic–inorganic based novel composite adsorbent for removal and detection of Se(IV) from contaminated water and showed adsorption capacity of 111.12 mgg^{-1} of Se(IV) is demonstrated. The presence of diverse competing ions did not affect the separation of Se(IV) (Awual et al., 2015). Loyo et al. demonstrated adsorption capacity of SeO_3^{2-} on the surface of Fe_3O_4 and Fe/Fe_3C NPs. The Fe/Fe_3C NPs showed a better adsorption efficiency than Fe_3O_4 NPs for the removal of Se(IV) from the water samples (Loyo et al. 2008). Gonzalez et al. described $MnFe_2O_4$ NMs for separation of Se from aqueous solutions at pH 6.0 for 5 min of reaction time (Gonzalez et al., 2010).

4. REMOVAL OF ORGANIC CHEMICAL SUBSTANCES FROM CONTAMINATED AND WASTE WATER USING NMS

The disposal of large amounts of domestic, agricultural and industrial waste contains potentially toxic organic chemical substances such as pesticides, phenols, polyaromatic hydrocarbons, and dyes, etc. These toxic substances when entering into drinking water or foods through contamination may cause mutagenic and carcinogenic effects on humans. Recently, NMs are being great attention to using as potential adsorbents to remove toxic and harmful organic substances from contaminated and wastewater.

4.1. Removal of Pesticides

The pesticide is an organic chemical substance used to kill, repel or control certain forms of unwanted weeds or pest in agriculture to prevent the damage of crops. They include insecticides, herbicides, and fungicides. However, both soils and water sources can become contaminated with excess use of these compounds. The acute exposure to these pesticides can disrupt the normal physiological functions of human and cause neurobehavioral disorders, reproductive abnormalities leukemia, malignant lymphoma, nausea, vomiting, hyperventilation and weakness (Hayes et al., 1991; Smith et al., 2002; Corsini et al, 2008). Hence, the removal of the pesticides from drinking water with respect to human health is important concerns.

More recently, Gkementzoglou et al. synthesized a highly specific molecularly imprinted polymer NPs and used for removal of atrazine pesticide from water (Gkementzoglou et al., 2016). Liu et al. prepared graphene-coated silica NPs by mixing GO with acid-treated silica in the presence of hydrazine hydrate. The strong π-bonding network of the benzene rings and interaction of the composite with the electron-donating abilities of the S, P, and N atoms helped in explaining the adsorption and removal mechanism of pesticides from water (Liu et al., 2013). Wu et al. synthesized a graphene-based magnetic nano-composite and used it as an effective adsorbent for the pre-concentration of carbamate pesticides (metolcarb, carbofuran, pirimicarb, isoprocarb and diethofencarb) from environmental water (Wu et al., 2011). Gao et al. utilized a novel nano-structured polyaniline-ionic liquid (i.e. 1-butyl-3-methylimidazolium hexafluorophosphate) composite film coated on steel wire through the electrochemical deposition and used it for the removal of pesticides such as hexachlorocyolohexane, dichlorodiphenyl dichloroethylene, dichlorodiphenyl dichloroethane, dichlorodiphenyl trichloroethane from water samples (Gao et al., 2011).

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4.2. Removal of Dyes

Dyes are another class of an organic chemical substance that widely used in many industries such as textile, cosmetics, plastics, leather, paper, plastics for coloring their products. The effluents from various industries are a major source for the disposal of dyes into the environment. Now, thousands of dyes are annually used for coloring the variety of the materials. The discharge of dyes after their use through the industrial waste results in the contamination of groundwater and drinking water supplies that may produce health risks. Dyes give undesirable color to the water and reduce the sunlight penetration and their degradation products being toxic or even mutagenic, carcinogenic (Lin, 1993; Perez-Urquiza, 2000). Therefore, a novel material is highly demanded to eliminate the dyes present in waste water or contaminated water.

Recently, Singh et al. demonstrated the photo-catalytic properties of semiconductor NPs for oxidation and degradation of dyes assisted with UV light (Singh et al., 2013). Patra et al. synthesized polysaccharide (agar)-based adsorbent through the modification of monometallic and bimetallic NPs (Fe, Cu, Pd, Fe/Cu and Fe/Pd) to remove cationic dyes such as methylene blue and rhodamine B. The NPs showed a 90% adsorption capacity for removal of dyes (Patra et al., 2016). Dadfarnia et al. used iron-basedmetal-organic framework loaded on Fe_3O_4 for the removal of methyl red (Dadfarnia et al. 2015). Singla et al. used a novel boron nitride NMs which showed a very high surface area and high adsorption capacity for brilliant green and methyl orange from water samples (Singla et al., 2015). Gautam et al. synthesized a novel bimetallic Fe-Zn NPs via a co-precipitation method and applied it for the removal of a carcinogenic dye such as malachite green and congo red from water samples (Gautam et al., 2015).

4.3. Removal of Phenol and Phenolic Compounds

Phenols and phenolic compounds are highly toxic to the human health at low concentrations. The major sources of these compounds are oil industry, municipal waste and coke plant effluents (Kolthoff et al., 1971; Kuriacose et al., 1987). In chlorinated water, phenol reacts with chlorine to form chlorophenol which can cause toxic effects on human or animals if the contaminated water is taken. The excess intake of phenol and phenolic compounds through the contaminated water may cause protein denaturation and paralysis of the central nervous system and also damages the kidney, liver, and pancreas (Knop et al., 1985). Thus, it is recommended to remove the phenol and phenolic compounds from waste water before entering the water stream.

For this, Mani et al. reported carbon-doped anatase TiO_2 NPs with high surface area employed for the removal of phenol from water under the simulated solar light (Mani et al., 2015). Yang, et al. demonstrated the separation of phenols through the H-bonding interactions between the target molecule and CNTs followed by π-electron polarizability play important roles on the adsorption of phenols from environmental water (Yang, et al., 2008).]. Zuo et al. presented the catalytic oxidation and removal of phenols from waste water using MWCNTs and MNPs in the presence of H_2O_2 (Zuo et al., 2009). Yao et al. reported the combined effect of cobalt oxide (Co_3O_4) and reduced GO NPs for the catalytic performance for the decomposition of phenol. The combined effect of both the NPs showed a better catalytic activity than individual NPs (Yao et al., 2012). Asmaly et al. presented the Fe_3O_4 MNPs impregnated with carbon fibers for the removal of phenol from water using Langmuir and Freundlich model (Asmaly et al., 2015).

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5. REMOVAL OF BACTERIA AND VIRUS FROM CONTAMINATED WASTE WATER USING MNS

Bacteria and virus are microscopic organisms present in contaminated and waste water that may cause water borne diseases. Thus, there is a need of novel technology for effective removal and inactivation of waterborne microbial pathogens from water bodies. For this, Zarpelon et al. prepared a thin film of AgNPs crosslinked with glutaraldehyde as a new material to act as a bactericidal agent for the treatment of industrial wastewater. The material showed a good inhibitory effect against *Escherichia coli* and also decreased the growth of coliform in water (Zarpelon et al., 2016). Jin et al. presented the use of Fe_3O_4 NPs modified with cetyltrimethylammoniumbromide [Fe_3O_4-CTAB] NPs as a bactericidal material in a water sample. The prepared Fe_3O_4-CTAB NPs are found to be good in capturing both Gram-negative *Escherichia coli* and Gram-positive *Bacillus subtilis* from water (Jin et al., 2015). Motshekga et al. developed a novel silver–zinc oxide bentonite chitosan nano-composite for complete inactivation of bacteria from water in short period of time (Motshekga et al. 2015). Zhan et al. prepared an amine-functionalized magnetic (Fe_3O_4–SiO_2–NH_2 NPs) and used for the removal of both pathogenic bacteria and viruses from water. The amine-modified NPs showed an excellent response in capturing a wide range of pathogens including bacteriophage, virus *(Poliovirus-1), S. aureus, E. coli, P. aeruginosa, Salmonella and B. Subtilis* (Zhan et al., 2014). Radzig et al. demonstrated the antibacterial action of AgNP on Gram-negative bacteria such as planktonic cells and biofilms. AgNPs stabilized with casein peptides strongly inhibit the biofilms formation and prevent the growth of various bacteria in water (Radzig et al., 2013). Ma et al. fabricated a novel nanofibrous microfiltration membrane system with nanofibers and employed for the effective removal of bacteria and viruses from contaminated water. Behra et al. exploited the use of porous polyethylene glycol microparticles functionalized with sugar ligands for capturing the specific bacteria from the water. Its selective and specific binding capacity is used for the separation of different strains of *Escherichia Coli*.

6. CONCLUSION

The uses of different NMs such as magnetic, carbon nanotubes, graphene/graphene oxide, titanium oxide, silica, silver, gold NPs are elaborately demonstrated for the removal of toxic metal ions, organic substances and disease-causing microbes from contaminated and waste water. The surface area and the functional groups attached to the NMs play an important role the removal of contaminates which depends on the pH, concentration of NMs and contact time of the sample. The electrostatic, π-π interaction and vander wall forces etc. are the main forces responsible for the separation of target chemical substances from water. The use of NMs is found easy, rapid and eco-friendly for selective and efficient removal of contaminants from water. These NMs are very stable and produce less amount of waste generation compared to another traditional method for removal of contaminants. In addition, these described methods are rapid and energy saving for adsorption of target environmental pollutants from contaminated and waste water.

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Chapter 25
Constructed Wetlands: Description and Benefits of an Eco-Tech Water Treatment System

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ABSTRACT

Constructed Wetlands are an alternative, promising technology for water/wastewater treatment and pollution mitigation. They belong to the wider category of natural treatment systems. The main principle is to exploit natural materials (gravel, sand, plants) and naturally occurring processes under controlled conditions for treatment purposes. Constructed Wetlands have been characterized as an environmentally friendly, sustainable technology which provides multiple economic, ecological, technical and societal benefits. It is a rising technology which can be effectively used for domestic, municipal and industrial wastewater treatment, as also for sludge dewatering and drying. This chapter presents an overview of this eco-technology; its different types, main design considerations and various advantages over conventional treatment methods.

INTRODUCTION

The use of natural processes is not something new in waste/wastewater processes. Practically, most known technologies and techniques are based on these processes, such as sedimentation, filtration, biological activity etc, and are often constructed with complex and energy-consuming mechanical equipment. The difference that separates natural treatment systems from conventional ones is that only natural components are used for the treatment. Naturally occurring processes are utilized under a controlled environment, without the input of external energy source, unless perhaps for pump operation. Among the various natural treatment systems such as facultative and oxidation ponds, Constructed Wetlands (CWs) appear as one of the most promising eco-tech treatment methods, which have been attracting increasing worldwide interest. Their excellent treatment performance, coupled with an environmentally friendly character and reduced overall costs are gradually placing Constructed Wetlands in the forefront

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of the scientific and marketing interest. This chapter discusses the multiple environmental, economic and technical advantages of these treatment systems and includes a brief description of their design and the wide range of their applications. These characteristics aim at presenting current research progress on sustainability issues in innovative wastewater treatment systems.

Background

Wetlands are considered today as natural systems with great ecological significance which provide habitat for numerous species and support their life. Natural Wetlands includes various benefits such as groundwater aquifer enrichment, control of flood incidents, absorption of carbon dioxide, heat storage and release, sediment trapping and other (Stefanakis, Akratos & Tsihrintzis, 2014). Their values can be translated in ecological, social, cultural and economic units (De Grot, Stuip, Finlayson, & Davidson, 2006). It was gradually realized that natural wetlands had always been capable of providing water purification and improving water quality, at least up until the point where industrial contamination had become so intensive. This observation initiated the investigation of re-assessing existing wetland purification potential. Natural wetlands have been utilized as disposal sites for secondary or tertiary wastewater effluents for many years, even some thousands years ago. Sewerage collection systems were constructed in the Zakros and Knossos Palaces during the Minoan era in the Greek Island of Crete, where nearby torrents and wetlands were used as disposal sites (Angelakis, Koutsoyiannis, & Tchobanoglous, 2005; Stefanakis et al., 2014). In modern times, the transition from Natural to Constructed Wetlands (CWs) was based on the potential exploitation of naturally occurring processes in a controlled environment for beneficial human and environmental usage and the healthy perpetuation of the natural environment. In this context, man-made Constructed Wetlands are designed to mimic and, thus, enhance the functions and operations of natural wetlands. While Constructed Wetlands generally offer the same functions and values as natural wetlands do, they also may appear as a more ecologically endowed system. Studies have shown that Constructed Wetlands possess a higher value in terms of flood and stormwater control, water quality improvement and biodiversity restoration (Ghermandi, Van den Bergh, Brander, De Groot, & Nunes, 2010). This may be because they are more easily integrated into the built infrastructure by urban planners, engineers, and landscape architects.

Today, the term "Constructed Wetlands" (also known as ""Treatment Wetlands" or "Reed Beds") refers to engineered systems which are designed to exploit under controlled conditions the processes that occur in nature (Stefanakis et al., 2014). Constructed Wetlands belong to the wider category of natural treatment systems which primarily rely on natural processes and/or natural components for wastewater treatment, where intensive use of external energy input can be avoided. Natural treatment systems are mainly classified into terrestrial, aquatic and wetland systems. Aquatic systems include stabilization or oxidation ponds and terrestrial systems slow rate systems and soil aquifer treatment (Stefanakis et al., 2014). Constructed Wetlands are in the middle of these two categories. The technology of Constructed Wetlands began with laboratory experiments in the Max Planck Institute in Germany in the 1950s. The first system in Europe was constructed in the 1960s and in the USA in the 1970s-1980s. Despite these early experiments and attempts, until the end of the 1980s Constructed Wetlands technology was not widely tested or utilized. Failure incidents of some of the first systems due to inadequate design, indicating lack of experience, and competition from conventional treatment methods in use for more than 80 years, were considered as the main initial obstacles for this limited expansion. However, over the last 20

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years the interest for alternative treatment methods has increased and the Constructed Wetlands technology has experienced a tremendous increase in both research and applications, due to the simultaneous increase of environmental awareness and sensitivity. Stefanakis et al. (2014) reported that the number of published scientific papers on Constructed Wetlands during the decade 2000-2010 has more than doubled, compared to the previous decade (1990-2000).

Constructed Wetlands represent one of the most interesting and attractive developments in environmental/ecological engineering. The philosophy behind this type of wastewater system is based on the decentralized approach in contrast to what had been regarded as the centralized approach of conventional biological treatment methods which dominate the wastewater market. This new approach also introduces new parameters and views in wastewater treatment, such as sustainability and overall environmental impact. The following section of this chapter presents an overview of constructed wetland classification, technology and description of its principal characteristics, with a focus on its advantages and benefits and its various wastewater treatment applications.

CONSTRUCTED WETLANDS TECHNOLOGY

Classification

Constructed Wetlands can be classified according to their functions and aims in three main application areas (Knight, 1997; Stefanakis et al., 2014):

- **Habitat creation:** these systems are designed to provide a revitalized wildlife habitat and to enhance the pre-existing ecological benefits of the technology such as attracting animals such as birds and creating a green area, while addressing the water/wastewater treatment and mitigation. In this category, four different types of CWs exist: ponds, marshes, swamps and ephemeral wetlands.
- **Flood control:** these systems operate as runoff receivers during flood incidents and increase the storm water storage capacity in urban areas.
- **Wastewater treatment:** systems designed and operated to receive and treat wastewater of different origin.

Another widely used classification of CW systems is based on the main characteristics of the system such as the direction of the water flow and the type of vegetation used, as it is depicted in Fig. 1. Thus, based on the flow path across the CW system, there are two general types (Kadlec & Wallace, 2009; Stefanakis et al., 2014):

A. Free water surface constructed wetlands (FWS CWs) and
B. Subsurface flow constructed wetlands (SF CWs).

A further classification of SF CWs can be made depending on the flow path direction; horizontal (HSF CWs) or vertical (VFCWs).

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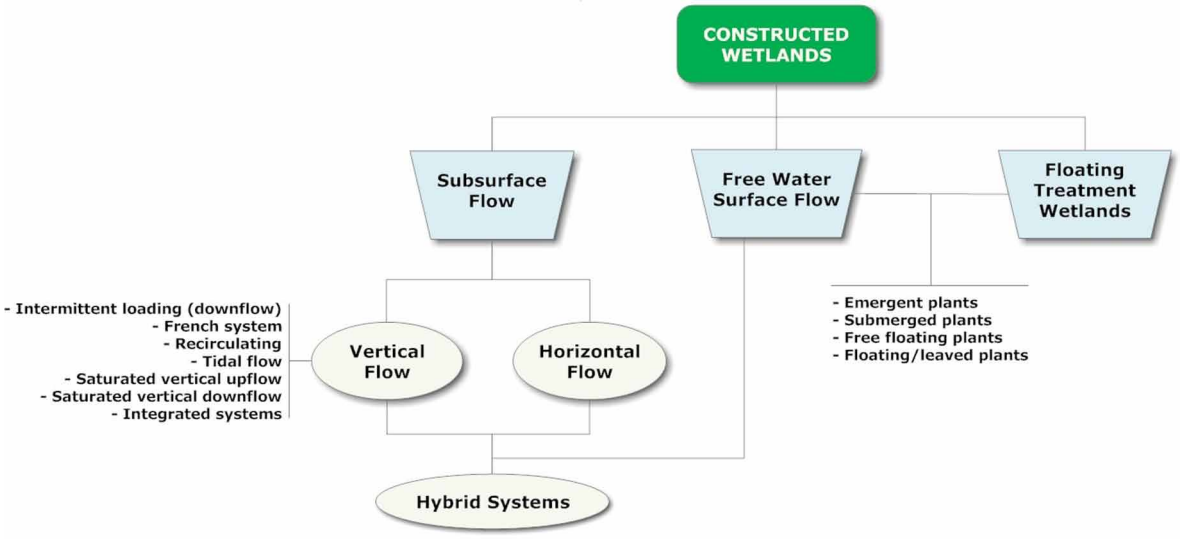
Figure 1. Classification of Constructed Wetlands.



The type of vegetation used in CWs is one of the major characteristics of the system. Thus, based on the vegetation type, CWs can be also classified as (a) emergent macrophyte wetlands, (b) submerged macrophyte wetlands and (c) floating treatment wetlands (FTWs) (Vymazal, 2007; Stefanakis et al., 2014). CWs with rooted emergent macrophytes are the most widely used.

Free Water Surface Constructed Wetlands (FWS CWs)

This type of CWs is widely used in North America, almost exclusively for wastewater treatment applications (Kadlec & Wallace, 2009). They are shallow basins or channels containing a soil layer (30-40 cm thick), in which the macrophytes are planted. Most common plants species used are common reeds (*Phragmites australis*), cattails (*Typha* spp), bulrush (*Scirpus* spp) and herbs (*Juncus* spp) (Vymazal, 2013; Stefanakis et al., 2014). The bottom of the basin (as in all CW systems) is covered by a geo-textile/geo-membrane or clay material in order to prevent wastewater leakage to the groundwater. Above the soil layer there is a water column (20-40 cm deep or deeper) which is exposed to the atmosphere and the solar radiation (Vymazal, 2013). Appropriate water level control at the outlet of the system regulates the depth of the water column; usually there is flexibility in the depth adjustment. The water flows through the plant stems and comes into contact with the top layer of the soil and the plant parts, which allows for the pollutant removal through various physical, biological and chemical processes. FWS CWs tend to attract mosquitos, especially when the water remains almost stagnant. This system performs well for suspended solids (SS) and biochemical oxygen demand (BOD_5) removal. Removal of nitrogen (N) and pathogens is satisfying, but phosphorus (P) removal is usually limited (Vymazal, 2007; Kadlec & Wallace, 2009; Kotti, Gikas, & Tsihrintzis, 2010; Stefanakis et al., 2014). FWS CWs have been applied for the treatment of primary and secondary municipal effluents, storm water and highway runoff and agricultural wastewater (Vymazal, 2013; Stefanakis et al., 2014). This type of CWs has higher area demands when compared with other types for the same wastewater characteristics (origin, flow). Since these systems have an open water surface they tend to resemble natural wetlands at a greater level.

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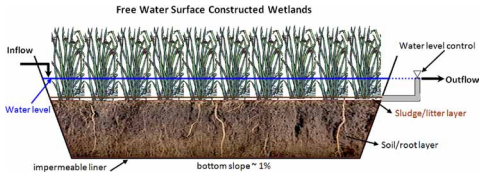
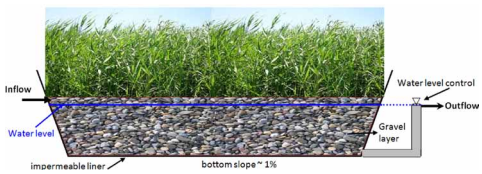
Figure 2. Schematic Representation of Free Water Surface Constructed Wetlands.



Horizontal Subsurface Flow Constructed Wetlands (HSF CWs)

HSF CWs are more widely used in Europe than in the USA (Stefanakis & Tsihrintzis, 2009a). These systems are basins containing gravel material, usually planted with common reeds (*Phragmites australis*) or other species such as *Typha* (e.g., latifolia, angustifolia) and *Scirpus* (e.g., lacustris, californicus) (Vymazal, 2011). The substrate used is rocks of different origin and composition. Unlike FWS CWs, in this CW type there is no water surface exposed to the atmosphere; the water level is kept 5-10 cm below the gravel layer surface and water flows through the pores of the substrate media and comes into contact with the media grains, the plant roots and the attached biofilm (Stefanakis et al., 2014). Thus, respective health risks due to possible human contact with the wastewater and mosquito issues are limited in this CW type (Kadlec & Wallace, 2009). The substrate layer thickness varies from 30 to 80 cm (Akratos & Tsihrintzis, 2007; Kadlec & Wallace, 2009). The bottom of the bed is usually covered with an impermeable geo-membrane and has a slight slope (1-3%) to allow the water flow. As for FWS CWs, the uniform distribution of the wastewater across the wetland width at the inflow point is a key parameter for the proper function of the system (Akratos & Tsihrintzis, 2007), while step-feeding of the wastewater along the wetland length has been found to enhance the system performance (Stefanakis, Akratos, & Tsihrintzis, 2011a). HSF CWs have the advantage of lower area demands compared to FWS CWs, although capital costs might be higher (Kadlec & Wallace, 2009; Stefanakis et al., 2014). This CW type has been proved to be very effective in the treatment of municipal wastewater, removing SS and organic matter (BOD_5) at high rates, although nutrient removal (nitrogen, phosphorus) is usually lower (Akratos & Tsihrintzis, 2007; Vymazal, 2007; Kadlec & Wallace, 2009; Stefanakis et al., 2014). Various modifications of the system design have been proposed in order to improve the performance such as effluent recirculation (Stefanakis & Tsihrintzis, 2009a), wastewater step-feeding (Stefanakis et al., 2011a), water level raising (Stefanakis & Tsihrintzis, 2009a) and effluent treatment with zeolite gravity filters (Stefanakis, Akratos, Gikas, & Tsihrintzis, 2009a). HSF CWs have been also applied for the treatment of industrial wastewater, e.g., mine drainage, dairy, swine, olive mills, landfill leachate, cork effluent, contaminated groundwater, hydrocarbons etc. (Vymazal, 2009; Santos et al., 2012; Stefanakis et al., 2013).

Figure 3. Schematic representation of Horizontal Subsurface Flow Constructed Wetlands.



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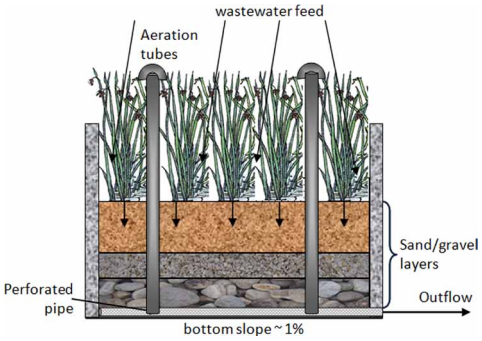
Vertical Flow Constructed Wetlands (VFCWs)

Until recently, this type of CWs was the least developed and applied. At the early stages of CW technology, FWS and HSF CWs were the dominant types, mainly due to higher overall costs for VFCWs construction and operation. However, the interest in VFCWs was gradually increased with time; especially when the higher oxygen transfer capacity of this CW type was realized compared to the horizontal flow beds. Thus, over the last 15 years research on VFCW systems was substantially intensified. Today, there are various modifications of VF systems which are either already applied or under investigation. VFCWs are mainly used in Europe, and especially in Denmark, Austria, Germany, France, and the United Kingdom (Kadlec & Wallace, 2009; Stefanakis et al., 2014). The most common setup is a basin containing several layers of gravels and sand with increasing gradation from top to the bottom (Stefanakis & Tsihrintzis, 2009b; 2012a; Stefanakis et al., 2014). The total thickness of the substrate varies from 30 to 180 cm (Stefanakis et al., 2014). Usually, the top layer of the bed is a sand layer. Plants are established in the top gravel layer or in the sand layer (if any). As for the other CW types, common reeds (*Phragmites australis*) and cattails (*Typha latifolia*) are the two most widely used plant species. The bottom of the bed is covered by a geo-membrane/geo-textile material and has a slight slop of 1-2%. VFCWs also contain perforated vertical aeration tubes which are connected at the bottom of the bed with the drainage collection pipeline system. These aeration tubes allow for the better aeration of the deeper parts of the bed (Stefanakis & Tsihrintzis, 2012a). The wastewater is applied in batches on top of the bed and drains vertically by gravity, while it should be uniformly distributed across the entire surface of the bed (Stefanakis & Tsihrintzis, 2012a; Stefanakis et al., 2014). VFCWs have smaller surface area demands compared to HSF and FWS CWs. Due to the better aeration capability, VFCWs are very effective in organic matter (BOD_5) and ammonia nitrogen removal, usually more effective than HSF CWs (Vymazal, 2007; Kadlec & Wallace, 2009; Stefanakis et al., 2014). Phosphorus removal remains limited and alternative modifications have been proposed for performance improvement, e.g., an additional stage with gravity filters containing bauxite, zeolite or other material for effluent treatment (Brix & Arias, 2005; Stefanakis & Tsihrintzis, 2012b). Their overall effectiveness enabled the use of this CW type for the treatment of wastewater with different origin, e.g., domestic, municipal, industrial, agro-industrial and landfill leachate (Stefanakis et al., 2014).

Figure 4. Schematic representation of Vertical Flow Constructed Wetlands.



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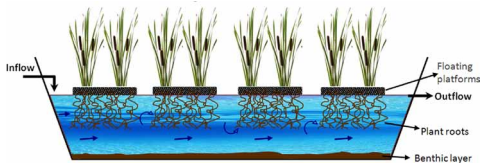
Floating Treatment Wetlands (FTWs)

This type is the latest version of CW technology, combining both a traditional CW system and a pond (Van de Moortel, Meers, Pauw, & Tack, 2010). These systems consist of a floating element (usually made of a plastic material) on which the plants are established; thus, it could be stated that these systems optically look like floating islands. As in the other CW types, the plants develop a deep and dense root system within the underlying water column (Tanner & Headley, 2011; Stefanakis et al., 2014). Since the combined system of the porous plastic basis and the plants floats on the water surface, the system is not affected by fluctuations of the water level. FTWs have been used for water purification in rivers, channels, lakes etc., as also for stormwater, domestic and municipal wastewater treatment (Van de Moortel et al., 2010; Stefanakis et al., 2014).

Sludge Treatment Wetlands (STWs)

These systems represent a special and very promising application of CW technology, for the treatment and management of excess sludge that is produced in conventional wastewater treatment plants. STWs appear as alternative systems to mechanical dewatering methods such as centrifuges or filter presses. They resemble vertical flow constructed wetlands (Fig. 4) in the design and construction, but they are modified systems for wastewater sludge dewatering and drying (Stefanakis & Tsihrintzis, 2012c; Stefanakis et al., 2014). As the vertical flow systems, STWs are rectangular or trapezoidal excavated basins filled with substrate materials planted with reeds (Nielsen, 2003). Usually the basin contains 1-2 gravel layers and on top a sand layer (Nielsen, 2005), although there have been systems designed without a top sand layer (Stefanakis et al., 2009b; Stefanakis & Tsihrintzis, 2012c). The total thickness of the porous media layers varies between 30-70 cm (Stefanakis et al., 2014). Sludge is applied on top of the bed in feeding cycles: a typical feeding scheme is 2-10 days of sludge feeding followed by 1-3 weeks of resting (Nielsen, 2003; Stefanakis et al., 2009b; Stefanakis and Tsihrintzis, 2012c). The bottom of the beds can be either constructed with concrete or excavated and covered with a liner, typically with a material of low-permeability as for the other CW types (i.e., HDPE geo-membrane covered in both sides with geotextile or clay) (Stefanakis et al., 2014). The bottom layer also contains a network of perforated plastic pipes for the collection of the drained water that flows vertically through the bed body. This bottom pipe network is connected with the atmosphere with vertical perforated plastic aeration pipes which are extended above the top layer and are open on their top end. STWs achieve high rates of sludge dewatering (volume reduction up to 96%; Stefanakis & Tsihrintzis, 2012c; Stefanakis et al., 2014), through evapotranspiration and draining processes (Stefanakis & Tsihrintzis, 2011).

Figure 5. Schematic representation of Floating Treatment Wetlands.



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Design Considerations of Constructed Wetland Facilities

CW beds are generally considered as easy to build and operate; however, the proper design of a CW facility is not as easy as it seems. Since it is a relatively new technology, there are not unanimously accepted guidelines or a widely applied setup. System design tends to differ not only from country to country but also among designers and experts/engineers. Personal experience is usually a key parameter. However, there are general rules and some basic design considerations which are used during the design process, including meteorological, topographical and operational parameters such as (Stefanakis et al., 2014):

- Climatic conditions of the area where the system will be installed,
- Topographical information in order to choose the most appropriate installation site,
- Geological structure of the area,
- Availability of the necessary land,
- Current and future wastewater flow and volumes,
- Any legal limits that apply in the area for the effluent quality – desired treatment performance
- Possibilities/desire for effluent reuse options,
- A nearby water body-effluent receiver,
- Total costs.

As it is obvious, most of these general parameters are common prior the implementation of any treatment technology. There are three main design parameters for constructed wetland systems which should be taken into account: (a) unit area demand (m^2/pe), (b) organic and hydraulic loading and (c) oxygen transfer capacity (Stefanakis et al., 2014). The unit area demand expresses the surface area demand (m^2) per person equivalent (pe). This parameter is generally accepted and serves as a good indication of the overall land area demands. Apparently, this parameter is affected by the climatic conditions. However, it is common than even for the same region different values are proposed based on the individual experience. Generally, VFCWs have lower area demands (1-2 m^2/pe) than HSF CWS (5-10 m^2/pe) (Stefanakis et al., 2014). Organic (e.g., g BOD_5 or COD/m^2/yr) and hydraulic (m^3/m^2/d or m/d) loads are also used and give a good idea of the system load. These parameters are very helpful in the determination of the optimum loading which will cause no operational problems. Finally, the oxygen transfer capacity (OTC) provides important information concerning the oxidation potential of the system, especially for organic matter decomposition and ammonia nitrogen nitrification.

Another important parameter which is mostly applied in horizontal CWs (either surface or subsurface) is the hydraulic retention time (HRT), which is described as the ratio of volume (m^3) to flow rate (m^3/d). Its value is crucial since it defines the available time for direct contact of the wastewater and the wetland elements (porous media grains, plant roots, biofilm) and, thus, the extent of the various removal/transformation processes. The selection of an appropriate HRT is directly related to the system surface area (and so to the unit area demand) and performance. Currently, there are many published studies and results from pilot and full-scale installations. For example, typical HRT in HSF CWs varies between 5-20 days, depending on the climatic conditions, the level of treatment etc. Dimensions of horizontal beds are also important; usually HSF and FWS CWs have a rectangular plan view with a varying width to length ratio of 1:3-5. Longer length than width is preferred in order to ensure plug flow hydraulics.

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Generally, designing and sizing a wetland bed varies from simple "rule of thumb" to more complex models. The plug-flow first order k (known as the kC* model) is often used, as also Monod-type equations (Kadlec & Wallace, 2009). A simple equation which is often used for the calculation of the required surface area for BOD_5 removal is the following:

$$A = \frac{Q\ [\ln(C_o / C_e)]}{K_T\ d\ n} \quad (1)$$

where, A = the surface area of the bed (m^2), d = the saturated depth of the bed (m), n = the substrate porosity (decimal fraction), K_T = the first-order areal rate constant (m/d), Q = the average daily flow rate (m^3/d), C_o the mean influent BOD_5 concentration (mg/L) and C_e the required effluent BOD_5 concentration (mg/L). For example, for a bed depth of 0.6 m at 10°C, K gets the value 5.2. K values depend on the biodegradability of the wastewater. Usually, BOD_5 is used as the main target parameter, but other pollutants such as suspended solids (SS), ammonia nitrogen and total phosphorus have also been used. The parameters used for the evaluation of CWs performance are the same pollutant indicators as for every wastewater treatment technology, such as organic matter (BOD_5 and COD), nitrogen compounds (total nitrogen, ammonia nitrogen, nitrate, nitrite), phosphorus (total phosphorus, ortho-phosphate), coliform bacteria (*E. coli*, feacal coliforms) and heavy metals. Physical characteristics (e.g., dissolved oxygen, electrical conductivity, pH etc) are also used to describe CWs operating conditions.

In Sludge Treatment Wetlands, the design is based on the quality of the raw sludge and the local climatic conditions, as well as on the annual sludge production of the wastewater treatment plant (Stefanakis et al., 2014). As for other CW types, the design and dimensioning of STWs follows mostly empirical observations and personal experience of the designer. Again, there are no commonly accepted guidelines and the design varies from country to country. The basic design parameter is the sludge loading rate (SLR; kg dm/m^2/yr), which expresses the annual dry mass (dm/yr) or dry solids (ds/yr) that will be applied to the bed per surface unit (m^2). It is directly related to the climate of the installation area. For example, proposed SLR for Denmark is 60 kg dm/m^2/yr for activated sludge and 50 kg dm/m^2/yr for sludge with higher fat content (Nielsen, 2003). Higher SLRs have been proposed for the Mediterranean basin: up to 90 kg dm/m^2/yr in Greece (Stefanakis & Tsihrintzis, 2012c), as also 45 kg dm/m^2/yr in Italy (Bianchi et al., 2011) and 55-110 kg dm/m^2/yr in Spain (Uggetti et al., 2009; Uggetti, Ferrer, Molist, & Garcıa, 2011). Stefanakis et al. (2014) presented an overview of SLRs applied in various countries around the world. The operational life time of STWs can last up to 30 years and more and it is divided in 2-3 phases of 8-12 years, based on the applied SLR. After the completion of each phase, the bed is left to rest for some period (a few months up to 1 year), then the accumulated sludge residual is removed and a new feeding cycle begins (Nielsen, 2003; Stefanakis & Tsihrintzis, 2012c; Stefanakis et al., 2014).

Two important design features of CW facilities are the plant species and the substrate media. The most common emergent plant species used are common reeds (*Phragmites australis*) and cattails (*Typha latifolia*) and also *Scirpus* spp, due to their wide presence in most parts of the world. However, other locally available species may also be used, for example in tropical regions bamboo has been tested in CW systems. Generally, the selected species should be well adapted to the local climatic conditions, tolerant against the various pollutants and with uptake capabilities of certain constituents such as nitrogen. It should be noted that indigenous species are always preferred for use in CWs and not exotic ones, to avoid ecological risks such as invasion of the new species and/or diseases (Stefanakis et al., 2014).

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The selection of an appropriate substrate media is also important for the CW system and, as plants, is connected with the system performance. The grain size should be carefully selected, especially for subsurface systems, since clogging problems due to low porosity and high hydraulic loads might occur and affect the system efficiency. An ideal substrate would also have the capacity of removing some constituents from wastewater by various processes (e.g., ion exchange, adsorption, precipitation). The substrate layer is also where the plants are established, thus, it supports plant growth and enhances system stability, provides filtration effects and together with the plants supports the various transformation/removal processes (Vymazal, 2007; Stefanakis et al., 2014). Media used in CW systems include natural materials (e.g., minerals, rocks and soils), synthetic materials (e.g., synthetic zeolites, activated carbon) and industrial by-products (e.g., slags, blast furnace) (Stefanakis et al., 2014).

Facility Layout

A full-scale CW facility comprises of several treatment stages. The first treatment stage is usually the pre-treatment stage. In this stage, large material (e.g., papers, leaves, plastics etc.) and coarse particles are firstly removed using mechanical equipment (e.g., screens and bars), along with a portion of the SS and organic matter. Most common pre-treatment methods are septic or Imhoff tanks and primary sedimentation tanks, although anaerobic digesters and stabilization ponds have also been used (Stefanakis et al., 2014). This pre-treatment stage is very important in CW facilities, since a good performance limits the clogging potential of the following CW beds. In case of industrial or agricultural wastewater, pre-treatment can be more complex and intensive due to the heavier loads of these wastewater types.

Different CW types can be combined in the second and third (or even fourth if necessary) treatment stages of a full-scale facility, usually HSF CWS and VFCWs (Stefanakis et al., 2014). These combined systems are also known as *hybrid CW systems*. The concept is to exploit the specific treatment advantages of each type in one facility and reach higher treatment efficiencies. For example, low nitrification capacity of HSF CWs (due to limited OTC) is counterbalanced by VFCWs (good nitrification capacity, high OTC). Additionally, HSF CWs can be used to provide denitrification of the nitrified effluent from VFCWs. The most common combination is a two-stage system of a first VFCW bed followed by a HSF CW. Stefanakis et al. (2014) presented several possible combinations of CW types in hybrid systems that have been tested, e.g., VF-HSF, HSF-VF, HSF-VF-HSF, VF-HSF-HSF, VF-HSF-FWS.

The two-stage VFCW system gains increasingly interest since it has been proved very effective. VFCWs operate with parallel beds in each treatment stage. The presence of parallel VFCWs beds is necessary to ensure the continuous operation of the facility, since VFCWs usually operate with intermittent wastewater application (2-4 days of feeding followed by 2-8 days of resting) (Stefanakis & Tsihrintzis, 2012a; Stefanakis et al., 2014). The number of parallel beds in the third treatment stage is lower, since the pollution load is respectively lower due to the prior treatment in the second-stage CW beds. A modification of the two-stage VFCW system has been developed in France, also known as the French system (Molle, Liénard, Boutin, Merlin, & Iwema, 2005; Stefanakis & Tsihrintzis, 2012a). This setup includes two stages of VFCWs but no pre-treatment stage (only screens are used). The wastewater is applied directly on the surface of the first-stage VFCW bed. The key here is that the first-stage beds contain only coarser material (no sand), in order to avoid clogging and gradually accumulate sludge on the surface. The advantage of the French system is that it may have lower costs since no pre-treatment is applied.

A final post-treatment stage is not a basic element in the design of CW facilities but it is often applied when stringent effluent quality criteria have to be met, especially concerning pathogenic micro-

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organisms. Of course, the goal is not to produce a final effluent appropriate for use as potable water, but to further improve the effluent quality and reach higher sanitation levels, in order to minimize or even eliminate the environmental impact. This final stage could include disinfection methods such as chlorination, ozonation or UV radiation. Maturation ponds or a final FWS CW system have also been used as a final treatment stage. A post-treatment stage could also improve the overall system efficiency, e.g., in phosphorus removal.

Facilities of Sludge Treatment Wetlands are similar to those of VFCWs. A STW facility consists of several beds which are alternately loaded with sludge. The presence of several beds allows for the application of feeding and resting periods in the beds and provides flexibility in the loading cycles applied which may vary during winter and summer months (Stefanakis et al., 2014). The number of beds in a STW facility depends on the sludge production of the wastewater treatment plant, the chosen SLR, the cycles of feeding/resting periods and the climatic conditions. For example, Uggetti et al. (2009) used 3 beds, Stefanakis & Tsihrintzis (2012c) 4 beds and Nielsen (2003) 18 beds, which correspond to 400 and 123,000 pe served, respectively.

Advantages of Constructed Wetlands Technology

As an alternative, ecological treatment technology, CWs provide a series of multiple significant advantages compared to conventional treatment methods such as activated sludge systems. Conventional treatment systems are in use for more than 100 years now, serving a different approach of wastewater treatment than CWs. The approach of conventional treatment systems consists in the construction of large, centralized facilities and respectively extended sewer networks for the collection and transport of wastewater. It is not difficult to understand that big end-of-the-pipe centralized plants and the accompanied sewer network represent high required investments. These facilities are also expensive in their operation and maintenance. Of course, this type of facilities appears as the only solution to provide wastewater treatment for large cities, capitals, and other populated urban areas. For these cases, high investment costs are considered as reasonable and unavoidable. However, the question is whether this approach of centralized treatment systems is even applicable in smaller cities, communities and rural areas. Over the last years, an alternative approach of wastewater treatment has risen; the decentralized approach.

Although there have been in the past huge investments in infrastructure for centralized plants, gradual population increase was not accompanied by respective increase in budgets to meet the needs for new wastewater treatment facilities. Insufficient funding was even more realized due to the aging of existing infrastructure, which means that additional investments are needed not only for new installations but also for the refurbishment and technological upgrade of existing facilities. This means that new, innovative and cost-effective methods are more welcome than in the past and the approach of decentralized treatment becomes gradually more attractive. CWs belong exact to this category and serve this philosophy. They are point-of-use treatment systems which can deliver effluents of the desired quality. They can be installed in many areas and regions with reduced overall costs. However, the CW technology should not be viewed as a direct and total competitor of conventional treatment systems. A complete replacement of centralized facilities with CW systems is practically infeasible, since the required land area would be very high; a demand which cannot be met in large densely populated urban areas. But CW systems appear as an ideal solution for small and medium communities, small cities, villages, single households or block of flats and generally rural, mountainous and remote areas, where sewer network does not exist

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Table 1. Main characteristics of conventional treatment systems (CTS) and Constructed Wetlands (CWs) (Stefanakis et al., 2014).

	Conventional Treatment Systems	Constructed Wetlands
Infrastructure	Many and complex mechanical parts	No mechanical parts (maybe only pumps)
Investment	High construction costs	Usually lower construction costs than CTS (especially if there is available land)
Operational costs	High	Very low to zero
Land area demand	Low	High demand (e.g., 2-10 m^2/pe)
Application scale	Small - medium	Medium - large
Performance	Continuous effluent of high quality	Similar with CTS, small fluctuations may appear with temperature variations
Raw materials	Use of non-renewable materials during construction (concrete, steel, etc.) and operation (electrical power, chemicals)	Almost exclusive use of renewable sources (solar, wind, etc.) - "ecological" character
Energy consumption	High	Low
Greenhouse Gas Emissions	High	Very low
Operation	Need for daily monitoring Useful lifetime up to 25-30 years	Need for periodical check only (e.g., on a monthly basis) – autonomous operation, Prolonged lifetime (>30 years)
Staff during operation	Demand for specialized personnel	No specialized personnel needed
Maintenance	High maintenance needs and costs - regular damages due to large/complex mechanical equipment	Low maintenance cost (only small mechanical parts – pumps)
Odors	Large open air tanks, odor production	Small problems only in free water surface systems
Insects	Usually no significant problems	Small problems only in free water surface systems
Response to flow variations	Higher/shock inflow rates negatively affect the performance	Robust to high flow variations
Robustness to toxic substances	Toxic pollutants may lead to system breakdown	Robust to some toxic constituents
By-products	Large daily volumes of sludge production, which needs handling and management on a daily basis	Zero production of by-products
Appearance	Unattractive, "industrial appearance"	Aesthetically accepted, green view

and the construction of a conventional treatment plant is economically unfeasible. For these areas, CW technology provides many technical, economic and ecological benefits, which are summarized in Table 1.

CWs are in general easy to build, simple to operate and provide treatment robust to flow fluctuations and pollutant concentrations. They appear as an ideal solution especially for small communities and settlements and for onsite treatment, where current requirements and needs for effective wastewater treatment are high. CWs facilities can satisfy general effluent discharge limits (e.g., BOD_5 < 30 mg/L, COD < 100 mg/L, total nitrogen < 15 mg/L), while effluents of even higher quality can also be achieved (Kadlec & Wallace, 2009; Stefanakis et al., 2014).

Although conventional treatment systems provide effective wastewater treatment for many decades now, they have certain disadvantages. Typical facilities of this type have an industrial appearance and are unattractive, thus, they are usually installed away from residential areas. Centralized plants include

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large and complex mechanical equipment such as ventilators for aeration, pumps etc., while extensive use of non-renewable materials (concrete, steel) takes place for the construction of the various basins, tanks and equipment. This means that construction of such facilities can be expensive and non-environmentally friendly, despite the fact that the aim is environmental-oriented (wastewater treatment). On the other hand, CW facilities do not include mechanical parts. The only mechanical equipment is pumps to transfer the water from one stage to the other, which - however - can be avoided with a proper design and exploitation of the topography of the installation area. Moreover, conventional treatment plants are energy-intensive systems and they require a large energy input for their operation. Facilities having many complex mechanical parts and equipment may also require high maintenance demands. This means that operational costs of such facilities are also high. On the contrary, minimum operational costs probably represent the main advantage of CW facilities. In CWs, the energy input needed is very small, usually only for the pumps that may exist in the facility. Energy requirements for the treatment processes are covered by renewable energy sources used by plants (solar, wind energy). At the same time, maintenance needs are also low, since the operation of a CW facility is practically autonomous; at the stage of full operation, a typical maintenance scheme applied is one visit at the site on a monthly basis. There may also be far less need for specialized personnel to run the CW facility, contrary to conventional plants where specialized staff is necessary. Global experience from many countries and professionals has shown that operational costs of CW facilities can be up to 90% lower compared to conventional plants. Moreover, CWs operate without the need for the addition of any chemical substances, which is not the case in conventional treatment plants.

Additionally, the treatment in CWs does not generate any by-product. Produced sludge is accumulated within the system. On the other hand, in conventional treatment plants large amounts of excess sludge are produced on a daily basis. This excess sludge needs to be managed, dewatered and stabilized in order to be further exploited. Although the sludge volume represents only a small portion (1-3%) of the total treated volume, its management and handling can reach up to 50% of the total facility costs (Stefanakis et al., 2014). It is then realized the significant advantage of CWs of no by-product production. To be accurate, though, it should be noted that occasional sludge removal (e.g., 2-3 times/years) should take place if there is a pre-treatment stage (e.g., sedimentation or Imhoff tank), but this cost is by far lower than the sludge production and handling cost in conventional systems. The only product that could potentially be viewed as by-product in CW facilities is the plant biomass. Usually, the produced plant biomass is harvested and collected once annually. However, this biomass can be exploited as biofuel for energy production or for compost production. Additionally, in most CW systems problems with mosquito and odor production are very low, especially in systems with subsurface flow, which is not the case in conventional treatment facilities where the open wastewater tanks for settling and/or aeration attracts mosquitos and insects and produce odors.

Disadvantages of Constructed Wetlands

Despite the various advantages of this technology, CWs have also some downsides which should be taken into account. The major one is that CWs require a larger land area compared to a conventional treatment facility. Although continuous research managed to reduce the total footprint of CW facilities and optimize their design (e.g., the use vertical flow systems and lately of aerated systems), area demands are still higher (e.g., 3-10 times) for CWs than for conventional systems (Stefanakis et al., 2014). Furthermore, false design could also result in odor problems and the appearance of a water surface in

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subsurface systems. However, it should be noted that if properly designed and constructed, CWs generally do not create odor issues.

Since the wetland technology still remains relatively new, the CW system is often viewed using the "black box" approach and simple regression equations are used for the design (Button, Nivala, Weber, Aubron, & Müller, 2014). On the other hand, it is known that most of the pollutant removal mechanisms are based on microbial processes (Faulwetter et al., 2009), which means that a better understanding of the fundamental processes taking place inside the system is necessary, in order to provide an optimum design and performance (Stefanakis et al., 2014). Thus, the design of CWs is still largely based on empirical data and professional experience. This also explains the fact that there are not yet widely accepted design guidelines for CW systems. Additionally, optimum performance is usually reached after one or two years of operation, when the plants are fully developed, while there might be some seasonal variations in the overall efficiency.

It should be noted that all the above mentioned drawbacks are currently under investigation by the scientific community. Intensified research over the last 10-15 years has managed to abate most of these issues and further improvements are anticipated in the future.

Sustainable Character of Constructed Wetlands

Based on the above, it is obvious that CW systems possess various and multiple characteristics which attach to this treatment technology an ecological character. They are often characterized as sustainable systems. Low energy consumption and use of natural materials (gravel, soil, sand and plants) are the two main treatment parameters in CWs. One of the largest projects using the wetland technology is the Everglades restoration project, where CWs were used to remove nutrients from agricultural runoff entering the Everglades (Guardo et al., 1995). This project is the largest restoration project in the USA for stormwater treatment and presented in the most emphatic way the sustainable dynamic and treatment capacity of CWs. Similar projects of sustainable design using the wetland technology have been developed for the removal of nonpoint-source pesticide pollution in river catchments (Schulz & Peall, 2001) and diffuse pollution at the catchment scale (Harrington, O'Donovan, & McGrath, 2013), the protection of coastal zone from human activities and pollution in China (Zuo, Wan, Qin, Du, & Wang, 2004), stream restoration (Wang, Gao, Guo, Li, & Zhang, 2012; Palmer, Filoso, & Fanelli, 2014), among others.

However, in order to characterize a technology as "green" there are specific factors which should be met such as effective treatment, robustness, no by-products, recycle/reuse of materials, minimum energy consumption – use of renewable energy sources, minimum/no use of chemicals and minimum environmental nuisance (Brix, 1999). The sustainable character of a treatment system is defined by its economic viability, technical feasibility, environmental protection and social acceptance (SunSanA, 2008). Additionally, it should close the flow cycle of materials, i.e., provide the option for safe reuse of the treated effluents. The approach of sustainable sanitation systems integrates aspects such as public health and hygiene, protection of the environment and natural resources, technological and operational parameters, financial parameters and socio-cultural aspects (SunSanA, 2008; Langergraber, 2013).

Health aspects are of crucial importance since they would determine the level of exposure risk to pathogenic microorganisms and other hazardous compounds. CW systems have been found to be effective in pathogens elimination (Kadlec & Wallace, 2009; Stefanakis et al., 2014). In VFCWs reported elimination rates reach up to 3 logs (i.e., 99.99%) (Stefanakis et al., 2014), while in FWS CWs respectively high rates are reported due to direct UV radiation and disinfection (Kadlec & Wallace, 2009).

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The level of environmental protection and natural resources preservation in CW systems is also high. Effective treatment and high removal efficiencies significantly decrease the pollution load that reaches the final receivers (surface and ground water bodies), thus, limiting the risk for ecosystem and aquatic life degradation. Moreover, the construction of CW systems takes place with natural materials (gravel/sand, plants) which are locally available worldwide and minimum use of synthetic or non-renewable materials takes place. This means that the production and provision of raw materials for CWs construction does not include significant energy-consuming and pollution generating processes. The minimum energy consumption in CW facilities also saves natural resources and minimizes pollution generation, especially when the energy source is non-renewable (e.g., fossil fuels). These environmental benefits can be translated to low levels of greenhouse gas emissions (CO_2, CH_4 and N_2O) (Langergraber, 2013; Stefanakis et al., 2014).

Quantification of these gas emissions for various wastewater treatment methods during both construction and operation phases is important for the estimation of the ecological impact and the global warming potential. Studies report that CW systems have a slightly lower environmental impact during the construction phase compared to other conventional methods (e.g., activated sludge, trickling filters), but a much lower impact for the operation phase (Georges, Thornton, & Sadler, 2009). Life cycle analysis studies on CW systems and comparison with alternative scenarios of using conventional treatment methods have also shown that the global warming potential of CWs is lower in terms of CO_2 emissions (Stefanakis et al., 2014). It is also interesting that in CW systems the major portion of the environmental impact occurs during the construction phase than the operation phase (Dixon, Simon, & Burkitt, 2003; Machado et al., 2007), while in conventional treatment plants the environmental impact of the operational phase is higher than the impact of the construction phase (Dixon et al., 2003; Ortiz, Raluy, Serra, & Uche, 2007; Renou, Thomas, Aoustin, & Pons, 2008; Stefanakis et al., 2014). Among the various CW types, FWS systems produce the lowest CO_2 emissions, VFCWs the lowest CH_4 emissions, while N_2O emissions are reported to be comparable in all CW types (Mander et al., 2014). It should be noted that hybrid CW systems, where different CW types are combined, achieve higher removal efficiencies and minimum greenhouse gas emissions at the same time. The ecological character of CWs is also enhanced by the fact that they promote biodiversity, they provide habitat for various wetland organisms, water savings and multiple hydrological functions (Langergraber, 2013).

Similar results are reported for sludge dewatering in Sludge Treatment Wetlands (Stefanakis et al., 2014). The comparison with conventional centralized facilities such as centrifuges, including all parameters of sludge management (transport, construction, raw materials, energy consumption), has shown that STWs have the lower environmental impact (Uggetti et al., 2011). As for CWs for wastewater treatment, the main impact occurs during the construction phase due to the raw materials used, while respective impact for the operational phase is minimum. If the basin for the CW is simply excavated or recycled concrete is used, when the impact of the construction phase can be reduced. Centrifuges have the highest environmental impact, since their operation requires a high energy input. The contribution of STWs to global warming is negligible. It is reported that the overall environmental impact of Sludge Treatment Wetlands is 500 times lower when compared with centrifugation technique and 2000 times lower compared to sludge transport to a centralized facility (Stefanakis et al., 2014). Moreover, studies have shown that the final sludge product after treatment in STWs (biosolids) is a well stabilized and non-phytotoxic valuable material which is safe for reuse and recycle, e.g., as fertilizer in agriculture (Stefanakis et al., 2011b; Uggetti et al., 2011; Stefanakis & Tsihrintzis, 2012d)

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CW systems are in general easy to build and simple in the design and operation (Kadlec & Wallace, 2009). This facilitates the efficient installation of CW facilities, especially in remote areas. Proper design and construction of a CW system allow it to perform in an effective and reliable manner. Problems such as bed clogging, water runoff from the surface or limited plant development may be caused by inadequate design or construction (Stefanakis et al., 2014). Typical problems such as pump/valve failure may occur in CW systems as in conventional plants (Langergraber, 2013). Increased maintenance time and more advanced skills may be required only in case of more complex CW modifications such as aerated beds.

The economic aspect is also an important factor in order to characterize a treatment method as sustainable. The major costs during the construction phase of CWs are, in general, for the earthworks (excavation and fill of the basin), the filter media to be used as substrates, the plants and the bottom liner (e.g., geomembrane/geotextile) (Kadlec & Wallace, 2009; Stefanakis et al., 2014). Most of items are usually locally available, which can decrease transportation costs, especially for short distances. The liner and mechanological equipment (e.g., pumps) may represent a high portion of the costs if they are to be purchased or imported. Labor costs also vary from country to country. Generally, construction costs of CW facilities are comparable or slightly lower with those of conventional treatment plants (Langergraber, 2013; Stefanakis et al., 2014). For small-scale applications (e.g., up to 1,000 pe) CWs offer an economic advantage in terms of investment but as the population served increases, the investment costs become comparable mainly due to the higher land requirements. However, the main economic benefit of CWs are the significantly reduced costs for operation and maintenance due to lower energy consumption and technical equipment used (Brix, 1999; Dixon et al., 2003; Langergraber, 2013; Stefanakis et al., 2014).

The social aspect of CWs as treatment systems is increasingly enhanced. The green, aesthetical appearance of CW facilities compared to the conventional treatment plants (Fig. 6) makes them more acceptable by the society. Many enterprises (e.g., industries, municipal-private companies) choose the CW technology for the treatment of wastewater produced in their premises as a mean to enhance their green profile and incorporate the CW installation to their corporate social responsibility plan.

Providing Clean Water for Better Health

Being a wastewater treatment technology, the main goal of Constructed Wetland systems is to purify wastewater and provide a final effluent of high quality. Degradation of the natural environment and ecosystems is a result of the various human activities and the respective production and uncontrolled discharge of wastewaters to surface- and groundwater. Wastewater treatment is today an absolutely necessary process not only to protect the natural environment and the habitat, but also to protect human health. Water pollution is an existent threat to human health, since surface water bodies (e.g., rivers, lakes) as well as groundwater and aquifers are used as potable water supplies. Therefore, it is crucial that wastewater generated by the various and multiple human activities is treated and purified prior the final discharge, in order to reduce and eliminate the pollutant load. Under this frame, eco-friendly systems such as Constructed Wetlands play a significant role. Their ability to provide wastewater treatment and sanitation in a sustainable way adds credits to their role in the protection of the ecosystems and human health. The further exploitation of the treatment potential of the Constructed Wetland technology will bring additional benefits for the society, since it will contribute to the issues of human health protection and natural environment conservation without causing an additional environmental impact.

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Figure 6. Typical view of a Constructed Wetland facility.

FUTURE RESEARCH DIRECTIONS

The CW technology is a relatively new technology, although first attempts were made almost 50 years ago. Actual interest and increasing research and applications mainly occurred only during the last 20 years and have been intensified over the last decade. This means that design optimization and basic understanding of the fundamental processes are still under investigation. Currently, there are not widely accepted design guidelines, although some general parameters and assumptions are used by the majority of researchers and engineers. Thus, the challenges in the field of CW technology are to further improve the design of the system and optimize their performance. Design optimization is crucial since it may allow for the decrease of the required surface area or footprint of the wastewater treatment facility. Furthermore, future studies under varying climatic conditions will assist in the development of design guidelines for extended regions. Additionally, the use of CWs for the treatment of more complex water sources such as industrial wastewater is another field of great interest. While it is has been proven that domestic and municipal wastewater can be effectively treated in CWs, recent applications for various industrial wastewater, such as tanneries, textile mills, landfill leachates, olive oil mills etc., reveal the great potential of the CW technology. Also, the development of reliable modeling tools for the performance prediction and design improvement of CWs will be a major step forward. Finally, it is realized that the various economic and environmental benefits of CW technology make them appropriate systems for water sanitation in developing countries, a topic which is expected to be further developed in the near future.

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CONCLUSION

The technology of natural treatment systems and especially of Constructed Wetlands is appearing today as one of the most attractive alternative technologies for wastewater treatment and sludge dewatering. These treatment systems provide multiple economic, environmental, technical and societal benefits over the conventional treatment methods such as activated sludge. Following the decentralized approach, the technology of Constructed Wetlands is particularly appropriate in areas where the implementation of a conventional treatment method is economically infeasible, such as in small-medium settlements and communities, rural, mountainous and remote regions and for onsite treatment for single households or block of flats. Especially for small-scale applications (i.e., up to 1,000 pe), Constructed Wetlands possess significantly lower investment costs. Their main economic advantage comes from their operation phase due to the minimum energy requirements and the low needs for maintenance and personnel. Constructed Wetland systems have been proved to provide very effective treatment of domestic and municipal wastewater. Their overall effectiveness enables their application for various industrial and agro-industrial wastewaters with very promising results. As natural treatment technology, Constructed Wetlands can be characterized as sustainable systems, fulfilling sustainability criteria such as effective sanitation, contribution to public health and hygiene aspects, environmental protection, protection of natural resources, simple, reliable and robust operation and social acceptance. The potential of this treatment technology is today widely recognized and further future expansion of the technology is anticipated in both developed and developing countries.

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KEY TERMS AND DEFINITIONS

BOD: Biochemical Oxygen Demand. An organic pollution indicator which expresses the part of organic pollution which can be removed biologically (using microorganisms).

COD: Chemical Oxygen Demand. An organic pollution indicator which expresses the total organic pollution which can be removed by using a strong oxidant agent.

CH_4: Chemical formula of methane. Atmospheric methane represents one of the greenhouse gases.

N_2O: Chemical formula of nitrous oxide. It is a greenhouse gas and an air pollutant.

Facultative Pond: A pond type of natural systems where wastewater is treated biologically under low oxygen conditions. The wastewater remains in this open-air pond for a prolonged period and then is transferred to the next treatment stages.

HDPE: High-density polyethylene, a material made from petroleum. It is used in the production of geomembranes that cover the bottom of tanks, constructed wetlands etc to prevent leaching of liquids to the groundwater.

Imhoff Tank: A V-shaped tank used as primary treatment for wastewater. Its design aims at the removal of solids and the separation from the liquid wastewater, as also the accumulation of sludge at the bottom.

Landfill Leachate: The liquid which percolates from landfill sites and which contains several contaminants, sometimes toxic chemicals.

Log: Logarithm, the mathematical operation that is the inverse of exponentiation. It is used to express the bacteria removal during wastewater treatment. Thus, 1log removal mean 90% kill of bacteria, 2log 99%, 3log 99.9%, 4log 99.99% etc.

Macrophytes: Aquatic plants that grow in water (or near water sources). Can be emergent, submergent or floating.

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OTC: Oxygen Transfer Capacity. An indicator of the oxygen amount that can be transferred to wastewater with different treatment technologies.

Oxidation Pond: A pond type of natural systems for wastewater treatment. They are large, shallow basins where wastewater is treated through natural processes such as bacterial activity, sunlight and algae. Mechanical aeration can also be used to increase the levels of oxygen required for the treatment processes.

Plug Flow: A flow type of a fluid inside a pipe, where it is assumed that the fluid has a constant velocity across the cross-section of the pipe and no back mixing takes place.

Zeolite Gravity Filter: Filters containing a natural rock (zeolite) which operate with gravity (i.e., the use of pumps is avoided). These filters are used in wastewater treatment to remove pollutants mainly through filtration and other processes.

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Chapter 26
Systems Based on Physical-Chemical Processes:
Nutrient Recovery for Cycle Closure

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ABSTRACT

High strength waste streams, namely rejected water from a wastewater treatment plant, livestock slurry, and agro-food wastewater, are characterized by its high organic matter and nutrient content which favours processes aiming to recover energy and nutrients, instead of removing them. In this regard physical-chemical processes are suitable technologies to attain these objectives. Among others, stripping coupled with absorption, struvite precipitation, membrane separation, and vacuum evaporation, are all physical-chemical processes aiming to concentrate nutrients in a stream that can later be reused as fertilizer. In this chapter the main physical-chemical processes will be defined and described in terms of the objective of each process technique, their theoretical fundamentals, environmental effects (air, water and soil emissions, resource depletion), technical indicators (efficiencies, energy consumption, etc.), and by-product characteristics.

INTRODUCTION

An increasing food demand and the sharpening of agricultural detrimental effects on the environment raise urgent technological challenges. The inadequate nutrient supply, mainly nitrogen (N) and phosphorous (P), that characterizes agricultural practices in most developing countries, lead to soil quality depletion, water bodies and atmosphere pollution (Vitousek et al., 2009; Galloway et al., 2003).

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On the other side, up to about 2-3% of the global energy consumption is ascribed to energy intensive fertilizer production processes (EU-BAT, 2006), with nitrogen fertilizers accounting for about 70% of it (Ramírez and Worrel, 2006). Almost all nitrogen fertilizers are synthesized from ammonia and around 80% of the world production capacity, estimated to be 109 Tg in 2003, is used for this purpose (EU-BAT, 2006). Direct energy requirements for the production of one Mg (tonne) of ammonia are between 40-45 GJ (Ahlgren et al., 2008) with an average cost of 100$ (Erisman et al., 2008). Moreover, fossil fuel use, mainly natural gas, is reported to represent 70-90% of these costs, thus exposing fertilizers and, indirectly, food sectors to international energy price fluctuations and instabilities (EIA, 2009).

Phosphorous, in its turn, is a mining resource with a very limited predicted lifetime; it is said that within the next 100 years it will be completed depleted (Zhang et al., 2015). This fact makes P a geo-strategic resource for most countries. Moreover, P recovery technologies and the subsequent marketing of phosphorous-rich solid products could have important positive environmental implications, as a replacement of inorganic-based P in the fertilizer industry would generate a global warming potential offset via reductions in climate emissions from P mining and production.

Management and technological solutions leading to an increase in nutrient use, and recycling efficiencies within agro-ecosystems, are receiving a renewed interest for their significant potential contribution in reducing fertilizer inputs and nutrient losses. Nevertheless, a development towards bio-base and circular economies is dependent on a more cost-effective nutrient recycling technologies from waste streams.

In this sense, both the quality and marketability of those end and by-products are relevant issues which could contribute to this economic balance. By-products from processing wastewater technologies (namely struvite, ammonia water, concentrates, etc.) are relatively new on the market, and legislations applicable to them are not always clear. Some products are not yet included and market operators are in doubt about their classification and requirements. Furthermore, due to associated logistic challenges, they have a considerably lower market price, even if also linked to market prices for mineral fertilisers (Foged et al., 2011). Besides this, end users are not always sure about the fertilization characteristics and harmlessness of these products; in this sense a lot of information is still missing.

In this chapter the main physical-chemical processes (Table 1) will be defined and described in terms of objectives of the technique, theoretical fundamentals, environmental effects (air, water and soil emissions, resources depletion, etc.), technical indicators (efficiencies, energy consumptions, etc.), side stream and by-products characteristics and destiny/use, etc. A detailed scheme of each technology and specificities for each waste stream application will also be presented.

MECHANICAL SEPARATION TECHNOLOGIES

Mechanical separation can be an effective technique to remove solids from a (semi) liquid stream obtaining a liquid fraction containing soluble components such as mineral nitrogen (N), potassium (K) and other ions, and a solid nutrient-rich fraction containing the majority of the organic matter, including a significant proportion of phosphorus (P) (Jorgensen and Stoumann, 2009). Decanting by gravity or natural settling is usually used to easily obtain these two fractions. However, the long times and large spaces required, makes this technology not always feasible. A quicker separation can be obtained using mechanical separators which are able to reach, at the same time, high removal efficiencies and a thick stream with high dry matter and most of the nutrients.

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Table 1. Main physicochemical process technologies to recover nutrients from wastewater

Physical base technologies	• Mechanical separation technologies	• Sieves • Screw pressing • Filter belt • Decanter centrifuge
	• Membrane filtration	• Nanofiltration • Ultrafiltration • Reverse osmosis • Other emerging technologies
	• Evaporation and Drying	
Chemical base technologies	• MAP (struvite) precipitation	
Physical-Chemical base technologies	• Electrocoagulation	
	• Stripping and Absorption	

Theoretical Fundamentals and Process Description

During the separation process, the distribution of nutrients between the two phases varies widely reflecting the solubility of the different compounds. For example, organic nitrogen is concentrated in the solid phase, while ammonia nitrogen remains at a similar concentration in the liquid phase. Phosphorous compounds, in their turn, are largely removed into the solid fraction, though pH can have a large effect.

Separation efficiencies of these mechanical separators may vary widely, due to the difference in the efficiency of each separator, and because separation efficiencies are affected by the variable physicochemical composition of the streams (Moller et al., 2002)

Most separation processes are either set up to produce concentrated sludge or clarified effluents but rarely both in a single stage operation. Ensuring a clear supernatant is often at the expense of a diluted thick phase; conversely, achieving a concentrate filter cake compromises the clarification process. If both are required, then a multistage process is needed (Burton and Turner, 2003).

The performance of a separation process is often quoted as the simple ratio of the mass of a given component in the solid or concentrated phase divided by the presence of that same component in the feed stream (Equation 1). However, it should be considered that any separation process is also a method of dividing a stream. In this regard, if the apparent removal of a given component is of 25%, but the concentrate stream represents 25% of the original volume, this equates to a non-effective separation (Burton, 2007). Martinez et al. (1995) aiming to incorporate this issue, defined efficiency in more meaningful terms (Equation 2);

$$\eta = (S \times X_s / X_f \times F) \times 100 \quad (1)$$

$$\eta = S/F(X_s/X_f - 1) \times 100 \quad (2)$$

Where η is efficiency, S is the concentrate solid stream (m^3/h), F is the feed stream (m^3/h), X_s is the concentration of a given component in S (kg/m^3), and X_f is the concentration of the same component in F (kg/m^3).

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Similarly, Moller et al. (2000) proposed a reduced separation efficiency index; where an index value of 0 indicates that the nutrients are distributed equally between the solid fraction and the liquid fraction, and a value of 1 indicates that all the nutrients are concentrated in the solid fraction.

However, the simple ratio of the mass balance is the efficiency index most commonly used.

Usual Applications, Equipments, and Environmental Aspects

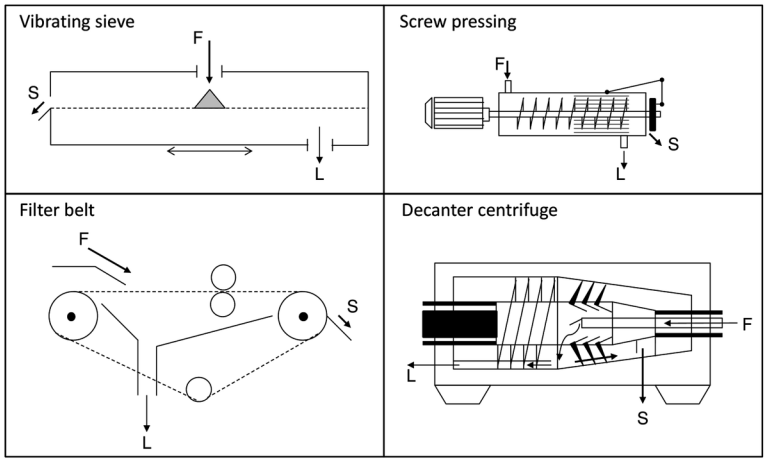
Mechanical separators are usually applied for the processing of streams with high un-dissolved solid content, namely livestock manure, sewage sludge whether raw or digested, agro-food wastewater, etc., and it is almost always a necessary first step if a further recovery technology is to be later applied.

The total solid content of a liquid stream is divided, in general terms, between those solids dissolved and those present as suspended matter. Beyond this, a useful division of the suspended matter can be made to outline the performance of the main groups of separating equipment available (Figure 1). The selection of one or another depends not only on the composition of the feed but on the final aim of the required processing technology (e.g. maximize nutrient recovery in the dry solid fraction, obtaining a liquid fraction without suspended solids, etc.).

There are different mechanical separators, the more common ones are described below (Flotats et al., 2011):

- **Sieves:** It consists of a screen of a specific pore size which allows solid particles smaller in size than the openings to pass through. The liquid flows through the screen and is drained off. There is a compromise between sieve size, separation performance, and risk of clogging. Sieve separators may be static or vibrant. Indeed, sieve clogging is one of the most common problems of static screens. Such risk is diminished in vibrant sieves due to vibration. If the flow is too high, a large amount of water can remain in the solid fraction.

Figure 1. Common mechanical separator equipments (F: feed, L: Liquid phase, S: Solid phase) (Adapted from Moller et al., 2000, Burton and Turner, 2003)



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- **Screw Pressing:** This is a process consisting in the application of pressure in order to separate the suspended and dissolved solids contained in a (semi) liquid, by filtration. The material to be separated enters into a cylindrical 0.5-1 mm screen by means of a screw. The liquid passes through the screen and is collected in a container surrounding the screen. At the end of the axle, the dry matter-rich fraction is pressed against a plate. The filter cake is compressed during pressure filtration, ensuring that the screw press produces a solid fraction with high dry matter content.
- **Filter Belt:** The filter belt separator also applies pressure to achieve separation. In this case the band filter is constantly turning on rollers to keep the material moving and to increase pressure on the material, whereby the liquid part will pass through the filter. The filter cake is continuously removed as the belt rotates, so that the loading and solid-fraction unloading areas are being constantly cleaned and changed over.
- **Decanter Centrifuge:** In decanter centrifuges, a centrifugal force is generated to cause the separation of solids from the liquid. There are two types of decanter centrifuges: vertical and horizontal. A horizontal decanter centrifuge uses a closed cylinder with a continuous turning motion (3000-4000 rpm). The centrifugal force separates solids and liquids at the wall, into an inner layer with a high dry matter concentration and an outer layer consisting of a liquid containing a suspension of colloids, organic components and salts. The solid and liquid phases are transported to either end of the centrifuge rotating the entire centrifuge at high speed and simultaneously rotating the conveyor at a speed slightly differing from the speed of the bowl (outer conical shell) (Flotats et al., 2011). The vertical decanter is designed and built primarily for high-temperature and/or pressurized operation. The vertical orientation lends itself to better and more reliable pressurization, with only one end to be provided with rotational seals. The amount of engineering required for pressurization and sealing makes the vertical decanters more expensive than the non-pressurised and open horizontal decanter. The availability of inexpensive vertical decanters is very limited, such that in some circumstances one has to select horizontal model even though a vertical one might have been preferred (Records and Sutherland, 2001).

Regarding possible environmental issues, some systems involve a high exposition of slurry to atmosphere, and thus, entail a risk of gaseous emissions in the form of volatile organic compounds (VOC) and/or NH_3, and odour problems. Nevertheless, this technology cannot be considered to have large environmental impacts.

Nutrient Recovery by Mechanical Separation Technologies

As mentioned, nutrient recovery efficiency in the thick fraction is dependent on the characteristics of the equipment, the composition of the liquid stream and the use of additives such as coagulant-flocculants or polyelectrolytes. The separation efficiency for removal of dry matter and phosphorus (P) is ranked as follows: centrifugation> sedimentation> non-pressurized filtration> pressurized filtration. In general, total separation of N and NH_4^+ follows the same pattern, but separation efficiencies are lower than for dry matter and P (Hjorth, et al., 2009).

In Table 2, a summary of the efficiencies of the different devices applied on livestock slurry is shown.

As can be observed, the range of efficiencies is quite wide, corresponding to a great variability in composition of this kind of streams and the adjustment of the different equipment.

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Table 2. Efficiency of different mechanical separators with livestock manure (adapted from Campos et al. 2004)

	Efficiency (%)[1]			
Mechanical Separator	**Dry Matter**	**COD**	**Nitrogen**	**Phosphorus**
Static sieve	0-40	0-40	0-10	0-10
Vibrant sieve	0-40	0-50	0-10	0-30
Filter belt	10-60	30-60	10-40	20-80
Screw pressing	20-60	30-60	10-40	30-80
Decanter centrifuge	20-60	30-60	10-40	40-80

[1]% of the component removed from the feed stream

By-Products Characteristics and Economics Aspects

The characteristics of solid and liquid fractions resulting from mechanical separators mainly depend on the separation technique and it can be assumed as well, that the availability of nutrients for the plants can be also affected (Fangueiro et al., 2015). Furthermore, the inclusion of a previous process (e.g. anaerobic digestion or acidification) will also have a great influence over nutrient speciation, removal efficiencies and the characteristics of the two streams obtained (Moller, et al., 2000; Fangueiro et al., 2009).

The two fractions obtained with different organic matter, nutrient and ion composition should be further processed and/or used as fertilizers if an appropriate management is applied. The liquid phase is usually processed to further recover nutrients or remove them, e.g. reject water from sludge dehydrating is usually returned to the head of the WWTP; on the contrary, the liquid fraction of livestock manure is often used directly as fertilizer. The solid fraction can be used directly as fertilizer; but before usage, it is preferable to stabilize the organic matter, for example by means of composting.

Investment and operational costs of these technologies vary a lot depending on the equipment and the use of additives or not. Investment costs range between 10.000 € for sieves and 150.000 € for a decanter centrifuge. Operational costs are most influenced by the use of additives. In this case, it moves between 1.5 €/t and 3 €/t when using polyelectrolyte additives (Flotats et al., 2011).

MEMBRANE FILTRATION

Membrane technology is a physical process for the separation of material mixtures in which a membrane acts as a filter, and the separated substances are neither thermally nor chemically nor biologically modified. This technology has grown in recent years due to growing concerns about water quality and pollution trends in relation to more complex global challenges such as rapid urbanization, increasing water demands in the domestic and industrial sectors, and problems associated with surplus nutrients in areas with high livestock density. In the last case, it could be partly solved by the use of membrane technology to concentrate manure nutrients in small volumes that could be exported as fertilizers to other agricultural regions. Membrane filtration offers concrete benefits in the production processes, such as the significant reduction in equipment size, efficiency boosting, energy savings, capital costs reduction, environmental impacts minimization, safety increase, and remote control and automation usage.

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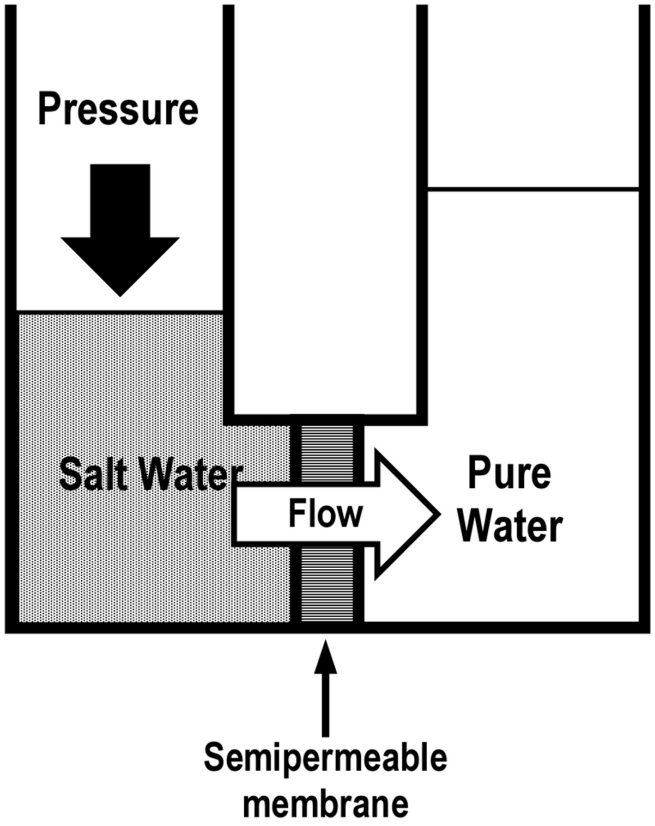
Theoretical Fundamentals and Process Description

Membranes are typically classified depending on their pore size, applied pressure, molecular weight cut-off, and permeability (Table 3). The commonly accepted classification in the field of water and wastewater treatment includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Depending on wastewater composition and characteristics, as well as operational requirements, different materials are used for membranes. Membrane materials can be organic (e.g. cellulose or polymer membranes) or inorganic (e.g. ceramic or metal membranes). Compared to organic membranes, the advantages of inorganic ones are a high resistance against heat and chemicals with, correspondingly, a high regeneration capacity, as well as a long service life. Disadvantages are, above all, the higher investment due to the membrane material, and more expensive module constructions (Sadr and Saroj, 2015). Figure 2 shows a schematic diagram of the reverse osmosis process.

From a structural point of view, they can be symmetric (isotropic) or asymmetric (anisotropic). Symmetric membranes have a uniform composition and structure throughout; such membranes can be either porous or dense. Asymmetric membranes, on the other hand, consist of a number of layers, each with different structure and permeability properties. A typical asymmetric membrane has a relatively dense thin surface layer supported on an open, much thicker, microporous substrate. The surface layer performs the separation and is the principal flow barrier through the membrane. The open support layer

Figure 2. Schematic diagram of the reverse osmosis process



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provides mechanical strength. Inorganic membranes can be either isotropic or anisotropic (Pinnekamp and Friedrich, 2006). The most important property of membranes is their ability to control the permeation rate of different species based on two main models (Table 3):

1. The solution-diffusion model, in which permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. The permeants are separated because of the differences in solubility of the materials in the membrane and the differences in the rates at which the materials diffuse through the membrane (NF, RO); and
2. The pore-flow model, in which permeants are transported by a pressure-driven convective flow through tiny pores. Separation occurs because one of the permeants is excluded (filtered) from some of the pores in the membrane, through which other permeants move on (MF, UF) (Baker, 2004).

Coarser membranes are associated with MF and the most selective membranes are associated with RO processes. Generally, suspended solids (including large microorganisms like protozoa and bacteria) are easily separated by MF whereas UF is used to remove particles down to size of around 20 nm. Moreover, NF is able to retain smaller organics and multivalent ions and RO is capable to remove all dissolved species (Table 3).

Often, membrane technologies are employed in a combination of physical, chemical, and biological processes, resulting in an efficient process configuration for a particular scenario of wastewater or waste treatment. For example, MBR technology combines activated sludge processes, or an anaerobic biodegradation process with MF, UF or RO.

Table 3. Membrane processes classification and operational conditions

Model	Membrane Process	Pore Size (μm)	Size of the Particles, Colloids, or Molecules to be Separated	Driving Force (Pressure Difference, Bar)	Application
Pore-flow	Microfiltration	0.1-5	Solids > 0.1 μm	0.1-3	Separation of solid matter from suspensions
Pore-flow	Ultrafiltration	0.005-0.1	200,000 – 20,000 D*	0.5-10	Separation of macromolecules or colloids, disinfection
Solution-diffusion	Nanofiltration	0.001-0.01	20,000 – 200 D*	2-40	Separation of dissolved organic molecules and polyvalent inorganic ions
Solution-diffusion	Reverse Osmosis	0.0001-0.001	< 200 D*	5-70 In special cases up to 120 bar	Separation of organic molecules and all of ions

*Dalton, numerically equivalent to the molecular weight in g/mol
(Modified from Pinnekamp and Friedrich, 2006)

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Usual Applications and Environmental Aspects

Although membrane technology was initially used almost exclusively for the desalination of sea and brackish water in arid zones, it has been tested and lately also applied for the separation of valuable materials from small water volumes and other waste streams: in biotechnology, in pharmaceutical and chemistry industries, in the metal-working industry, in the food and beverage industry, and in high strength wastewater such as livestock slurries. Specific applications of membrane processes for wastewater treatment are summarized in Table 4.

Due to its small footprint, flexible design and automated operation, membranes are a suitable option in developing countries for decentralized wastewater treatment and the extraction of valuable resources such as nutrients and energy.

Nutrient Recovery by Membrane Processes

High-rejection membrane processes such as NF and RO have demonstrated huge potential in wastewater nutrient recovery. RO has been applied for urine concentration in a source-separation toilet system, achieving a concentration factor of five and high concentrations of ammonium, phosphate and potassium (Maurer et al., 2006). NF separation also exhibited a medium to high rejection of a range of nutrients, such as urea (Pronk et al., 2006), ammonium, phosphate and potassium (Niewersch et al., 2014, Schütte et al., 2015). Häyrynen et al. (2009) studied the concentration of ammonium and nitrate in mine water by RO and NF membrane processes achieving retentions up to 96% for nitrate and 91% for ammonium. Retention of ammonium by NF membrane was 56.2% in this case.

Table 4. Membrane processes application in municipal and industrial wastewater treatments

Membrane	Municipal Wastewater Treatment	Industrial Wastewater Treatment
Micro and ultrafiltration	• Separation of activated sludge and water • Disinfection • Pre-treatment prior to a reverse osmosis plant • Phosphate removal after precipitation	• Waste water recycling and reuse as process water for different purposes • Treatment of landfill leachate combined with a biological stage • Recovery of water-based paint from spray booth effluents by concentration • E.g. in the metal-working industry: - Prolongation of the service life of electro-dipcoat bathes - Concentration of water-oil emulsions - Recycling of degreasing baths
Nanofiltration	• For further treatment after biological methods for wastewater reuse (few cases)	• Relief of ions exchangers downstream reverse osmosis units • Removal of color in the wastewater of the textile and the pulp and paper industry • Demineralization of wastewater containing surfactants
Reverse Osmosis	• For further treatment after biological methods for wastewater reuse (few cases)	• Concentration of drainage water from mines containing $CaSO_4$ • Dewatering of flushing water from photo laboratories for silver recovery • Treatment of waste water from textiles dyeing (cotton and polyester dyeing) • Concentration of cellulose washing water • Recovery of phosphoric acid • Treatment of wastewater from bleacheries • Treatment of landfill leachate • Treatment of livestock slurries

(Modified from Pinnekamp and Friedrich, 2006)

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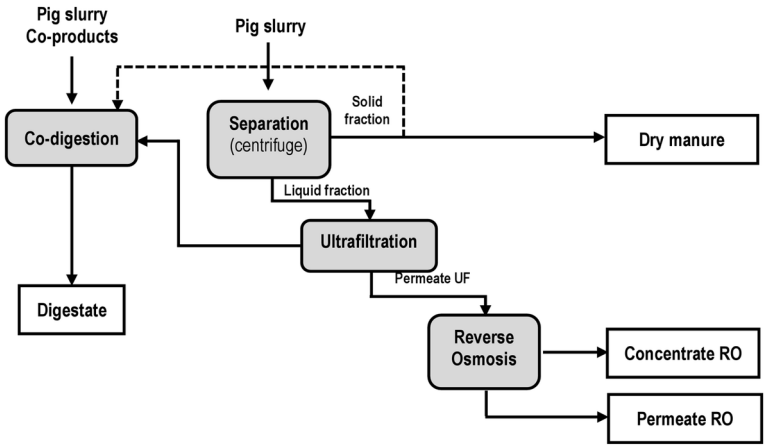
For manure nutrient recovery, ammonia and potassium retention requires NF or RO, which have demonstrated a very good performance, whereas MF and UF membranes basically act as very efficient solid-liquid separators that can isolate nutrients associated with particles such as phosphorus (Masse et al., 2007). Konieczny et al. (2011) recovered water from pig slurry utilizing an integrated system consisting of centrifugation followed by a two-step UF followed by NF. However, the amount of ammonium in the produced water was too high, resulting in regenerated water suitable for irrigation. Guo and Jin (2014) investigated anaerobically digested cattle manure treatments with RO pre-treated by UF. It was observed that ammonia was rejected with a rate of 77.1% at the first pass and only 54.2% at the second pass, most probably due to the pH increase in the RO feed. However, the concentration of NH_4^+ in the final permeate was around 63 mg/L from the initial 836 mg/L. Rejection of other species such as K, Na and Cl was observed to be as high as 90%. Beyond laboratory experiences, RO has been applied in several pilot experiences at manure treatment plants to separate the liquid manure fraction into water that can be discharged and a concentrated salt solution, the so-called mineral concentrate (Velthof, 2011).

Fouling of the membranes by deposition of salts and the growth of microorganisms is one of the main problems when using reverse osmosis of the liquid fraction of slurry. Fouling of NF and RO membranes impairs membrane performance and shortens the membrane lifetime, thereby restraining productivity in nutrient recovery. Therefore, in reverse osmosis solids and organic matter should be previously removed as much as possible from the liquid fraction. This includes techniques such as UF, dissolved air flotation, low pressure membrane filtration and using cloth or paper filters, resulting in process flowcharts as the one showed in Figure 3. Thus, although the use of reverse osmosis for nutrient concentration and manure treatment is technically feasible with the proper pre-treatment, the steep maintenance and operation cost is the main hindrance to the application of this technology in the livestock manure sector.

By-Products Characteristics and Economics Aspects

The typology and characteristics of end and by-products obtained in a processing plant including a membrane process depends on the process flowchart but, in general, there are three effluents: solid fraction, concentrate and permeate.

Figure 3. Treatment scheme of a manure treatment plant located in The Netherlands
(Modified from Velthof, 2011)



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The composition of the solid fraction is largely dependent on the separation technique, which leads to differences in the moisture content and, thus, to differences in nutrient contents of the solid fraction. This fraction contains most of the suspended solids, the organic matter and phosphorous. The levels of ammonium and potassium are largely determined by the levels of these nutrients in the untreated slurry. The composition of concentrates presents large differences depending on the processing plant, but in general, it can be said that they have a high content of N and K and low concentrations of P, as compared with the untreated slurry. The low content of organics could be classified as a mineral fertilizer. Finally, the permeate characteristics enable its direct discharge.

Based on the study carried out by Velthof (2011), the economic viability of plants treating animal slurry and other high strength streams with reverse osmosis heavily depends on the kind of slurry separator, mineral fertilizer prices, the price received from the providers of slurry, the prices of end products and of competitive products from slurry and fertilizers.

For example, the cost of the reverse osmosis installation unit is on average 7 to 8 € per ton of slurry treated. This applies to a lifespan of 10 years. The variability of the end products (low or high water content, much or little solid fraction) significantly affects profitability. Other factors affecting profitability are the further treatment of the solid fraction and the digestion of slurry. When the price paid by the providers of slurry is around 15 € per ton, or higher, plants are profitable. As a general practice in Europe, the costs of transport to the plant, weighing and sampling of the slurry are paid by the slurry supplier.

Emerging Technologies for Nutrient Recovery by Membrane-Based Processes

Forward osmosis, membrane distillation and electrodialysis are three emerging membrane-based processes considered suitable to overcome the challenges in nutrient recovery, which could potentially represent a paradigm shift in nutrient management:

Forward Osmosis (FO)

FO is a membrane operation developed from a natural process occurring in plants and human bodies. In FO, a semipermeable membrane is placed between two solutions of different concentrations: a concentrated draw solution and a more diluted feed solution. The driving force of the process is the chemical potential difference across the membrane which forces the water to flow from the low to high concentrated compartment, i.e. instead of hydraulic pressure; FO employs an osmotic pressure difference to drive the permeation of water across the membrane. In comparison with pressure-driven RO membrane filtration, FO has demonstrated a lower fouling propensity and a higher fouling reversibility (Blandin et al., 2016); also, a high rejection of phosphate and ammonium from activated sludge and wastewater by FO membranes has been reported (Huang et al., 2015; Xie et al., 2016). Moreover, FO has the potential to concentrate phosphate, ammonium, and magnesium in the source solution to facilitate struvite recovery due to the lack of hydraulic pressure and the occurrence of a reverse draw solute flux. These unique mass transfer properties of FO impel nutrient recovery from various waste streams such as urine, sewage, and sludge (Xie et al., 2016). Figure 4 shows a schematic diagram of the forward osmosis process.

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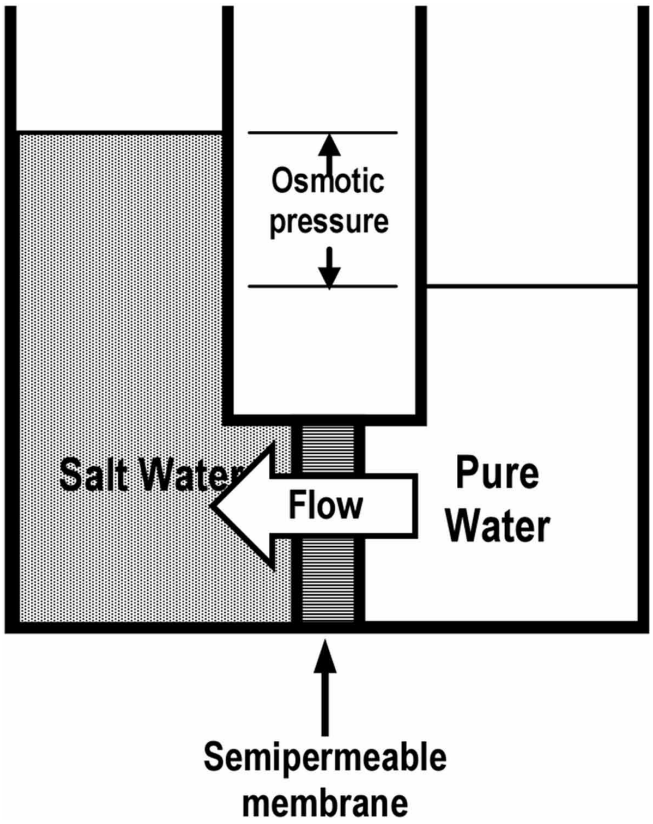
Membrane Distillation (MD)

MD using gas-permeable membranes (GPM) is another prominent technique, which is not yet completely commercialized. Its transport mechanism is based on the volatility and vapour pressure of the compounds to be separated. These components can be concentrated either in the feed stream or the permeate streams. For example, non-volatile inorganic nutrient ions, such as potassium and phosphate, can be concentrated in the feed stream to facilitate subsequent nutrient precipitation (Quist-Jensen et al., 2015). Ammonia recovery can be another important application of a GPM process in wastewater nutrient recovery. Dissolved ammonia (NH_3) can cross through the micro-porous hydrophobic membrane and concentrate in an absorption solution on the other side of the membrane. The membrane is submerged in the liquid and the NH_3 is removed from the liquid before it escapes into the air; NH_3 permeates through the hydrophobic membrane reaching the acidic solution located on the other side of the membrane. Once in the acidic solution, NH_3 combines with free protons to form non-volatile NH_4^+ ions that are converted into a valuable ammonium salt fertilizer $(NH_4)_2SO_4$, (Garcia-González and Vanotti, 2015). These MD processes achieved more than 96% in ammonia recovery in the form of aqueous solution.

MD offers a number of advantages over alternative pressure-driven processes such as reverse osmosis. As the process is driven by temperature gradients, low-grade waste heat can be used, and expensive high-pressure pumps are not required. Membrane fluxes are comparable to reverse osmosis fluxes, so

Figure 4. Schematic diagram of the forward osmosis process



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membrane areas are not excessive. Finally, the process is still effective with slightly reduced fluxes even with very concentrated solutions. This is an advantage over reverse osmosis, in which the feed solution osmotic pressure places a practical limit on the concentration of a salt in the feed solution to be processed (Baker, 2004).

Besides, gas-permeable membrane processes can be combined with other treatment technologies such as anaerobic digestion to improve their performance. The inhibition of methanogens by high NH_3 concentrations in manure severely inhibits the production of biogas. Hence, the use of gas-permeable membranes to recover NH_3 without damaging the carbonaceous material will improve the process.

One of the most innovative applications of gas-permeable membranes is its use coupled to bio-electrochemical systems (BES) with the objective of recovering ammonia from the anolyte without using energy-intensive stripping of the catholyte. NH_4^+ migration across a cation exchange membrane to maintain the charge balance, leads to a pH increase in the catholyte (pH >10) (Sotres et al., 2014), whence NH_3 can be recovered in an acidic solution using a hydrophobic membrane (Cheng et al., 2013).

Electrodialysis (ED)

ED is an electro-membrane process, in which ions are transported through ion exchange membranes from one solution to another under the influence of a potential gradient. The electrical charges on the ions allow them to be driven through the membranes. Charging a voltage between two end electrodes generates the potential field required. As the ion exchange membrane has the ability to selectively transport ions with a positive or negative charge and to reject ions of the opposite charge, the useful concentration, removal or separation of electrolytes can be achieved. Therefore, it is possible that the excess nitrogen and phosphorus, which are found as ions in nutrient-rich streams such as swine liquid fraction, can be removed by this technique (Fukumoto and Haga, 2004). The ion separation is attained by ion-exchange membranes that include cation-selective, anion-selective, and bipolar membranes.

The mechanism of an ED process provides a selective tool for wastewater nutrient recovery. ED processes selectively partition phosphate from nutrient-rich streams containing various ions as a concentrated phosphate solution, achieving a concentration factor of up to 7. Similar selective phosphate enrichments by ED processes were also observed in urine nutrient recovery, resulting in a purified phosphate concentrate (Pronk et al., 2006). Phosphate selectivity in an ED process can be further enhanced by either adjusting the feed stream to the alkaline pH range or increasing current density. Better performance was expected based on the ED separation mechanism, where multivalent phosphate migrates more slowly than monovalent ions under the current field (Xie et al., 2016).

EVAPORATION AND DRYING

The aim of evaporation and drying is to vaporize (applying heat) most of the water from a solution obtaining a concentrate that contains a desired product (in this case nutrients and organic matter). Apart from obtaining a concentrate with a lower water content and higher nutrient concentration than the original solution, another objective should be to obtain a purified condensate (water) that could be later reused (Bonmatí et al., 2003).

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Theoretical Fundamentals and Process Description

Evaporation could be performed at atmospheric pressure or under vacuum conditions. Vacuum evaporation is more common as the lower temperature for the process and the closed vessel used allow for a better emission control and an expected less energy consumption. When the pressure inside the evaporator unit is reduced below the vapour pressure of the liquid, the liquid evaporates and the consequent concentration of the treated substrate occurs; evaporated water, then, is condensed by cooling and collected in the condensate tank (Figure 5a) (Chiumenti et al., 2013).

One limitation of evaporators is that they only work with fluids. Grüter *et al*. (1990) defined three different zones of sludge consistency in a dryer: a wet zone where the sludge is free-flowing, a sticky zone where the sludge is pasty, and a granular zone where the sludge is crumbly. This constitutes a limit to the final concentration: slurry cannot be converted into a completely dry product. The limit is about 20–25% TS, depending on the corrosion and viscosity of the concentrate. Prior removal of suspended solids is also necessary. Should this not be done, concentration would be limited as the particles form a matrix and the concentrate ceases to be a flowing liquid (Have and Chiappini, 1993). A further drying process is necessary to increase the dry matter concentration.

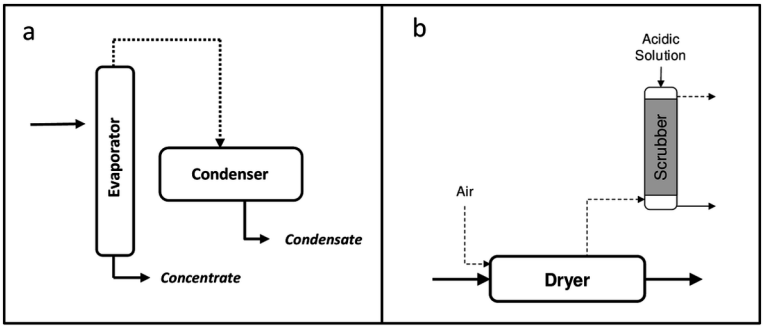
Drying works under the same principle, but in this case, the inflow is the solid fraction of a centrifuged slurry/sludge or the concentrate of an evaporation process. Most of the water (>85%) is removed applying heat, the concentrate reaching dry matter values >90%. In order to avoid the sludge sticky zone, dryers work in the granular zone (>60-65% of TS) where the concentrate is crumbly.

The dried product is often pelletized to increase its added value as fertilizer, pushing it through the holes of a matrix of the desired shape/size. Compression and temperature, as well as the composition of the raw material are the major factors affecting the process.

General Applications and Environmental Aspects

This technology is mainly implemented in the field of the treatment of residuals from industrial production, in some cases with the aim of recovering chemicals, like, for example, in the galvanic industry. Vacuum evaporation has been applied for years also for the treatment of landfill leachate. In the agro-industry sector, this technology has been tested on the dairy industry, for the recovery of proteins from serum, in the olive oil industry, for the treatment of wastewater from mills and olive husks. Other tests

Figure 5. Schematic diagram of the vacuum evaporation process (a) and drying process (b) (adapted from Flotats et al., 2011)



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have been performed on residues from the production of wood pulp and paper (Chiumenti et al., 2013). Regarding livestock manures, evaporation has been applied for processing pig slurry and the digestate from the co-digestion of biogas plants (Flotats et al., 2009). Although this process is applied usually at a large scale, there are some proposals for implanting it at a farm scale (Levasseur, 2004).

The increase in temperature causes the emission of several volatile compounds that can be present in the slurry leading to serious atmospheric pollution. Vacuum evaporation minimizes this effect since it occurs in closed systems, at lower temperature, and the exhausted gases can be easily treated. Considering its effects on air, water and soils, the process theoretically does not show air emissions, since the evaporated flow is recovered as a condensate. Thus, theoretically, this is a '0 gas emissions' process, including odours.

Adversely, drying is not usually operated in vacuum conditions and hence, all gaseous emissions from the dryer must be recovered (by filtration or scrubbing) to avoid ammonia (NH_3), organic volatiles (VOC) and odour emissions (Figure 5b).

Nutrient Recovery by Evaporation

To ensure the recovery of nitrogen in the concentrate flow steam, and guarantee its absence in the recovered condensates, the ammonia (NH_3)-ammonium (NH_4^+) equilibrium must be modified, by means of pH control (usually adding a strong acid). If pH inside the evaporator is maintained under pH 5.5 it is guaranteed that ammonium will be recovered in the concentrate. Adversely, at this pH values, other volatile organics such as volatile fatty acids (VFA) are present in its un-ionized form (volatile) and can be easily transferred to the condensate, with manifest implications (organic contamination) in the condensate and post-treatment requirements.

Theoretical studies performed by Marks *et al*. (1994) showed that at pH=4, 1% of ammonia and 75% of acetic acid are transferred to the condensate and that, at pH=10, 93% of ammonia and 1% of acetic acid are transferred. This demonstrated that if a liquid has a high ammonia nitrogen and VFA content, it is not possible to prevent the volatilization of both components by adjusting its pH to a given value. A two-stage evaporation process or a previous treatment is necessary to achieve this. Furthermore, the non-ionized volatile organic compounds (VOCs) cannot be fixed by modifying pH. A previous treatment (i.e. stripping or anaerobic digestion) to remove VOCs is necessary in order to prevent their emissions during evaporation (Bonmatí, 2001).

For pH regulation, sulphuric acid or other strong acid should be added (Bonmatí et al., 2003). The acid consumption will depend on the slurry alkalinity. Reagents do not need to be reagent-grade. Consequently, in some applications H_2SO_4 sub-products of low purity have been used.

As it has been mentioned, the processed stream requires a previous acidification step to avoid ammonia emissions. The use of a strong acid has different implications:

- The choice of constructive materials (resistance to high temperature and low pH) which requires high quality materials (e.g. stainless steel).
- Risk of accidents and the requirement of Health and Safety training courses for the workers.
- Introduction of S forms (if acidification is performed with H_2SO_4) which could later appear (at low concentrations) in the condensates.

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By-Products Characteristics and Economics Aspects

Two by-products are obtained in this process, the concentrate and the condensate. If the process is operated correctly, the concentrate will contain most of the nutrients. Phosphorous and potassium will remain in the concentrate, and, as mentioned, if pH is set below 5.5 the majority of nitrogen will also be found in the concentrate. Likewise, if heavy metals are present in the raw manure, they will be found in the concentrate stream and, depending of their concentration, could compromise the use of the concentrate as a fertilizer.

On the other hand, condensates may be free of nutrients but can contain remarkable amounts of organic matter, as the low pH process will favour the volatilization of VOC which will later be transferred to the condensate. A previous process to remove VOC, such as stripping or anaerobic digestion, is a possible way to obtain a cleaner condensate (Bonmatí and Flotats, 2003).

In terms of energy consumption, 21 kWh/m^3 of electric energy and between 107 and 353 kWh/m^3 of heat have been obtained in a pilot experience at a farm scale unit treating 0.5 m^3/hour (Flotats et al., 2011). On the other hand, the increasing number of evaporation steps could significantly decrease energy consumption. For this reason a full scale evaporation system usually consists in at least two steps. Energy consumption in single-effect evaporators is very high and makes up for most of the cost of the evaporation system. Each evaporation step added reduces the energy consumption by 33%; although investment costs increase.

However, with clearly different evaporator designs, the process could be attractive for slurries/manures with high dry matter content, especially over 30% (e.g. poultry) due to the smaller volume of water to be removed and the higher yields of dry product (Burton and Turner, 2003). In this regard, the use of the residual energy from a CHP engine or other processes could be a way to make this process feasible.

MAGNESIUM AMMONIUM PHOSPHATE (STRUVITE) PRECIPITATION

Typically, P in wastewater is removed biologically, using P- accumulating bacteria, or chemically, through precipitation by adding metal salts. Chemical precipitation introduces high costs and yields a large amount of chemical sludge to dispose of. Another option to recover nutrients is to create the physical-chemical conditions in the bulk solution (pH, ion strength, etc.) to favour the formation of different salts with low solubility products, and its subsequent precipitation to recover them. Among others, magnesium ammonium phosphate (MAP), usually called struvite, is the most common salt enabling the recovery of phosphorous and nitrogen from wastewaters.

Theoretical Fundamentals of Map Formation

Struvite is a white crystalline substance composed of nitrogen (ammonia, NH_4^+), phosphorus (phosphate, PO_4^{3-}) and magnesium (Mg^{2+}) in equimolar relation ($MgNH_4PO_4 \cdot 6H_2O$), also called MAP (Magnesium Ammonium Phosphate), which is considered as a slow releasing and valuable fertilizer, as it is sparingly soluble under neutral and alkaline conditions but readily soluble in acid (Yetilmezsoy & Sapci-Zengin, 2009).

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Struvite precipitation is produced in alkaline conditions when the concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} exceeds the solubility product, according to the following reaction (3):

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6\,H_2O \rightarrow MgNH_4PO_4 \cdot 6\,H_2O + 2H^+ \quad (3)$$

Struvite crystal development occurs in two chemical phases: nucleation and crystal growth. In the nucleation phase, ions are arranged in the characteristic pattern of a crystalline solid, forming foundation sites for deposition of crystallizing particles which then grow into detectable crystals (Ohlinger et al., 1999).

A combination of physical and chemical parameters controls the complex mechanism of struvite precipitation. One of the main factors is pH, as it changes the concentration of free ions available for reaction. When pH increases, Mg^{2+} and NH_4^+ concentrations decrease, as the first one complexes with hydroxides, and the second one increases its volatilization in the form of ammonia (NH_3). On the other hand, PO_4^{3-} concentrations increase as the pH increases. pH is also involved in controlling struvite solubility, being minimal with pH values between 9 and 10.7 (Doyle and Parsons, 2002). So, pH is usually increased to favour struvite precipitation, generally using NaOH or $Mg(OH)_2$. Alternatively, CO_2 stripping can be used to reduce the use of alkali (Cerrillo et al., 2015) for, when CO_2 is liberated from solution, the change in carbonate speciation leads to a pH increase.

The molar ratio of N, Mg, and P can limit the precipitation process if one of the components is lacking in the wastewater, as can be the case of magnesium in wastewaters from anthropogenic, livestock or municipal leachate, where it may be necessary to be added in order to optimize the struvite crystallization process. Low contents of soluble phosphate in the wastewater may require a prior solubilization process and, in some cases, the solids content of the influent can slow down the struvite precipitation process (Tao et al., 2016).

The reactor design (agitation and sedimentation properties) influences the size of the obtained crystals and the easiness to recover them, as fine struvite crystals are difficult to settle or separate. The size of the aggregates influence notably in the economic value of the product. The typical struvite precipitation reactor consists in a mixed crystallization reactor with two zones. The lower zone is the reaction zone, and the upper section is the sedimentation zone, which prevents the formed particles to leave the reactor (Figure 6). The reactor could also include an aeration system to favour CO_2 stripping and pH increase, and prevent mechanical mixing (Cerrillo et al., 2015). The process temperature needs to be taken into account as it influences the solubility of the salts: low or ambient temperatures are preferable as maximum solubility of struvite is attained at 50 ºC (Doyle and Parsons, 2002).

Finally, the ionic strength of competitive cations, such as Ca^{2+} and Na^+ that can form other salts, especially with phosphates, as newberyite ($MgHPO_4 \cdot 3H_2O$), bobierrite ($Mg_3(PO_4)_2 \cdot 8H_2O$) or hydroxiapatite ($Ca_5(PO_4)_3OH$) can hinder struvite obtainment (Cerrillo et al., 2015). Even depending on the relative concentrations of Ca^{2+} and Na^+, struvite formation may be inhibited (Doyle & Parsons, 2002; Moerman et al., 2009).

The analysis of the thermodynamics equilibrium and kinetics reaction can help to predict and explain the formation of struvite in different conditions (Crutchik and Garrido, 2016). However, industrial wastewater can be a complex matrix containing various compounds which might interfere with struvite precipitation, its quality as a fertiliser, and the length and shape of the crystals, as impurities block active growth sites by adsorption to crystal surfaces and inhibit crystal growth (Le Corre et al., 2009), leading to

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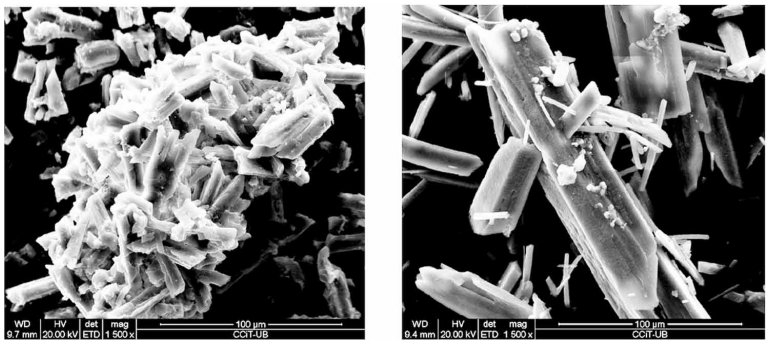
Figure 6. Lab scale struvite precipitation reactor (left), and pilot plant at SAT Sant Mer Biogas Plant (Vilademuls, Girona) (right)

a possible necessary detailed study for each wastewater. As an example, Figure 7 shows struvite crystals obtained with the liquid fraction of pig slurry and the crystals formed with synthetic water applying the same operational conditions.

Usual Applications and Environmental Aspects

Struvite precipitation technology has been studied and applied to different wastewaters, as food industry wastewater (Moerman et al., 2009), dairy manure (Uludag-Demirer et al., 2008), poultry manure (Yetilmezsoy and Sapci-Zengin, 2009), digested pig and cow slurry (Huang et al., 2011; Cerrillo et al., 2015) or even human urine (Liu et al., 2013). Most of these studies show that high amounts of NH_4^+ and PO_4^{3-} can be removed when adding the limiting reactive to wastewater (usually Mg^{2+} and PO_4^{3-}), and working at an optimal pH. Reported NH_4^+ and PO_4^{3-} recovery efficiencies vary depending on the substrate and the operational conditions, but are usually above 95% (Kataki et al., 2016).

Figure 7. Stuvite crystals obtained from pig slurry (left), and synthetic wastewater (right) (Bonmatí, A. ©)



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Apart from the benefits obtained when recovering P and N from wastewater, some environmental issues can be attributed to these systems if they are not operated correctly. Highly mixed reactors, or those equipped with air flow systems, can induce the removal of NH_3 from the solution, as the relatively high operational pH and agitation creates a removal pathway for dissolved ammonia to volatilize from the solution. Moreover, the air flow dilutes the concentration of the gas-phase NH_3 equilibrium and increases the driving force for dissolving NH_3 to separate the gaseous phase (Yetilmezsoy and Sapci-Zengin, 2009).

By-Products Characteristics and Economics Aspects

The positive value of struvite obtained from calf manure (Schuiling & Andrade, 1999), municipal wastewater (González-Ponce et al., 2009) or anaerobically digested pig slurry (Cerrillo et al., 2015), among others, has already been demonstrated. The advantages of struvite as a solid fertilizer relative to the direct land application of manure as a liquid fertilizer include ease of application, low transportation costs, reduced bulk storage, and the avoidance of odour and pathogen contamination issues (Tao et al., 2016). Moreover, struvite recovered from wastewater reduces the necessity of using chemical fertilizers obtained from phosphate rocks, a non-renewable geological reserve. Struvite dissolves slowly in the environment to release nutrients at a rate suitable for crop uptake. Its low solubility prevents struvite from contributing to typical fertilization problems such as crop burn and generation of nutrient-rich runoff (Nkoa, 2014).

Struvite production costs have been established between 4 and 15 \$/kg $N\text{-}NH_4^+$, depending on the ammonia concentration in the influent (Türker & Çelen, 2007). As the economic feasibility of struvite is heavily influenced by reagent costs, several low cost magnesium sources as by-products of industrial processes, such as magnesite pyrolysate (Huang et al., 2011), or other magnesium rich renewable sources such as sea water and brine (Liu et al., 2013), have been proposed to replace high grade magnesium. The investment for the precipitation reactor can be of around 0.12 €/$m^3_{REACTOR}$, according to Jaffer et al. (2002).

There are few crystallization plants at full scale, as there is still a lack of knowledge of struvite properties as a fertilizer by end users; and its quality, market value, difficulties in the crystallization process, pH control and reagent costs may be a hindrance to widespread struvite precipitation technology. However, some commercial full scale systems are already in the market, for example: PEARL, NuReSys, PHOSPAQ, AirPrex, etc. Commercial struvite recovery units handling municipal wastewater sludge are in operation in countries like Japan, Canada, England, USA, Australia, Sweden, The Netherlands and Italy (Kataki et al., 2016). Struvite sale price has been reported to be approximately 198-1885 \$/t in Australia and Japan (Le Corre et al., 2009), mainly depending on its purity.

ELECTROCOAGULATION

The objective of electro coagulation (EC) is to destabilize suspended, emulsified or dissolved particles within an aqueous media, by applying an electric current. Electricity destabilizes those particles favouring the aggregation of colloidal particles just like chemical reagents do in a conventional coagulation-flocculation process.

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Theoretical Fundamentals and Process Description

EC is an electrolytic process that has been already used for the treatment of various liquid wastes and consisting of dissolution of sacrificial anodes (iron or aluminium) upon application of a current between two electrodes. This provokes the dissolution of the electrode to yield metal ions (Fe^{2+}, Fe^{3+} or Al^{3+}) at the anode, which are involved in the neutralization of the negative charges on the colloids of the effluent. The cathodic reaction involves the formation of hydrogen gas and hydroxide ions which favour the formation of flocks; these flocks are then easily separated by decantation or filtration, depending on their density.

EC offers some advantages over chemical dosing: it has simple equipment requirements and can be readily automated; it reduces the chemical cost using cheaper materials; gas bubbling provides for a gentle mixing which promotes coagulation and helps form bigger flocks; and gas bubbling carries some particles up to the surface of the liquid in a kind of flotation, which may then be easily separated. The main disadvantages of this method are lack of a systematic approach to EC reactor design and operation, the need to replace electrodes at regular intervals, high electricity costs and anode passivation (Shalaby et al., 2014; Lin et al., 2015).

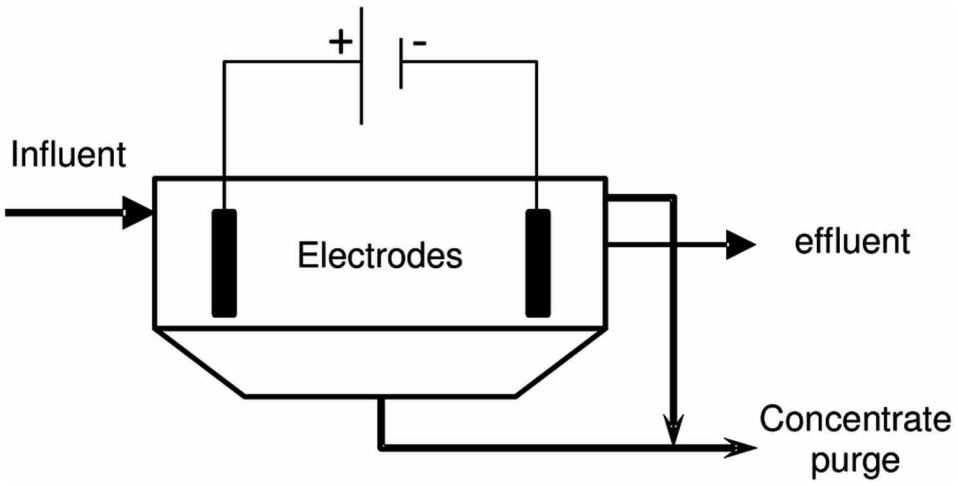
The EC process occurs in three steps. In the first step, a coagulant is formed due to anode oxidation. In the second step, pollutants are destabilized. In the last step, destabilized matters are aggregated. The most common electrode materials for electrocoagulation are aluminium and iron. These are cheap, readily available, and have proven to be effective (Gharibi et al., 2010).

If the effluent has a high enough electrical conductivity, the electrochemical process can generate an electrical field and/or produce a field 'in situ' by sacrificial electrodes, without adding additional ionic species The process alters the surface charge of the effluent and enhances P and solids settling.

When aluminium is used as electrode material, the reactions are as follows:

$$\text{Cathode: } 3H_2O + 3e^- \rightarrow 3/2\ H_{2(g)} + 3OH^- \tag{4}$$

Figure 8. Scheme of an electrocoagulation reactor



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Anode: $Al \rightarrow \ Al^{3+} + 3e^{-}$ (5)

Solution: $Al^{3+}\left(aq\right) \ + 3H_2O \rightarrow Al\left(OH\right)_3 + \ 3H^{+}\left(aq\right)$ (6)

When iron is used as electrode material, the reactions are:

Cathode: $3H_2O \ + \ 3e^{-} \rightarrow \ 3 / 2 \ H_{2(g)} + \ 3OH^{-}$ (7)

Anode: $4Fe\left(s\right) \ \rightarrow \ 4Fe^{2+}{}_{(aq)} + \ 8e^{-}$ (8)

Solution (with dissolved O_2): $4Fe^{2+}{}_{(aq)} + \ 10H_2O_{(l)} + \ O_{2(g)} \rightarrow \ 4Fe\left(OH\right)_3 + \ 8H^{+}{}_{(aq)}$ (9)

Overall reaction: $4Fe_{(s)} + \ 10 \ H_2O_{(l)} + \ O_{2(g)} \rightarrow \ Fe\left(OH\right)_{3(s)} + \ 4H_{2(g)}$ (10)

The release of hydroxyls and metal ions, and the formation of metal hydroxides cause the precipitation of different dissolved ions. As an example, phosphates precipitation reactions are as follows.

$\mathrm{H_3PO_4} + \ 3\mathrm{OH^{-}} \rightarrow 3\mathrm{H_2O} \ + \ \mathrm{PO_4}^{3-}$ (11)

$\mathrm{Al^{3+}} + \ \mathrm{PO_4}^{3-} \rightarrow \mathrm{AlPO_4}$ (12)

$\mathrm{Al} \ + \ \mathrm{H_3PO_4} \rightarrow \mathrm{AlPO_4} + \ 3 / 2\mathrm{H_2}$ (13)

In the solution, H_3PO_4 is neutralized by the hydroxyl ions released at the cathode (Equation 11). So, for pH lower than 6.5, aluminium phosphate is formed before aluminium hydroxide; consequently, the PO_4^{3-} ions obtained react with Al^{3+} ions produced at the anode (Equation 5). This results in the precipitation of aluminium phosphate (Equation 11). The overall reaction is best summarized by Equation 13 (Tchamango et al., 2010).

Usual Applications and Environmental Aspects

EC has been a promising technology aiming to destabilize and remove fine particles from water and wastewaters since the beginning of the 20th century. Presently, it is considered as a prospectively competitive technology for the removal of pollutants from supply water, urban wastewater, and also for the treatment of industrial effluents such as those generated in the agro-food industry, metalworking and textile industries (Lacasa et al., 2013). EC has been successfully used to remove different kinds of pollutants such as solids, nitrogen, organic compounds, heavy metals, dyes, hardness, chemical oxygen

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demand (COD), and important anions such as nitrate, fluoride and phosphate (Shalaby et al., 2014). Furthermore, it has demonstrated its superior performance in treating effluents containing suspended solids, oil and grease, and other similar substances (Zhao et al., 2010). Thus, EC is also effective at removing phosphorus and solids from digestates without any chemical addition.

Regarding its environmental side effects, the performance of some systems entails a high exposition of manure/slurry to atmosphere (high stirred systems), and thus, risk of gaseous emissions (COV) and odour problems could arise. Also during flotation (aeration) a high proportion of ammonia can be discharged into the air. It is therefore necessary to treat or collect the exhaust air coming from the flotation equipment.

Nutrient Recovery by Electrocoagulation

As mentioned, EC has proven to be a good option, in terms of efficiency, for the removal of several components such as total solids, COD, N and P. Tchamango et al. (2010) obtained N and P removals of 81% and 89%, respectively. Zhao et al. (2010) achieved P removals between 70-90%, whereas Lekuona (2004) reported higher P (>99%) but lower N (>60%) removals with electrocoagulation combined with a band filter, as can be seen in Table 5. The efficiency of the electrocoagulation process depends on many operational parameters such as the initial pH, initial pollutant concentration, temperature, nature of electrolyte and current density (Shalaby et al., 2014).

Besides, EC has been also successfully applied for removing nitrate NO_3^- from different liquid streams such as wastewater, groundwater (Lacasa et al., 2011), surface water (Koparal et al., 2002) and drinking water (Vasudevan et al., 2010), among others.

By-Products, Characteristics, and Economics Aspects

Settled solids resulting from EC have high nitrogen contents, phosphorus and other minerals, which can be used as fertilizer. Although the solids separated from the EC unit still contains considerable amount of water, they can be dried in the open air or by waste heat from the electric generator which is generally set up near the anaerobic digester. However, if the original influent contained heavy metals or other pollutants, they will end up in this solid fraction and its usefulness as a fertilizer could be compromised.

In terms of energy consumption, 20-22 kW·h per m^3 of pig slurry liquid fraction with about 1.1-1.3% TS has been reported (Lekuona, 2004). Additionally, EC represents an improvement in separation efficiency compared to other techniques (by electric supply) but sacrifice electrodes, consisting in iron plats, should be regularly replaced due to the release of Fe^{2+} in the slurry.

Table 5. Efficiency of EC for various components

	Concentration in Slurry (mg/l)	Concentration in Effluent (mg/l)	Removal (%)
Total Suspended Solids (TSS)	20,000-30,000	100-200	>99
Chemical Oxygen Demand (COD)	25,000-35,000	1,500-2,500	>90
Total N	2,000-3,000	600-800	>60
Total P	200-350	<2	>99

(Lekuona, 2004)

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As commented before, simple equipment is required for EC and it can be readily automated. Moreover, EC reduces chemical costs using cheaper materials. Therefore, the cost investment for this technology is mainly related to the cost of electrodes. The chemical and electrical costs come to 20¢$/m^3 and 6¢$/m^3, respectively (Zhao et al., 2010) when settling is used as dewatering strategy and a sacrificial electrode as chemical input.

AMMONIA AIR STRIPPING AND ABSORPTION

Ammonia air stripping is a physical-chemical process aiming to transfer volatile ammonia (strongly dependent on pH and temperature) from a liquid phase to a gas phase by means of liquid-gas (air or steam) intimate contact (usually in counter current), and its subsequent recovery in an acidic solution as ammonium salt, or by condensation. The process is usually performed in columns with packing material to favour the contact between liquid and gas (Frear et al., 2011).

Theoretical Fundamentals and Process Description

The amount of ammonia that can be stripped from a liquid waste or absorbed in the acidic solution is, to a great extent, dependent on two thermodynamic equilibria:

- Ammonia dissociation equilibrium in the liquid: $NH_{3\,(l)} \leftrightarrow NH_{3\,(g)}$
- And, ammonia gas/liquid equilibrium: $NH_4^+ \leftrightarrow NH_3 + H^+$

In the case of a diluted ammonia solution, Henry's Law can be applied to represent the equilibrium between phases (Equation 14).

$$y = \frac{K_H}{P} \cdot x \tag{14}$$

Where: y is the concentration of ammonia in the gas (molar fraction), x is the ammonia concentration in the liquid (molar fraction), P is the total pressure in the system (bar) and K_H is Henry's constant (bar).

Like all equilibrium constants, Henry's constant is strongly influenced by temperature. The temperature dependency of K_H can be expressed according to Dasgupta and Dong (1986). Ammonia equilibrium in aqueous solution is pH and temperature dependant (Equation 15).

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + \frac{[H^+]}{K_a}} = \frac{[NH_3 + NH_4^+]}{1 + 10^{pK_a - pH}} \tag{15}$$

Where: $[NH_3]$ is the free-ammonia concentration, $[NH_3 + NH_4^+]$ is the total ammonia concentration, $[H^+]$ is the hydrogen ion concentration, and pK_a is the acid ionisation constant for ammonia which can be expressed as function of temperature (T) by the following Equation (16) obtained by polynomial regression of data from Lide (1993); the higher the pH and temperature, the higher the free ammonia fraction.

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$$pK_a = 4{\cdot}10^{-8}\cdot T^3 + 9{\cdot}10^{-5}\cdot T^2 - 0.0356 \cdot T + 10.072 \quad (16)$$

As seen in Figure 9, if ammonia air stripping is performed at room temperature, a high pH is required to move the ammonia equilibrium towards free ammonia. However, with an increase in temperature a lower pH is required. pH is usually set between 9 and 10 by means of base addition or previous CO_2 stripping. On the other hand, ammonia absorption is clearly favoured when operating at pH values below 5, with almost no temperature effect.

Figure 10 shows a schematic diagram of the stripping-absorption technology. The process is usually performed in vertical columns where the liquid phase (ammonia riche stream) is introduced in the upper part while the gaseous phase enters in counter current from the bottom. To enhance liquid/gas contact the columns are usually filled with packing material (specifically shaped pieces of inert material). Stripped ammonia is recovered either by absorption in a second column, with a counter current acid solution, or by vapour condensation, obtaining NH_4OH or ammonia salts.

Up to 95% of ammonia reduction can be achieved under optimal conditions and almost complete ammonia recovery by absorption in acid solutions is possible with only a little acid stoichiometric excess (1.1:2 H_2SO_4:NH_3). With respect to the reagents used, NaOH, $Ca(OH)_2$ or other bases are added to increase pH (if CO_2 stripping is not enough), whereas H_2SO_4, HNO_3 or H_3PO_4 solutions are commonly used to absorb the NH_3 from the gas phase.

Figure 9. Free ammonia fraction as a function of pH at different temperature levels (data from Perry, 1992)

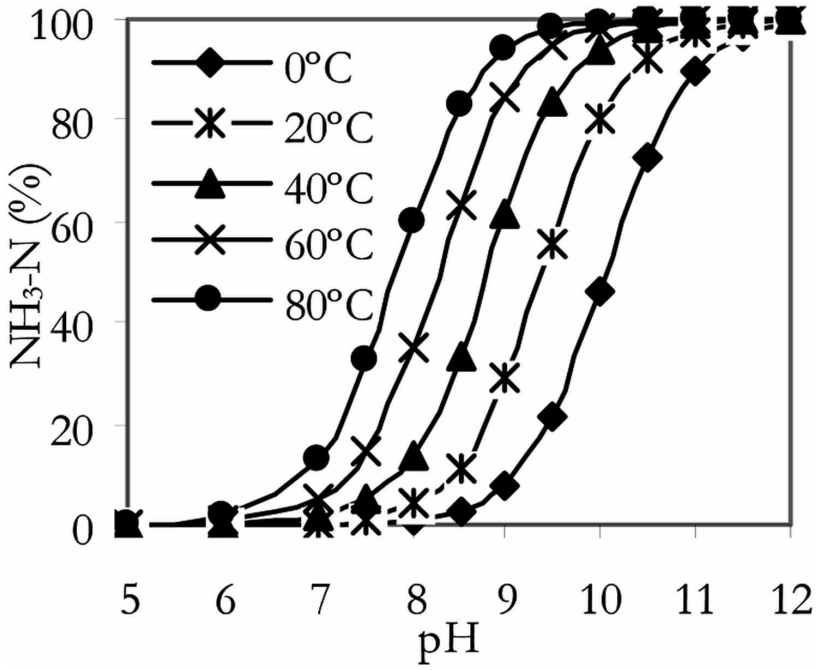

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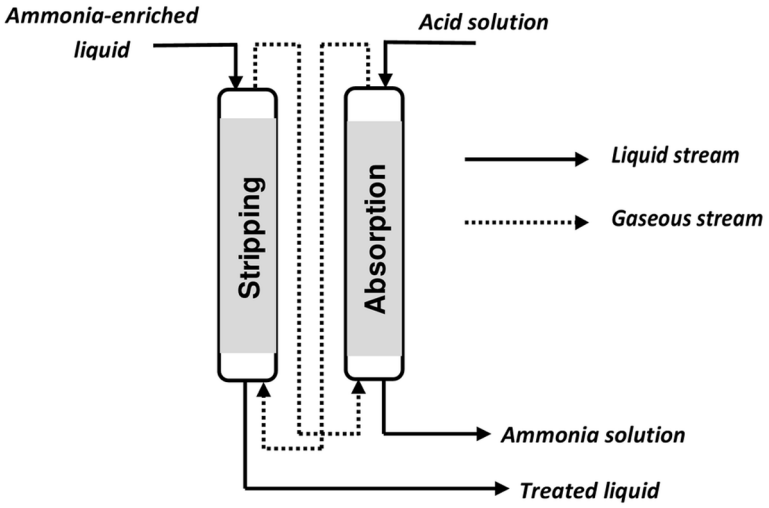
Figure 10. Schematic diagram of the stripping-absorption process



Usual Applications and Environmental Aspects

Ammonia stripping has already been successfully applied in anaerobic digestion (AD) supernatants from municipal wastewater treatment plants, landfill leachate, and industrial wastewater at a commercial scale. In the livestock sector, the process has been applied, both as pre- and post-treatment for anaerobic digestion, to pig slurries, cattle and fermented chicken manures, with a wide range of reported removal efficiencies. The use of digested slurry showed clear advantages compared with raw slurry, achieving efficiencies above 90% even without pH adjustment (Bonmatí & Flotats, 2003, Laureni et al., 2013, Jiang et al., 2014). However, not many cases can be found when it comes to farm-based AD systems. In the Lombardy Region (Italy), there are some facilities that have been implemented as part of a treatment chain mainly as post-treatment of the anaerobic digestion supernatant (Moscatelli & Fabbri, 2008) (Figure 11).

Figure 11. Ammonia stripping plant located in an agricultural biogas plant in Brescia, Italy - CRPA, 2015

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Nutrient Recovery by Stripping-Absorption

The removal efficiency of a stripping process depends on a number of operational parameters. As mentioned, the main parameters are pH and temperature, as they have a direct effect over ammonia speciation (NH_4^+/NH_3), but other parameters such as the characteristics of the inflow stream should be also taken into account. In this regard, a distinct relationship between the inflow characteristics and removal efficiency has not yet been clearly established, but the content of organic matter is likely to be the most relevant parameter (Laureni et al., 2013).

Slurries with an initial low organic matter ($< 10\ g_{COD}\ L^{-1}$) content led to higher N removal efficiencies ($> 90\%$) when stripping was performed at 50 ºC and pH was not modified. In contrast, nitrogen removal efficiency was limited to about 50% when organic matter concentrations were high, above 27 $g_{COD}\ L^{-1}$ (Laureni et al., 2013). Similarly, Bonmatí and Flotats (2003) compared fresh and digested pig slurries in terms of stripping efficiencies at high temperature (80 ºC). The authors reported higher N removals with anaerobically digested slurry (90%) than with the fresh substrate (63%). This behaviour could be explained by the capacity of the organic matter present to bind cations (e.g. NH_4^+) with the consequent reduction of the strippable ammonia available (Laureni et al., 2013).

The combination of ammonia stripping with anaerobic digestion processes presents other advantages besides diminishing the organic matter content. The biological process itself increases the ammonia content; part of the organic nitrogen is hydrolyzed to ammonia; and it slightly increases pH reducing alkali requirements. Furthermore, as stripping is usually performed at high temperatures, the biogas produced during anaerobic digestion can partially or totally provide for the necessary heat for stripping at high temperature.

By-Products Characteristics and Economic Aspects

Stripping/absorption processes resulted in a liquid ammonia solution or solid ammonia salts, produced after a crystallization process. Both, products could be used directly as fertilizers or sold for other industrial applications (WWT of paper industry). However, the products recovered should have a marketable quality, in terms of nutrient concentration and organic matter contamination.

Organic matter contamination of the recovered ammonium solution, in terms of TOC and VOC concentration, strongly depends on the initial organic matter content of the treated slurry and, to some extent, on the operational pH. The higher the organic matter content, the higher the contamination; and oppositely, the higher the pH, the lower the contamination (Laureni et al., 2013).

Investment costs could be set between 0.25 and 0.5 M€ for treating 10-15 m^3/h, and operational costs amount to 0.66€/m^3 for NaOH and 0.21 €/m^3 for H_2SO_4 as well as 2.5-4.5 €/kg of stripped nitrogen (only for the stripping column). At least an equivalent range of values should be considered for the absorption step (Flotats et al., 2011). The by-product obtained (ammonia salts) can be used as raw material for the production of liquid fertilizers. An ammonium-sulfate solution with low organic contamination and a nitrogen concentration of 6% w/w, can be sold at a price of about 0.35 € kg^{-1} N (Laureni et al., 2012).

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CONCLUSION

In the current juncture of increasing raw materials and energy sources scarcity, organic waste (e.g. livestock manure and other industrial wastewaters) arises as an attractive resource which, if processed properly, can yield renewable energy and be a source of added-value products (e.g. nutrient fertilizers) while, in turn, reducing the environmental impacts associated to its management.

The development and implementation of cost effective processing technologies aiming to recover valuable products as nutrients, is crucial to redirect the development towards a circular economy. In this chapter, the main process technologies already in operation, as well as the new technological developments have been reviewed, showing that these technologies are ready but have different hindering issues which should be overcome before it can spread worldwide. Operational costs, the quality of the recovered products and the need to open the market for this kind of products are the main limiting factors. Nevertheless, these recovering technologies present good potential to be widely implemented in a near future.

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Chapter 27
Constructed Wetlands for Industrial Wastewater Treatment and Removal of Nutrients

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ABSTRACT

Constructed Wetlands (CWs) are low-cost and sustainable systems for wastewater treatment. Traditionally they have been used for urban and domestic wastewater treatment, but in the last two decades, the applications for industrial wastewater treatment increased due to the evolution of the technology and the extended research on the field. Nowadays, CWs have been applied to the treatment of different kind of wastewaters as such as refinery and petrochemical industry effluents, food industry effluents including abattoir, dairy, meat, fruit and vegetables processing industries, distillery and winery effluents, pulp and paper, textile, tannery, aquaculture, steel and mixed industrial effluents. In this chapter, the authors present the main types of CWs, explain how they work and the expected performances, and describe the principal applications of CWs for industrial wastewater treatment with particular attention to suspended solids, organic matter and nutrient removal. A review of these applications as well as some case studies will be discussed.

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INTRODUCTION

In this chapter, the authors refer to the use of constructed wetlands (CWs) for industrial wastewater treatment and their efficiency for nutrient removal. CWs are engineered systems that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils, and their associated microbial assemblages to achieve wastewater treatment (Vymazal, 2014). "Modern treatment wetlands are man-made systems that have been designed to emphasize specific characteristics of wetland ecosystems for improved treatment capacity" (Kadlec & Wallace, 2009). "Besides treatment wetlands", constructed and engineered wetlands can cover a broad range of objectives such as improving biodiversity and environmental conditions related to, wildlife use, irrigation of agriculture lands, improving river water quality, or riverine restoration. Some misleading names have been given to the technology including green filters, biofilters and even sand filters or artificial wetlands. As CWs have evolved with time and applications, other terms like engineered wetlands have appeared that might include the use of devices that upgrade the performance using energy input.

CWs are low-cost and ecofriendly technologies, that take advantage of natural processes to remove pollutants from the water, generally avoiding the use of chemical products and the input of high amounts of external energy. On the other hand, CWs may require a large surface, which is its major drawback. As a result; they are included in the group of extensive technologies for wastewater treatment.

The first research into CWs for wastewater treatment took place in Germany, in the 1950s (e.g., Seidel, 1961), with special focus on phenols removal. From the beginning, the first applications of CWs dealt with urban wastewater, but in the last two or three decades, they have been applied for industrial and agricultural wastewater, as well as stormwater runoff and the treatment of landfill leachates (Vymazal 2011a).

CONSTRUCTED WETLANDS: HOW DO THEY WORK?

Pollutant removal in natural wetlands takes place due to the combination of physical, chemical and microbial processes. The processes involved in pollutant removal are sedimentation, sorption, precipitation, evapotranspiration, volatilization, photodegradation, diffusion, plant uptake, and microbial degradation (for instance, nitrification, denitrification, sulphate reduction, carbon metabolization, etc.) among others.

Types of Constructed Wetlands

There are several types of CWs, depending on the hydrology, the type of macrophytic growth and the direction of the flow inside the wetland. As a result, if the hydrology is considered, the principal types of CWs are surface flow (or free water systems) or subsurface flow systems (Figure 1). According to the macrophytic growth, there are emergent, submerged, free-floating and floating leaves. Finally, the direction of flow inside the CW can be vertical, horizontal or mixed flow.

The most widespread CWs are the surface flow systems (FWS), the horizontal subsurface flow systems (HSSF) and the vertical subsurface flow systems (VF). For improving the performance and the removal of pollutants and nutrients, a combination of these systems can be used, known as hybrid systems. The hybrid systems can combine several features in only one or in several sequential steps.

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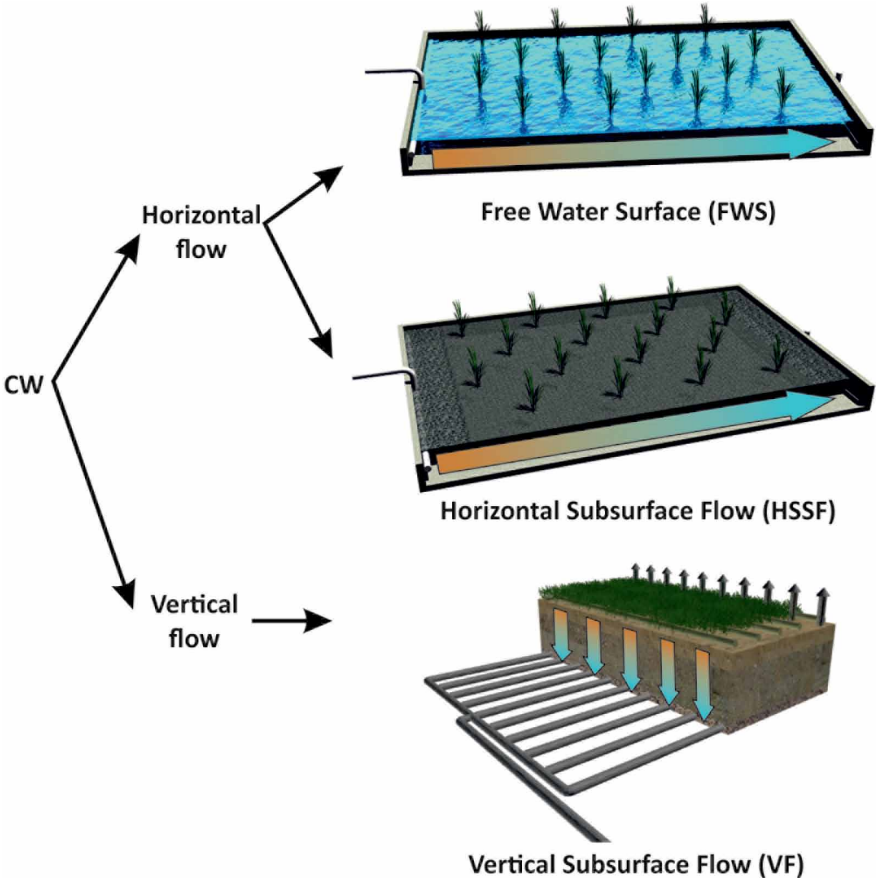
Figure 1. Schematic representation of types of CWs, depending on the flow regime



Free Water Surface Systems (FWS)

The FWS system CWs are shallow beds (often from 20 to 40 cm), planted with aquatic vegetation. The pollutants are removed as wastewater goes exposed to the atmosphere through the planted beds, due to several processes including sedimentation, oxidation, reduction, precipitation, sorption and biological degradation.

This type of FWS is often used for tertiary treatment, to polish effluents from a previous physical-chemical or biological wastewater treatment. The FWS systems have several characteristics:

- Simple to operate and low-cost systems.
- Low removal rates.
- Demand large surface requirements (up to 20 m^2/PE^1).
- Risk of odors forming (if they receive untreated sewage directly) and freezing in winter.
- Can host vectors.

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Horizontal Subsurface Flow Systems (HSSF)

HSSF systems are cells filled with media (from 30 to 60 cm deep) in which aquatic vegetation is planted (Figure 1). This kind of wetland is saturated, and the water column is not exposed to the atmosphere, usually remaining about 5 to 10 cm under the surface of the bed and therefore avoiding fouling odors and the proliferation of vectors.

Water is distributed in the inlet zone by perforated pipes or Thompson channels. The inlet of the wetland is filled with coarse gravel (30-100 mm size), to improve influent distribution and delay the possible clogging in the inlet zones. The bed media is generally gravel (5-20 mm size), where the biofilm develops and at the same time, the media serves as a support for the vegetation. At the outlet zone and the bottom of the bed, a collection pipe is placed to evacuate the treated waters. The pipe is also embedded with coarse gravel to facilitate the effluent collection. After the bed, there must be an outlet sump where a pipe is connected to the collection pipe and can regulate the water level in the wetland by a swivel joint or a flexible pipe.

In a HSSF wastewater goes through the wetland and the media in a horizontal path, coming into contact with aerobic, anoxic and anaerobic zones. The oxygen from the air is transported through the stems and leafs of the vegetation to the rhizosphere, where an aerobic-anoxic microcosm is present (Brix & Schierup, 1990). Normally, the amount of oxygen in HSSF CW treating typical wastewaters is not enough to degrade all the organic matter via aerobic processes much less to allow high dissolved oxygen concentration into the wetland. Therefore the processes responsible for the degradation are mainly anoxic-anaerobic. Some characteristics of this system are the following:

- High resistance to freezing conditions.
- Less surface area needed than FWS (5 m^2/PE).
- Higher removal rates than FWS, although this is dependent on operational conditions.
- Risk of clogging problems in the inlet zone.

Vertical Flow Systems (VF)

The subsurface VF systems are cells filled with coarse sand or fine gravel, usually from 60 to 100 cm deep, and planted with aquatic vegetation (Figure 1). Most VF systems are unsaturated and fed sequentially in short pulses and then a drainage period takes place. The wastewater is loaded homogeneously onto the surface of the wetland, trickles vertically through the filter media and is collected at the bottom by drainage pipes. Additionally, passive aeration pipes from to the drainage pipes to the atmosphere to improve the oxygen transfer to the bed. Due to aeration pipes, pulse loadings and drained periods, the oxygen transfer can reach much higher values, if compared to HSSF or FWS systems. VF CWs have aerobic conditions and therefore higher organic removal rates as well as the capacity to nitrify.

The wastewater distribution system of VF CWs consists of a manifold of pipes installed on the surface of the bed. The media filling the bed can be either by one layer or even several sand layers. At the top and the bottom of the bed, a layer of about 20 cm of coarse gravel is placed to facilitate the distribution and evacuation of the waters.

Some other characteristics of VF CWs are the following:

- Less surface area needed (2-3 m^2/PE).

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- No clogging problems (if well designed and operated).
- Demands a good influent distribution system.

A modification of VF is commonly called "the French system" or French reed beds (FRB). It is basically a 2-step CW but with some differences, mainly the stratification of the substrate layers and the distribution system. It can treat wastewater directly, without primary treatment. In the FRB the 1-step VF demands parallel beds that are loaded sequentially and used as primary treatment and the bed retains suspended solids as well as other particulate pollutants. As times goes by and after loading, a layer of stabilized sludge accumulates on top of the wetland. After 8 to 10 years, the sludge layer is removed and can be further composted or applied directly to land as fertilizer. After the first step and according to the effluent needs the vertical bed can be followed by a new set of vertical flow beds or a horizontal flow bed.

The recirculation of treated effluents back to the pumping well or to the sedimentation tank improves the overall system performance and enhances the removal of nitrogen. The recirculation of treated water dilutes and makes the water loaded onto the filter more homogeneous. Additionally, the recirculation of treated water helps maintain the presence of water during vacation periods ensuring the survival of the plants and bacteria/biofilm. The optimal recirculation rate is circa 100%, i.e. the recirculation of half of the effluent back to the pumping well (Arias *et al*, 2011).

Tidal Flow Constructed Wetlands

Other type of CWs developed during last decade are the tidal-flow constructed wetlands (TFCWs), which have enhanced the organic matter and ammonia removal by overcoming the lack of oxygen in conventional CWs (Sun *et al*., 2005; Wu *et al*., 2011). However, the total nitrogen removal efficiency in TFCWs is not ideal because of the high oxygen content that limits the denitrification processes (Ju *et al*., 2014; Cui *et al*., 2012).

The "tidal flow" principle includes four operational procedures (fill, contact, drain and rest) that constitute the main difference with conventional CWs (Sun *et al*., 2006).

Engineered Wetlands

As reviewed by Wu *et al*. (2014), different operation strategies and innovative designs can be used in order to intensify the performance of CW systems. These strategies include recirculation, aeration, tidal operation, flow direction reciprocation, earthworm integration, short-term fluctuations in the water table, step-feeding, circular-flow corridor wetlands, towery hybrid CWs, baffled subsurface CWs for the intensifications of the performance.

Aerated wetlands are subsurface flow wetlands, both horizontal and vertical flow, but with artificial aeration implemented in the bed where the air is pumped into the wetland by means of compressors. Forced bed aeration (FBA®) wetlands were patented in USA by Scott Wallace and are gaining ground and are being used more due to their versatility and better capacity to treat industrial waters. Aerated wetlands testing different regimes of aeration "on" and "off", nitrification or denitrification processes can be enhanced.

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Pretreatments for CWs

The most frequently used pretreatments for CWs treating domestic wastewater and, frequently used for treating industrial wastewater, are septic tanks (ST) and Inhoff tanks (IT). Often, these primary treatment technologies are not efficient enough for removing suspended solids, and can promote clogging in CWs, especially when high organic loads are applied. The use of anaerobic digesters and CWs is gaining importance in latest years for treating different industrial wastewaters. Both systems are low-cost, robust and effective in wastewater treatment. According to Álvarez *et al*., (2008) an average and 95 percentile TSS concentrations of anaerobic treated wastewater were below 60 and 100 mg/L, respectively, for all configurations reported suggesting that anaerobic treatments might be an option when using CWs.

Removal of Pollutants in CWs

Solids are removed in CWs mainly by physical processes such as sedimentation and filtration. The removal of solids takes place in the inlet zone of HSSF (1/3 or 1/4 of the total length) and in the surface of VF CWs. These processes are favored by the low velocity of the water and the sieving in the interstitial spaces of the granular media inside the CWs.

Organic removal processes are complex and vary, with the interaction of several physical, chemical and biotic mechanisms involved. Particulate organic matter is retained like solids, as described before, and hydrolyzed in simple substrates that can be assimilated by heterotrophic, anaerobic and facultative bacteria. Aerobic degradation of organic matter takes place close to the water surface and the rhizosphere, while facultative and aerobic degradation occurs in the bottom of HSSF and FWS systems. The rest of the bed is dominated by anaerobic organisms and as such anaerobic processes are responsible for further transformations.

Pathogens are removed by complex processes, including filtration, sorption, died off due to environmental conditions and predation.

Under aerobic conditions, heavy metals (HM) retention and accumulation in wetland substrate is mainly due to the formation of metal hydroxides (i.e. Fe and Mn hydroxides; Singer & Stumm, 1970). Under anoxic or anaerobic conditions, precipitation of metal sulphides is the main process contributing to the removal of HMs in CWs. In anaerobic conditions, sulphate reduction leads to the formation of hydrogen sulphide and most HMs react with sulphide to form highly insoluble precipitates (Stumm & Morgan 1981).

Removal of Nutrients in Constructed Wetlands

The most important mechanism to remove nitrogen from wastewater in CWs is nitrification-denitrification process. The process begins with nitrogen from organic compounds like proteins, transformed both in aerobic and anoxic conditions into ammonia, (ammonification). Nitrification consists on the oxidation of ammonia into nitrite and nitrate by autotrophic bacteria. This process occurs in aerobic conditions. Denitrification is the conversion of nitrate to dinitrogen gas (N_2) by heterotrophic bacteria. This process needs organic matter and anoxic conditions.

Recently, the presence of anaerobic ammonium oxidation (anammox) processes has been described in CWs as another path to remove nitrogen (Saeed and Sun, 2012b). Anammox is a reaction that oxidizes ammonium to dinitrogen gas using nitrite as the electron acceptor under anoxic conditions. When

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partial nitritation (NH_4^+ to NO_2^-) and anammox is combined, only about one half of ammonium needs to be oxidized to nitrite first, then anammox bacteria use the remaining ammonium as electron donors for autotrophic denitrification of the nitrite produced (van der Star *et al*., 2007; Kartal *et al*., 2010). Anammox process consumes 60% less oxygen than nitrification-denitrification cycle and no organic carbon source is required (He *et al*., 2012).

Other processes involved in nitrogen removal are plant uptake, volatilization, dissimilatory nitrate reduction, and biomass assimilation. The latest process takes place through incorporation of NH_4^+ in the heterotrophic biomass to fulfil nutrient requirements. In stationary systems like CWs, biomass accumulation could lead to clogging problems, so biomass assimilation is not expected to be an important process in CWs for removal of nitrogen.

The presence of phosphorus in wastewater is mainly in the forms organic phosphorus, orthophosphate, and polyphosphate. Soluble reactive phosphorus is taken by plants and transformed to biomass, in the form of vegetal tissues and/or organisms. Sorption by sediments, sand or gravel media is the most important phosphorus removal process in CWs. Precipitates and co-precipitates of Al, Fe and Ca occur under certain circumstances mainly depended on pH, but can be redissolved under altered conditions (Kadlec & Wallace, 2009).

Nitrogen Removal in CWs

If organic matter concentration (carbon source) is sufficient, denitrification might be an important process to remove nitrogen in FWS systems. Unvegetated open water does not promote denitrification, resulting in rate constants about one third of those for vegetated systems (Arheimer & Wittgren, 1994). Smith *et al.* (2000) have shown nitrate removal proportional to the number of shoots in a *Schoenoplectus* spp. planted wetland. These considerations lead to the conclusion that fully vegetated marshes with either emergent or submergent communities are the preferred option for denitrification.

Since HSSF CWs are saturated reactors they have limited nitrification capacity, on the contrary the conditions are best for denitrification processes and therefore total nitrogen removal is effective only if a previous nitrifying system is implemented. However, low loaded HSSF systems can remove influent total nitrogen because near all the nitrified ammonia is effectively removed (nitrification-denitrification), or by the existence of other removal mechanisms.

In VF CWs, ammonia oxidation to nitrate is highly dependent on the organic and nitrogen surface loads and on the VF operation regime, mainly the pulse frequency and volume as well as the duration of drained periods. If well designed and operated, VF systems can reach more than 90% of nitrification, both for urban and industrial wastewater. With aerobic conditions, total nitrogen removal in VF systems is poor or null, due to very limited denitrification rates. Partial recirculation of VF effluent to previous septic tanks or anaerobic reactors can enhance total nitrogen removal (Brix & Arias, 2005; Torrijos *et al*., 2015).

In TFCWs ammonium cations (NH_4^+) are first adsorbed on matrix, pores, and surfaces when wetland cells are flooded. Second, as wetland cells drain, matrix pores are immediately filled with air and the absorbed ammonia is nitrified by bacteria. Finally, in the next flood cycle, nitrate (NO_3^-) and nitrite (NO_2^-) desorb into bulk water, where they are denitrified into atmospheric nitrogen (Austin, 2006; Chang *et al*., 2014). Therefore, the flooded time of TFCWs plays a key role in forming effective anoxic conditions that are favorable for reducing oxidized nitrogen and to improve total nitrogen removal (Li *et al*, 2015b).

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The Role of Plants in Constructed Wetlands

Nutrient transformation and sequestration in low-loaded systems, organic matter production and plant uptake of nutrients, as well as root-zone oxygen and organic carbon release systems have been identified as key factors (Brix, 1997; Tanner, 2001; Vymazal, 2011b). According to Tanner (2001), wetland plants promote the enhancement of nutrient removal, mainly by favoring transformations to gaseous forms and sequestration in accumulating organic matter. Recent studies reported that nitrogen removal is usually better for planted systems (Hijosa-Valsero *et al*., 2012; Pedescoll *et al*., 2013a; Webb *et al*., 2013; Huang *et al*., 2013; Seeger *et al*., 2013; Lv *et al*.,2013; Chen *et al*., 2014).

Carballeira *et al*. (2016) reported a linear correlation between ammonia nitrogen removal rate (g N/m^2·d) and biomass production (g volatile solids VS/m^2·d) in HSSF CWs treating domestic wastewater. According to that correlation, biomass production explains 91% of additional nitrogen removal in planted systems. Unplanted CW removed 0.34 g NH_3/m^2·d while planted systems removed an additional 13.4% per each g VS/m^2·d of above-ground biomass produced or the equivalent 36.6% additional per each kg VS/m^2 year.

The contribution of plants, in terms of nitrogen removal has been reported within the range 0.5-40.0% of the total nitrogen removal (Drizo *et al*., 1997; Shamir *et al*., 2001; Healy and Cawley, 2002; Meers *et al*., 2008; Kantawanichkul *et al*., 2009; Bialowiec *et al*., 2011, Saeed and Sun, 2012b). Chen *et al*., (2014) reported that N mass balance showed that denitrification, sedimentation burial and plant uptake respectively contributed 54%-94%, 1%-46% and 7.5%-14.3% to the N removal in CWs, mainly stored in aboveground biomass. Zheng *et al*., (2015) reported that plants harvesting in the first year improved nutrients removal by plant uptake (41.9 g N/m^2 and 3.7 g P/m^2 versus 37.3 g N/m^2 and 3.2 g P/m^2) as well as in the substrate layer (216.9 g N/m^2 and 8.0 g P/m^2 versus 191.0 g N/m^2 and 5.7 g P/m^2) during the second year.

Phosphorus Removal in CWs

In FWS, phosphorus is removed, due to three processes in wetlands: sorption, utilization to build a larger biomass compartment and storage as newly created, refractory residuals (burial). Sorption and biomass storage have a limited phosphorus retention capacity. Moreover, there are secondary processes like particulate settling that can rapidly remove high amounts of phosphorus from runoff water with a high level of suspended sediments (Kadlec & Wallace, 2009).

Similar phosphorus removal processes take place in subsurface flow CWs (HSSF and VF), biomass accumulation, sorption in the gravel media and sediment accretion. Sorption mechanisms are limited to the gravel media capacity, which can be high, but only when considered in a short term. In this sense, latest research in new materials with higher phosphorus sorption capacity has been done.

Like in HSSF systems, phosphorus removal in VF systems takes place mainly by sorption in the filter media. VF systems are designed principally to remove organic matter, solids and ammonia. As a result, phosphorus loading rate is bigger than the capacity of plants to accumulate phosphorus as vegetal biomass.

The biological removal of phosphorus by microorganisms in tidal flow CWs has never been considered as a significant factor in CW design. However, results from Li *et al*. (2015a) suggest that the cycling of phosphorus in CWs might depend significantly on the type of operations employed. Nevertheless, further investigations on the detailed mechanism of phosphorus removal are needed before any concrete conclusion can be made regarding phosphorus removal efficiency in tidal flow CWs.

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Influence of Filter Media of CWs on Phosphorus Removal

A review of different filter media used for phosphorus removal was elaborated by Vohla *et al*. (2011). These researchers reported that the most commonly used materials are described as natural materials, industrial byproducts and man-made products. Most of the studied materials had a pH >7 and high Ca (CaO) content. Several industrial byproducts achieved the highest P removal capacity, including some furnace slags (up to 420 g P/kg), followed by natural materials (maximum 40 g P/kg for heated opoka) and man-made filter media (maximum 12 g P/kg for Filtralite-P®). Some important factors such as saturation time, availability at a local level, the content of heavy metals, and the reuse of the saturated filter media as a fertilizer should be taken into consideration regarding the applicability of filter materials.

Moreover, a good hydraulic conductivity and the chemical composition of the adsorption media are key factors for CW design. Since phosphorus is removed via sorption and precipitation, Ca, Fe and Al content of the filter media is important for P removal. Even if a medium with high P binding capacity has been selected, it may be saturated after a few years (Arias *et al*., 2001). An easy, practical and sustainable solution might be to install a separate well filled with replaceable high binding P capacity media after the treatment for P removal (Brix *et al*., 2001).

Recovery of Nutrients in Constructed Wetlands

Recovery of nutrients by CWs is generally not very effective, comparing with other wastewater treatment systems and will depend on the type of CW and the water quality. For example, harvesting of plants for uptaken nutrient recovery might be interesting, but it is only feasible for large surface areas. Another example for carbon and nutrient recovery can be sludge treatment wetlands (STW).

STW is a type of VF, and were developed to treat sludge produced as a result of activated sludge wastewater treatment. The required specific surface area can be roughly assumed as 0.25 to 0.50 m^2/PE (Kainz, 2006). These systems consist of several parallel beds filled with three or more layers with a bottom gravel drainage layer, an intermediate layer with coarse material and a soil/sand layer for favoring the vegetation establishment (commonly reeds, *Phragmites australis*). In STWs homogenized sludge is pumped intermittently and sequentially to the different beds by alternating dosing regimens and allowing resting periods for the different beds. The resting periods will depend on the design conditions, but the intervals between loadings must be sufficient to allow the drainage of trapped water from the sludge. As sludge is accumulated and built up, the rhizomes will develop in the sludge and penetrate, increasing dewatering by evapotranspiration process.

After the sludge storage capacity of the bed is filled, the sludge from the STW is stable. This process reaches a final product with a dry solid content higher than 25%, and is suitable for direct reuse. As an example, the sludge produced in the Helsinge STW after 10 years of operation resulted in total phosphorus content of 30-35 g/kg dry solids and total nitrogen content of 20-25 g/kg dry solids (Nielsen, 2015).

Nutrients concentration in biosolids depends on the wastewater composition and treatment, and on subsequent sludge management. Nitrogen comes from biomass present in the sludge and form wastewater residues. In a study carried out by Uggetti *et al*., (2012), total Kjeldahl nitrogen (TKN) values in biosolids ranged from 0.03 to 0.25% TKN/TS (TS total solids), being significantly lower than in activated sludge (Andreoli *et al*., 2007). TKN values were significantly higher (2.30-2.53% TKN/TS) in compost of sewage sludge (Ruggieri *et al*., 2008; Sanchez *et al*., 2010). Uggetti *et al*., (2012) reported a certain nitrogen reduction in STW, due to sludge mineralization, ammonification and plant uptake.

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The main sources of phosphorus in sludge are biomass formed during wastewater treatment, residues and phosphate-containing detergents and soaps. Uggetti *et al*., (2012) reported a decrease in total phosphorus values from the influent (2.7-3.0% TP/TS) to treated sludge (0.07-0.39% TP/TS), probably due to phosphate immobilization in microbial cells (Elvira *et al*., 1996).

STATE OF THE ART OF CONSTRUCTED WETLANDS TREATING INDUSTRIAL EFFLUENTS

Industrial Applications of Constructed Wetlands

CWs were initially used for treating domestic wastewater. But in the last two decades, industrial wastewater has been treated with hybrid CWs, both surface and subsurface flow. CWs started treating industrial effluents like petrochemical, dairy, meat processing, abattoir, and pulp and paper factory effluents. Brewery, tannery and olive mills wastewaters have been recently added to CWs applications. So, CWs can be applied to several and different kinds of industrial wastewaters, including acid mine wastewater with low organic matter content and landfill leachate. Vymazal (2013) reported industrial wastewater treatment with hybrid CWs systems with influent concentrations up to 10,000-24,000 mg COD/L and up to 496 mg NH_4^+/L. But there are not general rules to select the most suitable type of CW for a certain industrial wastewater or even urban wastewater. Every single case must be studied particularly due to several conditions: type of wastewater, land availability, the amount of flow and pollutant load, outlet discharge limits, etc. Some recommendations to be taken into account could be:

- Good pretreatments like anaerobic digesters (UASB, HUSB) to remove solids and avoid or at least delay clogging of media. A degreaser is necessary if wastewater contains huge grease concentration.
- If the industrial wastewater has a low volume to be treated and land availability, the simplest type of CW like HSSF can be a suitable solution.
- If high surface loading rate needs to be applied, VF or aerated wetlands are recommended.
- For the removal of nutrients, hybrid systems including VF and HSSF are specially indicated.

In this section, the authors will revise a few of the industrial effluents treated by CWs.

As shown in Table 1, the efficiencies can vary extensively, depending on the wastewater characteristics and the system design features and operational conditions. Regarding environmental conditions, CWs can work in extreme weather conditions ranging from the coldest temperatures to tropical conditions.

It seems hard that natural systems like CWs can work treating industrial wastewater, for instance, refinery, pulp and paper, tannery or textile effluents, where hardly biodegradable compounds are present. In wastewater with a high BOD/COD ratio, CWs can perform well as a secondary or tertiary treatment, with good pretreatments that can reduce the organic loads. For these types of wastewaters, the conventional primary treatment and activated sludge or SBR reactors as secondary treatment are the most common used systems. The variety of different industrial wastewater treated by CWs is high, and the latest research in the field is increasing this range of possibilities. The evolution of CWs has been enormous, from the simple FWS to the intensified systems. The treatment technology of CWs has evolved into a reliable technology which is nowadays successfully used for many types of industrial effluents (Vymazal, 2014).

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Table 1. Application of several types of CWs for the treatment of industrial wastewater

Type of Wastewater [a]	Type of CW (n) [c]	HLR (cm/d)	Treatment Efficiency (%) [d]						Others Pollutants Assessed
			TSS	COD	BOD	NH_4^+	TN	TP	
Refinery	FWS (8)	0.1-128	44-95	54-93	50-98	84-94	19-22	43-68	Phenol, HM, mineral oils, TKN
	HSSF (4)	2-3			99	98			Hydrocarbons
	VF (2)	3.4-10	47	50			53		Hydrocarbons, HM
	Hybrid	2-13		30-50			48-80	50-60	Hydrocarbons, HM
Pulp and paper	FWS (5)	1.5-22	33-84		6-77		29	32-54	NO_3^-,
	HSSF (6)	2-15	55-68		27-90	31-88		14-31	Phenol, Resin and fatty acids
Woodwaste	FWS (2)	1.2-4.7		6-50	60				Tannins, lignins
Tannery	FWS (1)			30		95			HM
	HSSF (3)	3-10	65-72	59-65	48-73	73			TKN, HM, turbidity
	Hybrid (1)	6	55	98	98	86		87	
Textile	HSSF (3)	10-45	88	70					Color, sulfate, HM
	VF (2)			64					Colorants
	Hybrid (2)	1-6	93	84	66		52		Color, colorants
Aquaculture	FWS (2)	7.7-9.1	89-91		65-82	47-75		82-86	NO_3^-
	HSSF (8)	1-790	81-95	12-94	72	7-61	21-69	43-89	TKN, NO_3^-
	VF (4)	16-39	39-82	26-99	53-99	62-86	48-96	17-84	NO_3^-
	Hybrid (4)	1-300	66-71	27-94	24-98	86-98	67	24-87	NO_3^-, TKN
Winery	HSSF (7)	2.5-48	30-97	49-99	92	54	58		S_2^-, TKN, phenols, tannin
	Hybrid (4)	2-3	75-89	71-98	70-99	90	81-90	60-72	S_2^-, TKN, PO_3^{4-}
Destillery	HSSF (3)	2.7-58		64-80	84-85	2-10		79	TKN, NO_3^-, SO_4^{2-}
Abbatoir	FWS (2)	1.4-4.6	94-95	42	85	54	30	74	NOx-N, TKN
	HSSF (6)	1.7-7.2	44-99	65-98	77-98	20-82	18-75	37-79	TKN, PO_4^{3-}
	Hybrid (1)	0.6	94	97	97	99	74		
Dairy/cheese	HSSF (8)	0.1-4.4	62-96	92-97	34-98	9-92	44-80	45-81	TKN
	Hybrid (4)	0.7-10	40-90	72-96	55-90	62-82	40-90	30-88	
	VF (3)	10		73-86		43-72			TKN, PO_4^-, color, phenol
Food industry [b]	FWS (4)	1.4-39.5	52-93	68	89-99	22-99	72-92	21-77	TKN
	HSSF (4)	1.0-4.3	81	11-92	89-94	43-95		18	TKN,PO_4^-,NO_3^-
	VF (1)	2.5-7.4	88	87		80			
	Hybrid (2)	0.3-3	83	93-94		47-72	54-90	83	
Laundry	HSSF (3)	3.7	83		61		62	32	LAS
Mixed industrial	FWS (2)	10-19	81	61	89	53		35	HM
	Hybrid (2)	36.5	89	67-81	66-69	24	30	62	PO_4^-
Steel industry	HSSF (2)	1.-2.6		50-77		77		6	HM
	VF (1)			55		67		93	HM

[a]Other industrial effluents with one reported case are brewery (HSSF), olive mill (FWS), chemical industry (VF), explosives (FWS), coke (HSSF), coal gasification (FWS), lignite pyrolysis (HSSF), tool industry (FWS and flower farm (hybrid).[b]Sugar, potato, fish/seafood and mixed food industry. [c]Number of cases. [d]Ranges of available values (note that not all the reported cases include data about all these parameters). Acronyms: HM, heavy metals, TKN, total Kjedahl nitrogen, LAS, linear alkylbenzene sulfonates.

(modified from Vymazal, 2014)

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CWs for Dairy Parlor Wastewater Treatment

CWs have gained a place in dairy parlor and wastewater treatment from different farm activities. Table 2 summarizes main results for some applications.

Three cases are shown in this section. Newman *et al*. (2000) designed a FWS of 400 m^2 for dairy parlor wastewater treatment from a farm with 100 milk cows. Real BOD_5 concentration was much higher (2683 mg/L) than expected and the treatment was not sufficient due to effluent values of 692 mg/l with a 74% BOD_5 removal. After this experience, an estimation of pollutant loadings when designing the systems is not recommended by those authors.

Mantovi *et al*. (2003) described a two-stage HSSF system in series to treat a mixture of domestic and dairy parlor effluent, previously treated in an Inhoff tank and a well with plastic filter for the removal of sedimentable suspended solids. Removal efficiency was satisfactory, with values of more than 90% in organic matter (TSS, COD and BOD), 48.5% of TKN and 60.6% of TP.

The 16-years of expertise of van Oirschot (2015) treating dairy wastewater is described in this section. In rural areas from the Netherlands and Belgium the main sources of wastewater discharged into fresh water are untreated widespread domestic and dairy farms wastewater. Several projects were developed, testing different additions to the substrate for their efficiency in the removal of phosphorus. The ratio BOD/COD in wastewater coming from milking parlors, seems to be greater than domestic wastewater, and low N-values due to the presence of milk. Results of nitrogen and phosphorus removal of 13 CWs treating dairy farms were 84.2%, 78.7%, 47.9% and 72.3% for TKN, NH_4^+, TN and TP, respectively.

These results from van Oirschot (2015) show a high removal of organic matter and organic nitrogen, as well as a significant reduction of total phosphorus. Denitrification occurs to about 50%, good if considering that is single-stage VF being used. This denitrification rate is higher than the same CW treating domestic wastewater, due to the relatively high C/N ratio of the dairy wastewater. In VF systems, it seems that the lack of carbon in the lower anaerobic parts of the wetland is the main cause for the low denitrification rate. The total P concentrations of 6 CWs at dairy farms with $CaCO_3$ and iron additions in the substrate ranged from 8.8 to 29.1 mg P/L and 0.14 to 8.8 mg P/L in the inlet and the outlet respectively.

Cheese Production Wastewater

Gorra *et al*., (2014) reported the performance of a HSSF from a medium-sized cheese factory which processes 8 ± 4 m^3 of milk. The local climate conditions were a mean air temperature of 12ºC and mean total precipitation of 430 mm. The system consists of a pretreatment by means of sedimentation tank (45 m^3) and a HSSF CW of 200 m^2 of total area and planted with common reed (*Phragmites australis*). The CW is divided into five sections, each one filled with a different material: (1) gravel from metamorphosed limestone, (2) ground ceramic wastes, (3) by-products from magnetite extraction, (4) zeolitite and (5) a horizon of a Dystrict Endoskeletic (Siltic) Cambisol. The input average flow was 10 ± 2 m^3/d, with a maximum during spring of $12 \pm 1 m^3$/d and a minimum of $8 \pm 2 m^3$/d during summer. Different volumes of influent treated have influenced the retention time, which for such reason varied from 15 to 5 days (average value about 7 days). Average SLRs were 40 (BOD_5), 10 (TN) and 0.5 (TP) g/m^2·d, while maximum SLR reached approximately 100 (BOD_5) and 25 (TN) g/m^2·d. The average mass removal was 55%, 55%, 59% and 58% for TN, organic N, NH_4^+ and TP, respectively.

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Table 2. Results of dairy farms wastewater treatment with CWs

Reference	Country	Source of wastewater	Pre-treatment	Treatment[a]		T (ºC)	Efficiency (%removal)		Surface loading rate SLR (g /m²·d)		HRT (d)	Surface rate (m²/ cow)	Effluent concentration (mg/L)	
Tanner *et al*., 1995	Argentina	Dairy parlor (pre-treated)		HSSF	40 cm	7-22	92-76 (BOD) 76-83 (TSS)		0.9-4.1 (BOD)	1.9-8.5 (TSS)	2 – 7	-	11-27 (BOD) 30-36 (TSS)	
Geary & Moore. 1999	Australia	Farm (pre-treated)	Pond	FWS / HSSF	24 cm/52cm		61 (BOD) 27 (TKN)	43 (Norg.) 28 (TP)	5.6 (BOD) 5.7 (TKN)	3.2 (NH_4^+) 1.5 (TP)	oct-14	2.7	90 (BOD) 105 (NH_3)	49 (TP)
Kern & Idler. 1999	Germany	Dairy and domestic (1:7)	Septic tank	VF	1.5 m		86 (COD) 35 (TN)	67 (NH_3) 55 (TP)	18.2 (COD) 2.8 (TN)	2.1 (NH_4^+) 0.3 (TP)	3	-	89 (COD) 63 (TN) 25 (NH_4^+) 32 (NO_3^-) 4.7 (TP)	
Newman *et al*. 2000	USA	Dairy parlor		FWS		3-20	94 (TSS) 85 (BOD)	68 (TP) 53 (TKN)	17.0 (BOD) 9.0 (TSS) 0.68 (TKN)	0.19 (TP)	41 (<12)	4	692 (BOD) 130 (TSS) 52 (NH_4^+) 14 (TP)	
Knight *et al*. 2000	USA: 38 cases	Farm		FWS (/HSSF)					<10.3 (BOD) <10.3 (TSS) <2.8 (NH_4^+)				Secondary and partial nitrification	
Mantovi *et al*.. 2003	Italy	Dairy parlor and domestic[b]	Imhoff tank	2xHSSF	100 cm		Global (IT +CW) > 90% (TSS, COD, BOD) 48.5 (TKN) 60.6 (TP)		12.7 (BOD) 27.0 (COD) 10.8 (TSS)	2.0 (TKN) 0.42 (TP)	10	1.9	28 (BOD) 60 (TSS) 98 (COD) 33 (TKN) 5 (TP)	
Dunne *et al*.. 2005	Ireland	Farm		FWS			99 (TSS) 99 (BOD)	96 (NH_3) 93 (SRP)	3.6 (BOD) 1.0 (TSS)	0.03 (SRP) 0.07 (NH_4^+)		114	20 (BOD) 1.6 (NH_4^+) 11 (TSS)	
Lansing & Martin. 2006	USA	Farm		CW Hybrid (11 units in series)			99 (BOD) 99 (NH_3)	79 (PO_4^{3-})			10	-	5.2 (BOD) 0.07 (NH_3) 0.53 (NOx)	4.4 (PO_4^{3-})
Healy *et al*.. 2007	Ireland	Dairy parlor	Septic tank	ISF / VF with recirculation			99 (BOD) 86 (TN)		30 (COD)			5	BOD removal and complete nitrification	

[a]IT: Inhoff tank, ISF: Intermittent sand filter .[b]Domestic effluent means a dilution of dairy parlor effluent in this case, reducing 70% concentration. Effluent from holding room is separated to the slurry tank, not contributing to reported concentration. Pretreatment, IT (40 PE), includes a filter and reaches removal rates of 64% TSS, 48% COD and 35% BOD in the original mixed effluent.

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Most of the influent nitrogen was in the form of organic N (>85%), while ammonium and nitrate were around 8-14% and 2-4% respectively. The average removal of biochemical oxygen demand (BOD_5) was higher than 90%.

The treated effluent had a final quality that would allow the use for direct irrigation in agriculture.

Tannery Wastewater

CWs have been used for secondary or tertiary treatment for the treatment of tannery wastewater as a cost-effective and environmentally friendly technology. Calheiros *et al*., (2014) reviewed the tannery sector in Portugal and the performance of CWs for treating this wastewater. Depending on the kind of treatment, tannery wastewater has different BOD/COD ratios, ranging from 0.23 and 0.66 for water that had primary treatment, and from 0.1 to 0.65 for water after secondary treatment. As shown by the ratio, these waters are not easy biodegradable, if compared to domestic wastewater or even with most industrial wastewater. When considering CW as part of a treatment system an efficient pretreatment and the primary treatment and precious treatments are of upmost importance before the wastewater is conducted to the CW (Calheiros *et al*. 2007). The reported treatments for tannery wastewater CWs are conventional primary treatments and an activated sludge as a secondary treatment.

Regarding the construction and establishment costs CWs correspond to circa 10–20% of the conventional secondary biological treatment and the running costs account for approximately 10% (Daniels, 2007), although it may vary according to the country where the system is implemented. Dias *et al*., (2006) reported that in the Portuguese scenario the capital costs, with pretreatment included, are equivalent to a conventional treatment, however, concerning the operation and maintenance cost the same authors state they are at least 6–20 times lower.

Efficiencies of CWs treating tannery wastewater in Portugal ranged from 2.3 to 160 g COD/m^2·d and 0.6 to 61 g BOD/m^2·d removed.

Focusing on the phosphorus and nitrogen removal in tannery wastewater, Kadlec *et al*. 2000 reported that the performance is lower when compared to the organics removal, although in some way expected for this type of systems. For instance, Calheiros *et al*. (2008), reported that for an inlet of 0.21–0.43 mg P/L the outlet was 0.18–0.35 mg P/L and for an inlet of 63–87 mg NH_3/L the outlet was 40–56 mg NH_3/L. Removal of PO_4 reaching 61% (inlet 15 ± 7 mg/L, hydraulic retention time (HRT) of 12.5 d) has been reported for the treatment of tannery wastewater by CW in Bangladesh (Saeed *et al*. 2012a). High removal of NH_4^+ (99%) from tannery effluents has been reported by Kucuk *et al*. (2003) for an inlet of 20 mg/L at a HRT of 7 days.

Greenhouse Gas Emissions (GHG) in CWs

Greenhouse gases namely CO_2, CH_4 and N_2O are emitted from both natural and constructed wetlands. During the mineralization of organic matter, CO_2 production is desirable but, on the other hand, CH_4 and N_2O emissions must be avoided due to their high greenhouse effect potential (they have a global warming potential of 34 and 298 relative to CO_2 over a 100 year time horizon (Myhre *et al*., 2013).

HSSF CWs have the bottom as the principal anaerobic environment, and the zone close to the water surface and the rhizosphere as aerobic zones. Both organic and hydraulic loading rates are key operational variables that can influence the importance of anaerobic and aerobic roles, together with water level as a design variable. As a result, these factors determine the influence on methane generation and emission (Pedescoll *et al*., 2011).

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Methane emission rates from CWs treating different types of wastewaters can vary from -208 to 36,792 mg $CH_4/m^2 \cdot d$ (Pei-Dong *et al*., 2002; Wang *et al*., 2008) but more usual range is from 0 to 2000 mg $CH_4/m^2 \cdot d$. Some important factor affecting the measured gas emissions are the position on the length of the wetland in the direction of flow, and the season of the year (Tanner *et al*., 1997; Mander *et al*., 2003; Johansson *et al*., 2004; de la Varga *et al*., 2015).

According to the literature review reported by Mander *et al*., (2014), CO_2 emissions are significantly lower in FWS than in HSSF CWs, with average values of 2208 and 4440 mg $CO_2/m^2 \cdot d$, respectively. Additionally, in VF systems, methane emissions were significantly lower than in HSSF and FWS (average values of 97, 178 and 142 mg CH_4 $m^2 \cdot d$, respectively). For N_2O emissions, no significant differences were found for several types of CWs (average values for FWS, VF and HSSF of 2.2, 2.9 and 3.1 mg $N_2O/m^2 \cdot d$, respectively). As a conclusion, Mander *et al*., (2014) reported that hybrid systems (VF, HSSF and/or FWS) perform better for treating wastewater and reducing direct greenhouse gas emissions. The emissions are affected by the loading, the operation mode as well as the local climatic conditions.

The emission factor for methane might be defined as the ratio of carbon emitted as methane to the total organic carbon influent to the CW (CH_4/TOC_{in}). Mander *et al*., (2014) reported that the greatest emission factor for methane was found for FWS (average of 16.9%), followed by HSSF (4.5%) and VF (1.2%). These researchers reported that significant differences of emission factor for N_2O (percentage ratio of N_2O emitted to influent total nitrogen TN) were found for HSSF (0.79%), FWS (0.13%) and VF (0.023%). Moreover, according to Mander *et al*., (2014), a significant correlation between the influent rate of total organic carbon (TOC) and the methane emission rate and between the influent rate or total nitrogen (TN) and N_2O emission rate for all types of studied CWs was found as well.

Data about gas emissions from CW treating industrial effluents is still scarce. Tanner *et al*., (1997) found an average methane emission rate of 225 mg $CH_4/m^2 \cdot d$ (standard deviation SD of 28-482) in a HSSF treating dairy wastewater, with a surface loading rate from 2.5 to 4.2 g $BOD/m^2 \cdot d$. Maltais-Landry *et al*., (2009) reported an average methane emission rate of 20 to 120 mg $CH_4/m^2 \cdot d$ in an aerated HSSF pilot plant treating fish factory effluent. De la Varga *et al*. (2013b) reported methane emissions ranging from 143 to 1899 mg $CH_4/m^2.d$ for HSSF system treating winery wastewater while carbon dioxide emissions in this system ranged from 1783 to 6137 mg $CO_2/m^2 \cdot d$.

Economics of CWs

CWs include mainly two types of costs: capital costs (construction, engineering and indirect costs) and operation and maintenance (O&M) costs. The main difference between FWS and subsurface flow system is the amount of gravel media which affects the construction costs. Although it is not possible to stablish universal cost guidelines, every system shares a similar set of construction components. Kadlec and Wallace, (2009) reported some equations for calculating costs of FWS and HSSF systems depending on surface needed or flow rate. As an example, for a 1 ha FWS system, total costs would be $480,000 (for 2006 USD), which means $48/m^2$.

Area:

FWS: $C=194A^{0.690}$ $R^2=0.79$ $0.03<A<10{,}000$

HSSF: $C=652A^{0.704}$ $R^2=0.75$ $0.005<A<20$

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Flow:

FWS: $C=518A^{0.729}$ $R^2=0.79$ $1<Q<5{,}000{,}000$

HSSF: $C=561A^{0.498}$ $R^2=0.76$ $0.5<Q<10{,}000$

where:

A= wetland area, ha

C=cost, 2006 dollars in thousands

Q=flow rate, m^3/d in thousands

DiMuro *et al*., (2014) reported a study in which a comparison of economic and environmental costs of a constructed wetland vs. a sequential batch reactor (SBR) was assessed. The selected industry was the wastewater treatment facility of a large industrial complex containing several manufacturing units involved in the production of plastic resins and other organic chemicals. Wastewater and storm water captured in containment areas are routed through the wastewater treatment system. The input variables for the design of both systems were flow rate ($6.9 \cdot 10^6$ m^3/year), total organic carbon (TOC, 500 mg/L), COD (1500 mg/L), BOD_5 (875 mg/L) and TSS (918 kg/d). The financial results indicated that the total net present value savings calculated for implementing the CW instead of the SBR reactor was $282 million over the project's lifetime (30 years). The Life Cycle Assessment (LCA) demonstrated that the lower energy and material inputs to the CW resulted in lower potential impacts for fossil fuel use, acidification, smog formation, and ozone depletion and likely lead to lower potential impacts for global warming and marine eutrophication.

CASE STUDIES

Winery Wastewater Treatment

Winery wastewater is generated by the various processes and operations carried out in wine production, and wastewater comes mainly from the water used to wash equipment and bottles and from the cooling processes.

Winery wastewaters contain COD concentrations ranging from 500 to 45000 mg/L and total suspended solids (TSS) from 12 to 7300 mg/L, while BOD_5 is about 0.4-0.9 of the COD value (Shepher *et al*., 2001; Petruccioli *et al*., 2002; Masi *et al*., 2002; Mosteo *et al*., 2008). The concentrations of nitrogen and phosphorus compounds in winery wastewater are usually low and the pH varies from 3.5 to 7 (Serrano *et al*., 2009).

Conventional biological treatment systems do not effectively treat wastewater generated by wineries (Petruccioli *et al*., 2002; Mosteo *et al*., 2006), as wastewater from these facilities are highly concentrated in terms of COD and show highly variable flows and loadings, both daily and seasonally. CWs have also been considered as a means to treat this wastewater (Masi *et al*., 2014). Wetlands remove efficiently

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organic matter, excess nutrients and other pollutants. CWs are robust and can assimilate large and highly variable flows and organic loadings and neutralise low pH.

As a complement and to ensure the best performance, anaerobic pretreatment such as hydrolytic upflow sludge bed (HUSB) digesters are recommended. HUSB is an intensive, efficient and low-cost technology for domestic wastewater and industrial wastewaters (Álvarez *et al*., 2008) that can also be applied to the pretreatment of winery wastewater (de la Varga *et al*., 2013a).

Winery Wastewater Treatment in Hybrid CW System in Spain

In this section the authors summarize the results obtained on a full-scale hybrid CW with an anaerobic digester as primary treatment, followed by CW which combined VF and HSSF units for treating winery and a touristic and restaurant wastewater component (which provided higher nutrients concentration than a normal winery). (Serrano *et al*., 2011; de la Varga *et al*., 2013b). The wastewater was previously pretreated in an HUSB digester (de la Varga *et al*., 2013a). The system installed showed an average removal efficiency of 76, 26 and 21% of TSS, COD and BOD respectively. The anaerobic digester mainly initiated the ammonification of organic nitrogen compounds and the acidification of organic matter.

Description of the Plant

The full-scale plant was designed to treat the wastewater coming from a winery with a production capacity of 315000 L of white wine. The touristic and restaurant component increased nutrient concentration of wastewater.

The constructed-wetland system consisted of a HUSB anaerobic digester 6 m^3 in volume, a VF CW 50 m^2 in area and three HSSF CW at 100 m^2 each. The water depth for HSSF1 was 0.3 m, while the depth for HSSF2 and HSSF3 was 0.6 m, respectively. CWs were planted with three to four units/m^2 of *Phragmites australis* (VF) and *Juncus effusus* (HF) and started up on April 14th 2008.

CW Performance and Efficiency

Average influent temperature was 20.2±4.5 ºC, while effluent temperature was in general 3 ºC lower (17.2±4.6 ºC in average, ranging from 12 to 28 ºC). Average influent pH was 6.41±0.95, while effluent pH was 6.7±0.5 (ranging from 5.4 to 7.4), and then the wastewater increased pH in 0.5 units passing through the HSSF wetlands.

The average surface loading rate (SLR) to the VF ranged from 43 to 466 g COD/m^2d and from 22 to 296 g BOD_5/m^2d, while COD removal ranged from 29% to 70% and BOD_5 removal from 36% to 68%. Thus the VF unit reached high surface removal rates of up to 153 g COD/m^2d and 107 g BOD_5/m^2/d.

Influent TSS levels to HSSF were generally low as they had been efficiently removed in the preceding steps of the plant (mainly in the HUSB reactor). Therefore, SLR of suspended solids remained low (ranging from 0.5 to 5 g TSS/m^2·d) and solids have been efficiently removed in HSSF units, which reached TSS effluent concentrations below 44 mg/L (17 mg/L on average) and TSS removal efficiencies of about 74%.

Influent COD and BOD_5 were highly variable, ranging from 50 to 4000 mg COD/L and from 12 to 2400 mg BOD_5/L (n=68). Higher influent concentrations and flows were registered for vintage phases of years 2008 and 2009, respectively. This led to highly variable SLR to the HSSF units, ranging from

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4-85 g TCOD/m^2·d and from 2 to 49 g BOD_5/m^2·d. TCOD and BOD_5 removals were generally between 60 and 80% but clearly decreased when the influent concentration or the SLR applied increased.

Regarding nutrient removal, variable concentrations of nitrogen and phosphorus compounds were present in the influent, due to touristic and restaurant component of the wastewater. Influent TKN of VF CW was between 19 and 109 mg N/L (average of 52.9 mg N/L) and the VF effluent ranged from 11 to 63 mg N/L (average of 26 mg N/L). Ammonium concentration ranged from 1 to 101 mg NH_3/L in the VF influent (average of 28 mg NH_3/L) and from 0.6 to 76 mg N/L (average of 19 mg NH_3/L) in the VF effluent with an average removal of 32% (made on average values). This relatively low nitrification might be due to high organic load in the VF CW which primary consumed the oxygen present and subsequently reducing nitrification. Phosphate in the VF influent ranged from 0.28 to 5 mg P/L (average of 2.3 mg P/L) and from 0.9 to 6.3 mg P/L (average of 2.4 mg P/L) in the VF effluent. HSSF effluent concentrations of TKN, ammonia and phosphate ranged from 12 to 52 mg N/L (average of 25.2 mg N/L), from 2 to 52 mg (average of 12.5 mg N/L) and from 0.3 to 6 (average of 1.9 mg P/L), respectively. Removal of nitrogen compounds and phosphate in HSSF units was reduced, ranging from 6 to 29% on average. Limited data indicates that polyphenols removal averaged 39% in HSSF units.

The full-scale hybrid CW system successfully treated winery wastewater. Surface removal rates up 41 g COD/m^2·d, 25 gBOD_5/m^2·d and 4.4 g TSS/m^2·d were reached by the overall (VF + HF) system. Overall percentage removals ranged from 54% to 93% of COD, 45% to 95% of BOD_5 and 75% to 94% of TSS. The overall system also removed up to 1.4 gTKN/m^2·d (52%), 0.7 gNH_3/m^2·d and 0.04 g PO_4^{3-}/m^2·d (17%).

Upgrading of a CW System for Winery Effluents in Italy

The Cecchi system in Italy (Masi *et al*., 2002; 2014) consisted of an Inhoff tank, a single stage of HSSF of 480 m^2 and a FWS of 850 m^2. Due to growing production of the winery, the treated flow increased from 35 m^3/d to 70 m^3/d. An upgrading of the treatment plant was developed in 2009, with a French reed bed (FRB), followed by four parallel HSSF, with the existing FWS and optional sand filter before discharge into fresh water (Gena River). Results from a 3 years period show a COD reduction of up to 96% even at peak loads while COD average removal efficiency was 75%. For the HSSF unit, average removal was 87%.

Further Considerations about CW Design Criteria for Winery Wastewater Treatment

Hybrid systems of CWs can themselves treat winery wastewater, as well as a complement to other systems like sequential batch reactors (SBR) or activated sludge. For small wineries producing less than 100.000 L wine/year, a septic tank +HSSF CW with more than 5 days of HRT during peak flow period can ensure a proper treatment for fresh water discharge or for irrigation purposes (Masi *et al*., 2014).

A good pretreatment or primary treatment to decrease the solids and the organic particulate matter is important. For small wineries, a septic tank could be enough if a sort of resting period of 10 months with lower organic and hydraulic loads takes place. For bigger wineries, this first stage (SBR, FRB, etc.) should remove 40-50% of pollutants from the raw wastewater.

Some of the wineries have additional nutrients in the wastewater, like black waters from employees, small households or restaurants. No supplementation of nutrients has been necessary, as well as neutralization of low pH. If we do so, performance of CWs might be increased, and this is a good point for future research.

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HIGHWET Project for Food Processing Industry

The research project "Performance and validation of HIGH-rate constructed WETlands" (HIGHWET), under the European call FP7-SME-2013-1, was developed during years 2013 to 2015. There were two pilot plants, one located in Spain to treat domestic wastewater, and the other "real" plant was implemented in Denmark, to treat the discharges generated from a food production factory, a house inhabited by the factory owners and a small dairy factory.

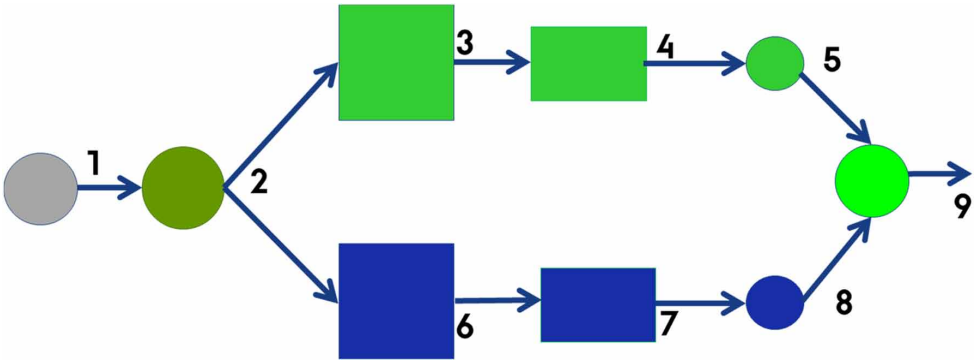
The final design includes a combination of the anaerobic treatment HUSB reactor, aerated *CWs* and conventional CWs. In addition, the system was fitted with reactive media to improve phosphorus removal in order to achieve discharge limits.

Figure 2 presents the layout and the different units of the treatment plant. During the project, inflow was limited to 1000 L/d to control the process. After a pumping well, water is conducted to the primary treatment, which is a HUSB reactor. Then, the system is split in two treatment trains. The first one (aerated train) is composed by an aerated VF, an aerated HSSF and a phosphorus removal well, filled with tobermorite. The second train (conventional train) has a conventional VF, an aerated HSSF and a second phosphorus removal well, with polonite. Both VF beds have an area of 16 m^2 while the HSSF beds are of 3 m^3 followed by wells of 1 m^3. The aeration systems installed in the beds supply air to the beds using individual blowers that provide atmospheric air to increase the oxygen availability and improved the aerobic depletion processes of pollutants. The aeration time to each wetland cell can be regulated depending on the operation planned. The aerated train treated 80% of the total flow, and conventional train treated 20% of the total flow.

Operation of the Plant

During the plant operation, pollutant loadings, aeration times and hydraulic loadings by recirculation of VF effluent to the pumping well after the HUSB reactor were changed to determine the capacity of the plant. In this sense, five campaigns were carried out under different operational conditions. As the

Figure 2. Sampling points along the treatment trains 1) inlet; 2) after the HUSB, 3) after the aerated VF; 4) after the aerated HF bed; 5) after the P removal filtered filled with tobermorite 6) after the non-aerated bed 7) after the aerated bed 8) after the P removal filter filled with Polonite 9) final effluent



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wastewater produced at the site did not reach the projected organic and nutrient loadings, a system with a prepared solution was installed to increase the pollutant and hydraulic loads. The loading solution was prepared using a blend of pig manure, molasses, starch, urea and fertilizer.

After plant start-up (campaigns 1 and 2), several monitoring campaigns with high nutrient loadings were carried out (campaigns 3, 4 and 5). During campaigns 3 and 4, aeration schemes were changed in order to increase the total nitrogen removal, and during campaign 5, recirculation (increasing to around 80% the hydraulic load to each bed) from the VF effluent to the well after the HUSB was implemented. Following, the efficiency reached during campaign 3 is presented (Table 3). Similar results were obtained for campaigns 4 and 5.

The third campaign took place in May when temperatures increased and the local weather was mild. The vegetation growth was better in the aerated beds, due to higher water flow that allowed major nutrient availability. On the other hand, plant growth in the passively aerated beds was poor. The water temperature did not change too much, compared to the winter temperatures, due to low temperatures at night. As expected, anaerobic conditions were prevalent before and after the HUSB digester. After this primary treatment, dissolved oxygen was close to saturation generally, except in aerated beds when aeration regime was decreased to improve denitrification.

Total suspended solids were efficiently removed, with a concentration in the final effluent below 3 mg/L. A high COD percentage was removed at the HUSB reactor, and further COD removal was high in both VF beds which reached similar effluent concentrations. Along the system, biological oxygen demand (BOD_5) was removed to very low concentrations.

During the third campaign, the HUSB reactor removed around 20% of NH_4^+, so NO_3^- was denitrified effectively in this stage. After the HUSB reactor and in both treatment trains, N-removal was effective producing nitrified effluent with a NH_4^+ concentration below 1 mg/L. The results show that the NH_4^+ nitrified in the aerated VF bed is also denitrified during the shut-off time after the oxygen supply. The conventional VF bed does not show the same denitrification rates as the aerated bed and the effluent from the bed has a NO_3^- concentration of 40 mg/L. Even though NO_3^- seems high in the outlet, concentration in

Table 3. Pollutant concentrations at the different sampling points during campaign 3. Concentrations are presented in average. BDL: Below detection limit

Sampling point	TSS (mg/L)	COD (mg/L)	BOD_5 (mg/L)	NH_4^+ (mg/L)	TN (mg/L)	TP (mg/L)
Inlet	117	5268	4167	250	382	25.1
After HUSB	25.2	2055	1383	197	201	18.2
Aerated train						
After aerated VF	22.6	211	44	5.2	11	5.2
After aerated HSSF	33.6	156	6	0.12	9	4.0
After tobermorite	33.8	156	6	0.14	11	2.2
Conventional train						
After VF	86.5	174	3	0.10	42	2.9
After aerated HSSF	101.7	82	2	BDL	40	1.2
After polonite	102.7	61	2	0.7	45	0.5

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the inlet was much higher and denitrification was considerable in the passive VF. Total nitrogen followed the same dynamics as the nitrogen species. Phosphorus removal was effective in both tested materials, but the P concentration in the effluent after tobermorite material was higher than the Danish limits.

In all campaigns, the percentage of total nitrogen removal was higher than 80%. The HUSB reactor removed between 30% and 40%, corresponding to NO_3^- denitrified. The aerated VF bed performance of total nitrogen removal was better for periods with discontinuous aeration compared to continuous aeration, as well as with recirculation of nitrified VF effluent. The non-aerated VF nitrified quite well, and removed total nitrogen as well, which means that some parts of the bed have good denitrifying environmental conditions.

CONCLUSION

Constructed wetlands are engineered systems that have been designed to utilize natural processes involving wetland vegetation, soils, and their associated microbial assemblages to assist in treating wastewater. In CWs, removal of pollutants takes place due to physical, chemical and microbial processes including, among others, sedimentation, sorption, precipitation, evapotranspiration, volatilization, photodegradation, diffusion, plant uptake, and microbial degradation (i.e. nitrification, denitrification, sulphate reduction, carbon metabolization, etc.). The most used types of CWs are the FWS, the HSSF and the VF. For improving the performance and the removal of pollutants and nutrients, a combination of these systems, the hybrid systems, may be used. CWs are also used to recover nutrients from the macrophyte biomass and particularly from sludge in the sludge treatment wetlands. Nowadays, CWs have been applied to the treatment of different kind of wastewaters as such as refinery and petrochemical industry effluents, food industry effluents including abattoir, dairy, meat, fruit and vegetables processing industries, distillery and winery effluents, pulp and paper, textile, tannery, aquaculture, steel and mixed industrial effluents.

The reached efficiencies can vary depending on the wastewater characteristics and the system design features and operational conditions.

Regarding environmental conditions, CWs can work in extreme weather conditions ranging from the coldest one to tropical conditions. TSS, COD and BOD_5 are potentially removed in any kind of CWs if proper design and loading rates are provided.

On the other hand, nitrogen removal requires the combination of adequate oxic and anoxic/anaerobic conditions which can be provided by hybrid systems and other intensified systems involving water recirculation or artificial aeration.

Phosphorus removal requires extensive application of CWs (large footprint) or specific filtering substrates to absorb phosphorus compounds.

As reviewed, CWs are particularly suitable for the treatment of dairy parlour wastewater, cheese production wastewater and other food industry wastewater, as well as for tannery and winery wastewater.

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KEY TERMS AND DEFINITIONS

Hydraulic Loading Rate (HLR): Amount of influent wastewater per unit of wetland surface. It is often expressed as mm/d, which means $L/m^2 \cdot d$, or cm/d.

Hydrolytic Up-Flow Sludge Blanket Reactor (HUSB): Up-flow anaerobic reactor in which only hydrolysis and sedimentation of particulate organic matter and solids are aimed, avoiding methanogenic reactions.

Surface Loading Rate (SLR): Amount of a certain pollutant applied to a wastewater treatment system per surface and time units.

Surface Removal Rate (SRR): Amount of a certain pollutant removed in a wastewater treatment system per surface and time units.

ENDNOTE

[1] PE: People equivalents.

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Section 3
Tools and Technologies

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Chapter 28
Economic Instruments for Sustainable Environmental Management

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ABSTRACT

Environmental pollution has been continuously threatening the world. In the combat with environmental pollution problems, waste management authorities, in compliance with the "User Pays Principle-USP", apply the "Polluter Pays Principle-3Ps" to the waste generators. Thus the resource users and the waste generators will be paying a fee for the resources and services they are using. They can be summarized as water fee, wastewater discharge fee, effluent permit fee, air emission fees, solid waste disposal fee, landfill tax, and hazardous waste tax and product charge, Advance Disposal Fee (ADF), Ozone-Depleting Chemicals (ODC), government product charge and road user fees. The main purpose of charging a fee is to encourage the users and the polluters to reduce the amount of pollutants they are generating and disposing into the environment. These fees can also be named as "a pollution charge fee", "user charge fee" or "product charge fee". This chapter outlines the many existing waste fee models.

INTRODUCTION

Environmental pollution has reached to such a high level which causes global disasters that threaten the public health and natural resources. The natural resources such as water, minerals and fuel are not limitless. Extraction of virgin materials and usage of these amenities carelessly will eventually end up as waste in the form of disposals/emissions to land, air and water (European Commission, 2011a; Söderholm, 2011). Throughout the world the waste amounts are growing, and so is the sensitivity and concern about how to deal with them and the corresponding environmental problems (Bruvoll, 1998). According to the research studies conducted, global municipal solid waste amounts will increase at an annual rate of 2.4 per cent through the year 2019 (Beede & Blom, 1995). The waste management au-

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thorities have been having difficulties both in handling and financing the environmental protection and clean-up activities lately. On the other hand waste management is also important for achieving several other environmental quality objectives including "reduced climate impact" and "a non-toxic environment". Waste management in many countries has undergone significant changes during the last decades (Finnveden, et.al., 2013; Broome, 1992).

In the combat with the generated environmental pollution problems, several policy instruments such as "Polluter Pays Principle-3Ps" in compliance with the "User Pays Principle-USP" can be effective and possible to implement. Thus people will be paying a fee for the services they are using. This fee can also be named as "a pollution charge fee", "user charge fee" or "product charge fee". Although all of these terminologies are used interchangeably, they have subtle differences in their meanings. A pollution charge fee is a fee based on the quantity of pollutants that are disposed into the environment. A user charge fee is a fee paid for using natural resources or for the collection and/or disposal of pollutants (European Commission, 2011b). A product charge fee is a fee imposed on products that are having negative impacts on environment. While "tax" is used for the revenue rising instruments, "fee" and "charge" are the applications used to offset costs to the government. Those charges and fees collected are retained to be used to supplement the budget allocated for the protection of environment and management of wastes (ISWA, 2011; Kocasoy, 2014).

Most environmental taxes are designed to fund environmental protection activities. The economic rationale behind them is that those who generate and cause environmental pollution should bear the costs of both damages to the environment and the administrative costs incurred. To be economically efficient, environmental taxes should include both of these costs. The fee should cover all the costs of the collection, treatment and final disposal of wastes as well as the costs of the administrative work and the operation of the waste management, treatment and disposal facilities. The most important issue in the design and the application of the waste fee model is the "fairness"

ENVIRONMENTAL FEES-TAXES

In the following sections various environmental fees and fee models will be discussed. After the discussion of some of the environmental fees such as water fees, wastewater discharge fees, air emission fees, permit fees, air toxics and ozone-depleting chemicals emission fees, solid waste disposal fees and landfill fees, criteria in the design of the solid waste disposal fees and the different fee models will be explained in detail.

Water Fees

Water fees are classified as user fees for groundwater, surface water or drinking water supplied by waterworks and as fees for direct or indirect water discharges. The idea behind the water user fees is that water is not a free unlimited resource but rather a scarce commodity that should be priced to avoid inefficient use and environmental pollution. The water fees are designed to raise budget to recover costs of providing service rather than the allocation of the scarce resource among competing needs (Bruvoll, 1998; Smith, et al., 2011).

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Direct Water Discharge Fees

The rationale for discharge fees is being in compliance with the Polluter Pays Principle. While discharge fees in some countries varied according to discharge volume and toxicity, at some others fees are charged according to discharge volume alone. The criteria used by different countries in setting fees include the purpose of the water use, the characteristics of the receiving water, and the type of the facility releasing the discharge. (Toj, 2008).

Indirect Water Discharge Fees

Households and businesses that discharge their wastewater into Publicly Owned Treatment Works (POTWs) are subject to indirect discharge fee. Fees for Publicly Owned Treatment Works (POTWs) are sometimes based on the size of the population that is connected to the local sewage system. Most of the time, the water and wastewater utilities that service households or businesses are one and the same. Then a single invoice includes both water use fee and discharge fee. In most cases water used is measured but wastewater discharged is not. They are assumed to be equal in volume to water usage, consumption. Some discharge fees for large businesses are based not only on water use but also on discharge toxicity. This is an incentive for the businesses to reduce the volume and the toxicity of their discharges.

The effect of the water user fee on the reduction of water usage and consequently polluting potential depends largely on the elasticity of the demand for water, that is whether demand is responsive to changes in price or not. If the demand is inelastic, an increase in user fees will not affect consumption behavior in a significant way. If demand is elastic, however, consumption behavior is going to be changed by raising the water usage fee. Although water demand is often assumed to be inelastic, research studies conducted indicated that household water demand is inelastic in winter but elastic in summer. The researches also showed that water demand by industrial and agricultural users is sensitive to price changes (Piotr & Malecki, 2010).

To promote water conservation, there are suggestions about the use of rate schedules that impose higher rates per certain cubic meter after the consumption of certain volume of water.

Effluent Permit Fee Structures

The primary purpose of effluent fees is to discourage high volume of wastewater discharges to prevent receiving water media pollution. Then the second purpose is to raise revenue for the administrative costs of the effluent permit program. Most of the time fees are based on easily measured parameters that are related to discharge characteristics. At most of the cases fee structures have broad classes for discharge volume or toxicity level, or both. Since these structures impose the same fee within a set volume or toxicity bracket, polluters have no incentive to limit discharges unless they can move from a lower fee bracket to a higher one.

At some countries the annual permit fee is determined by a worksheet that assigns points on basis of several factors such as flow volume and type; pollutants released; heat load; potential public health threat; facility complexity and the designation of a facility as major or minor depending upon how many people it employs. The points are multiplied by a rate factor of certain dollars per point for municipal facilities and higher amount of dollars per point for industrial facilities to determine total annual fees (Speck, 2006).

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At some other countries annual fees are based on the threat to water quality and the complexity of the permit. The characteristics are classified at three categories as categories I, II, and III for the level of threat to water quality; and as categories a, b, and c for the complexity of the permit. Permit holders with an I-a rating (the greatest threat to water quality and the most complex permits) pay the highest fees and III-c permit holders pay the lowest fees annually. Some countries also charge Bay Protection and Toxic Clean-up fees to dragging operations, boat construction and repair facilities and beach replenishment activities in addition to the annual permit fee. The highest Bay Protection Fee is charged to the I-a permit holders while the lowest fee is charged to the III-c permit holders (Ocean Conservancy, 2007; Moore et.al, 2001).

The effluent fee system in which the most harmful pollutants are taxed at the highest rate per unit volume has potential incentive for the polluters to reduce both the quantity and the toxicity of pollutant releases (Nordic Council of Ministers, 2006).

Air Emission Fees

Countries use emission fees as an air quality management tool. Most of them impose fees for issuing air emission permits. Some of them also charge fees on Volatile Organic Carbon (VOC) emissions.

The authorities impose permit fees to recover the administrative costs. They charge a fee of certain dollars/Euro per unit weight of emissions of air toxics. The rate increases as the pollutant amount moves to a higher bracket. Each level of pollutants has different rates. Some countries base their fees not only on the pollutant level, but also on the pollutant's potential harm to the environment. Facilities that exceed their allowable emission levels must pay excess emission fees. The excess emission fees for the pollutants such as Sulphur oxides (SOx), nitrogen oxides (Nox), Volatile Organic Carbons (VOCs) and particulate matter are about the same as the regular fees while emission fees for carbon monoxide, asbestos, cadmium, hexavalent chromium, chlorinated dioxins, 1.3 butadiene and lead is approximately twice as high (European Commission, 2011a; Söderholm, 2009).

Solid Waste Disposal Fees

Variable rate programs are used for the design of the solid waste disposal fees. Application of the solid waste management fee is a relatively new trend for the household wastes. The primary purpose of these fees such as the household waste collection fees/taxes, landfill fees/taxes, and hazardous waste disposal fees/taxes is to discourage waste generation and encourage recycling. Unfortunately, they also are incentives for the disposal of waste illegally or to transport waste to other locations where disposal is cheaper (Pires, et. al., 2011).

According to Fischer and his colleges (2012) there is some variation regarding the waste types covered by the landfill tax, but this variation is not very large between countries. Tax is charged on construction and inert wastes; residues, hazardous waste and biodegradable waste. In some countries the tax only covers non-hazardous waste (European Commission, 2011b).

The landfill tax level varies between countries. Different tax levels have been depending on the waste type. Inert waste types, residues from incineration of waste or construction waste generally have a lower tax level than mixed municipal waste. Also most countries operate with only a limited numbers of tax levels (1-3), while some countries have more differentiated tax system. Increased taxation levels have a considerable economic incentive for diverting waste away from landfills to other treatment forms (Mayers, 2011).

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The main aim of the tax is to reduce the amount of waste that is landfilled, and to make the environmentally friendly handling of waste more attractive. Several tax rates are charged to reach the aim and as the tax rate increases, the diversion of waste from landfill increases (Kinnaman, 2010).

Hazardous Waste Tax

Taxes charged to hazardous waste have different rates based on the final removal method. Some countries charge higher tax rates for landfilling than for incineration. In some other countries, taxes per ton vary according to the type of waste. All the taxes are based on the tonnage of the hazardous waste to be treated. Removal fees vary by quantity removed with rates fixed within a given range of tons per year.

There are two fees applied to raise revenue and to encourage waste minimization. The fee of the tonnage of hazardous waste sent to landfills is lower than the incineration. Although this leads to the decline in the tonnage sent to the landfilling, it is difficult, however, to determine to what extent this decline is due to the fees, because there are many other factors that influence the generation and disposal practices. According to a research conducted, due to the differences in the disposal type, the amount of waste incinerated rose, but it did not increase as much as the amount of waste sent to landfills declined. Also according to another research about the impact of the landfill and incineration taxes on the generation of four types of chlorinated solvent wastes from metal cleaning industry, the quantity of the hazardous wastes sent to landfills or incinerators was very sensitive to the tax. The other outcome of the research was that taxes encouraged generators to choose incineration or other treatment options rather than landfilling as their waste management method. However, the estimated impact of these taxes was minor because the fees were low in comparison to the total costs of waste management (Watkins, et al., 2013).

The social cost of hazardous waste generation should also be reflected at these taxes in order to maximize the efficiency of the taxes. This cost depends on the factors, such as the type of waste, method of disposal, geographic location which are difficult to assess and incorporate into the fee structures. Beside these, if taxes are too high, illegal dumping will be encouraged and it will cause enough environmental damage to offset the increased efficiency achieved by fees (Mayers, 2011).

Product Charges

Product charges are imposed on either a product or some characteristic of that product whose disposal causes environmental pollution. These are charges on chemicals, fuels, transportation and transport equipment. Fees charged to the products are a kind of advance disposal fee of the product for its proper disposal after the completion of its useful life. Therefore they have minimum effect on incentives for the reduction of the products.

Another mechanism is the take-back responsibility of the manufacturer who is responsible for the proper disposal of the wastes. This is called as the "extended producer responsibility" (Monomaivibool & Vassanadumrongdee, 2011; Watkins, et al., 2013).

Ozone-Depleting Chemicals

After the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer the production of ozone-depleting chemicals (ODCs) such as chlorofluorocarbons (CFCs) is taxed. The magnitude of the tax is determined by multiplying a base rate per unit weight of ozone-depleting chemicals produced or imported

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by an ozone depletion factor that is set by the Montreal Protocol. The ozone depletion factors indicate each chemical's damage to the ozone layer and vary according to the type of chemical. For example, methyl chloroform has a factor of 0.1, whereas Halon-1301 has a factor of 10.0, which means that methyl chloroform is less harmful to the ozone layer than the Halon-1301. The producers and importers of these chemicals as well as the products that contain these chemicals are responsible for paying these taxes.

Unlike most product charges, ODC tax has a significant incentive impact on the reduction of the ODCs consumption. They are either substituted or recovered for reuse (Mayers, 2011).

Government Product Charges

Some governments have imposed charges on some products such as beverage containers, refrigerators, furniture, tires, fertilizers, motor oil, pesticides and solvents. These charges are in the form of advance disposal fees (ADFs). Some governments also impose litter tax on the sale of some products which are commonly found in litter (Beck, 2007; Carlozo, 2008). Many governments impose severance taxes on the removal of minerals from the ground.

Another product charge is the tax imposed on the tires. Because of the lack of substitutes for tire, the incentive effect of tire charges on the buyers of tires is minimal. On the other hand, the system encourages the proper disposal of tires. Governments use the tire fee revenues to subsidize recycling of tires as well as the development of markets for end uses of used tires, such as rubberized surfaces, noise barriers, blasting mats, and rubberized asphalt pavement and for the clean-up of tire disposal sites.

Litigation has been pursued against manufacturers of products that damage the environment. In fact, entire communities have filed class action lawsuits to sue polluters, and these cases are typically based on two tort theories: negligence and nuisance. (Novotny, et.al, 2009).

There are also some governments charging fees for "hard-to-dispose materials "such as antifreezes and lubricating oils (Watkins, 2013).

Advance Disposal Fee (ADF)

Concern about toxic waste resulting from some technology products such as computers, telephones, and televisions, has given rise to the implementation of a legislation which is a consumer funded Advanced Recycling Fee (ARF). It is obtained at the point of purchasing the products. These fees are intended to pay for the costs of recycling the item and the cost of disposing any non-recyclable material properly. The fees, compared to the cost of the products, are minimal (Thompson, 2002; Hogg, 2012).

Some countries also imposed a low tax to a variety of containers. Containers made of plastic, plastic-coated paper, and glass that had average recycling rates of at least 50%; and glass, plastic, aluminum and steel containers having respectively 35%, 25% and 50% recycled content are exempt from this tax (Edjemo & Söderholm, 2008).

Although low ADF tax imposed on "white goods," such as refrigerators and freezers does not have a significant incentive effect, it generates revenues to manage the disposal of white goods.

Another aspect of the ADF is the option for the companies to work with other firms in the same sector to raise recycling rates, to increase the recycled content of packaging to obtain exemptions (Nicolli, et.al, 2012; Nakatani, et.al, 2010).

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Road User Fees

Tolls, which are the most common type of road user fees, are mostly unrelated to environmental protection. They are generally used for the road construction and maintenance.

However, the tolls designed according to the heavily usage of the road and the tolls varying according to the time of the day help the coverage of social costs of traffic congestion. One of these costs is the increased emissions per kilometer travelled. Congestion pricing is an important environmental management tool. The economic gains from congestion pricing can be more effective than any other traffic management tool. (Florida Department of Revenue, 2015).

Toll fees designed according to the time of the day should be announced in advance, so motorists can plan their trips accordingly. Drivers, by using windshield-mounted transponders, can pay toll-lane use without stopping at toll booths. Some countries exempt the vehicles having three or more occupants, public transportation vehicles, zero-emission vehicles, and vehicles with a disabled-person license plate paying the tolls.

SOLID WASTE FEE DESIGN

Waste management authorities at many countries are charging solid waste collection fee based on the volume or weight generated by the household. EPA is also encouraging variable rates. Variable rate programs are applied in different forms such as prepaid garbage bags required for collection, or collection fees that are based on the number of containers, the size of containers, or both of these characteristics. Some other communities have weight-based systems. Most popular ones are mixed programs that combine a fixed rate programs which entitles households to allow the collection of a pre-specified amount of waste and then incremental rates for amounts in excess of the maximum amount covered by the flat rate These programs are relatively easy and inexpensive to implement and they have the potential to reduce illegal dumping (Dahlén & Lagerkvist, 2010; Kocasoy, 2015).

Collection systems that require periodic billing are likely to be more expensive to administer than bag systems. On the other hand, the disadvantage of the bag system is the torn of the bags if they are handled improperly or opened by animals.

Charging waste fee has many constraints. People in some countries are not ready to pay for the waste they are generating and for the related services they are using. There are different models of waste management fees. Each of them has advantages and disadvantages. There is not a single model which can be accepted as “fair” by everybody.

There are many issues, which differ from region to region, to be considered in choosing the fee model. The issues to be considered in the development of a “fair-suitable fee model” are as follows:

- Fairness,
- Independence of fee-models and the collection system,
- Fixed and variable costs to be covered,
- Social effects,
- Administrative costs,
- Behavior / attitude of the residents and
- Influence of the waste authority (Hauer et.al, 2011; Ljunggren, 2011).

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General Requirements

There are many requirements to be met in developing waste fee. Some of them are legal requirements while the others are economic, financial and social aspects. The general requirement/request is the "fairness". Although there is not a single model that can meet all these requirements completely, the model developed and applied should be practical, suitable and appropriate for the region. General requirements of waste management fee models can be summarized as follows:

- The User Pays Principle should be applied,
- The fee should be based on the system's policy such as dispose or recycle,
- Each model should encourage people to generate less waste,
- Each waste generating facility should be within the public waste collection region,
- Some commercial and institutional waste generators prefer to take the responsibility of collection and disposal of the wastes themselves - "self-disposers",
- It should be simple, so that it can be applied very easily. It should be transparent and reduce both the regulation and the administration requirements,
- The fee should cover both the collection and disposal costs, there should be no differentiation between them,
- Fee should be collected either monthly or yearly,
- Differentiation between the "household waste" and the "commercial waste" should be made according to the waste composition and/or the amount of the waste (Hauer, et.al, 2011; Tyskeng, 2012).

Interrelation between the Collection System and the Fee Model

The waste fee model applied should be in compliance with the type of the waste collection system. The waste fee should be based on the measurable quantity such as weight or the volume of the waste of the identifiable generator. The generator cannot be identified if the waste is collected from the containers placed at the curb-side.

If the waste is determined according to the data which changes very often such as the floor space, number of the residents using the same single house or the value of the premise, the data should be updated periodically which causes the increase of the administration cost. Therefore the waste fee should be based on the data which do not change frequently and can be understood clearly by the public. If the collection system applied based on the collection of the containers of single premises, the fee can be based on either the volume of the containers or the number of emptying the containers during the collection period.

Specifications of the Different Fee Models

It is not possible to apply a fee model which will satisfy all people in the community. (Ohio EPA, 2015). There are many requests from different stakeholders which cannot be met by a single fee model. Some of the issues of the applied fee models are explained in the following sections.

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Fairness

The fairness of the fee model applied is very important for the acceptance of the public. It should be kept in mind that every fee model has some kind of unfairness for some stakeholders. Decision makers should be careful not to have the waste fee based on the data that is difficult and costly to obtain. For example, measurement of the weight or the volume of the waste of every single premise is much more costly and requires more effort than the measurement of the mass of the waste of the whole city by just weighing the collection / transportation vehicles at the disposal site. Also identification of the quantity of the waste disposed by the different residents of the multi-storage buildings using a single container requires additional effort. The easiest method is the application of the waste fee based on the volume of the waste container multiplied by the number of emptying. For the multi-story buildings, the administration of the property-building can break down the cost based on the floor space or the number of the residents in the premise which can be decided and accepted by the owners (Kocasoy, 2014).

Distance of the Settlement Structures to Collection Points

Another issue of fairness is the distance of the source of the waste generation to the disposal site. The collection cost of the wastes from the houses at open fields is much higher than the ones which are very close to the treatment/disposal areas of the wastes. This reality does not justify charging higher waste fee to those premises at the open field. The fairness of this issue is debatable.

Premises Which Are Used Only for Part of the Year

Another common issue is the application of waste fee for the houses (holiday premises) which are occupied only for part of the year. The waste fee of these houses should be calculated based on the periods/ months that are used. Authorities should assure that no service is given at the months that the buildings are claimed to be empty.

Generated Waste Quantities/Volumes

Waste fee, determined according to the amount / volume of the waste generated, can be applied only if each premise has its own waste container and if there is no collection bins at public places. Thus the quantity of the waste generated / collected can be decided by the size of the container and the frequency of emptying the container. The actual weight / volume of the waste in the container is not considered in this method. Additional measurements should be made to determine the actual amount of waste in the containers which makes the waste collection more expensive.

Waste quantity has effects only on the variable costs which is just a small part of the waste management costs. The fixed costs such as the costs of the collection vehicle, the salary of the driver and the waste collection staff and the fuel used do not depend on the waste quantity such as if the container is full or only 50 percent full. If the waste fee is determined according to the measured weight or volume of the waste generated at a premise, additional administrative costs will occur (Dahlén & Lagerkvist, 2010).

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Comparison of the Different Fee Models

The comparison of the advantages and disadvantages of the different models of the fee application are as follows:

1. Fee Model Based on Waste Quantity:
    a. It is the application of the "User Pays Principle". People pay according to the amount of the waste they are generating. It is a fair system.
    b. Disadvantage of this system is that people tend to avoid paying by using public or neighbors' bins or by illegal dumping.
    c. Each premise has to have its own waste container which should be used only by the inhabitants of the house.
    d. Size of the container of the premise and the frequency of the emptying of it should be known.
2. Average (Flat-Rate) Fee:
    a. No incentive for reducing the waste generation as well as for illegal dumping.
    b. The User Pays Principle is not applied.
    c. It is easy to administer if the waste fee is the part of another fee- such as water fee- of the premise.
    d. It is easy to administer if the fee is fixed by known data such as the area of the building, rate of the building and number of the inhabitants living at the premise, etc.
    e. It is more difficult if such a data is not available or if it changes frequently such as the number of residents.

Affordability

Costs of the waste collection and disposal is much more lower than the costs of other public services, such as water supply, waste water treatment and discharge, transport, telecommunication, etc. This is true for all countries of different economic levels. People generally are not willing to pay for the cost of services of collection, transportation and disposal of solid wastes although the fee is lower than the costs of other services. It is irrespective of the level of economic development of the society. It is not the matter of "non-affordability". It is very easy to dispose waste "illegally" without paying any fee which most of the time is not possible for the other services such as the electricity or telephone, etc. (Söderholm, 2010).

Social Effects

The social situation should be also considered when the fairness of the waste fee applied is discussed. The social factors such as families with low income, houses used by a single person, families with many children, and families with newly born babies using disposable diapers etc. should be considered from the point of view of fairness. All of the groups have excuses to pay reduced waste fee; but it is recommended not to make any differentiations at the waste management fee for certain groups or legal entities. If it is necessary to support a special group, this support should be given by other methods, not by reducing the fees.

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Administrative Costs

Each fee model discussed needs some data on which the waste fee is based. It is preferred to have a simple fee model which has low administrative costs. Data, such as number of the people in a resident, which changes very often is both difficult to monitor and to manage and also costly. Therefore it is preferred to base the waste fee on data, such as the size/area of the premise, living space which is stable and easy to obtain and has low cost. The minimum data required are the names and addresses of the owners as well as the person who is responsible for the payment of the waste fee of the premise. For more sophisticated fee models, more additional data should be collected and kept up-to- date which will cause extra costs.

Fixed and Variable Costs

Fixed costs are the costs occurred irrespective of the amount of the waste disposed into the waste containers. The main portion of the waste management budget is spent for the fixed costs which cover the collection costs, administrative costs, collection of recyclable goods and costs for public relations. The variable costs include just a small part of the collection cost and the treatment cost of the collected waste. The variable costs are much less than the fixed costs. As the cost of the waste treatment becomes less, the ratio of the fixed costs to the variable costs increases. This indicates that quantity of the waste has a limited effect on the waste management costs. In some waste fee models, fixed and variable costs are charged separately

Citizens' Behavior and Steering Effect

The possible steering effects should be taken into consideration in the design of the waste management fee. It is known that people have the tendency to avoid paying a fee or try to pay a lower fee when they have opportunities to do so (Söderholm, 2010).

Waste fee also should cover the costs of the collection and the administration of the recyclable and hazardous wastes. No extra fee should be charged for them.

There is always a tendency of using the containers allocated for recyclable wastes for the municipal solid wastes. If the same attitude continues in spite of warnings, these containers should be replaced with the municipal solid waste containers and the waste fee should be raised. Thus, the people in that district will start to use these recyclable containers properly.

So the steering effect can be summarized as;

- The fee model should have financial incentive for the reduction of the waste generation,
- The fee should cover the collection of the bulky, recyclable and hazardous wastes.

Influence of the Competent Authority in the Development of the Municipal Waste Management

There should be a single organization within the municipality or the region as an authority for the management of the solid waste in the region. The organization should have the responsibility of all issues related to the solid waste management such as collection system, public awareness, waste treatment, identification / definition of the wastes to be collected separately and recycling methods. This organization should also be responsible for setting the waste fee (Pires, et.al, 2011).

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Another issue is the identification of the responsible authority for the collection of the waste fee. There is a debate about the collection of the waste fee by the private or the public organizations.

Handling the Commercial Wastes of the Companies

In some countries commercial waste generators do not require the services offered by the municipalities, such as collection of bulky or hazardous wastes, taking collection bins from the premises, collection of bio-wastes and special wastes as electronic equipment etc. (Francesc, 2011; Monomaivibool & Vassanadumrongdee, 2011). Thus, the waste fee charged to the commercial waste generators will be less than the fee tariff of the private households. The waste fee for the commercial waste generators will be calculated according to the services given to them. Since the municipality is collecting wastes over a large area with close distances between collection points, the price offered by the municipalities will be lower than the fee offered by private companies specialized on only commercial waste collection. Thus a cost–efficiency can be realized by the municipalities by combining the wastes generated at residential and commercial premises. Thus, the municipalities have a kind of contribution to the fixed costs from the commercial premises which in turn cause the reduction of the average costs (Pires, et al., 2011).

DESIGN OF THE WASTE FEE

In the design of the waste tariff, the authority should take many issues into consideration. Among these, the most important one is the simplicity and the fairness of the selected models. The steps of designing the tariff for the waste fee can be summarized as follows:

- **Simplicity**: The fee model decided should be simple and it should be explained to people very easily.
- **Fairness**: The tariff should be fair to everybody. It should reflect the "User Pays Principle" so the waste generator can believe in the fairness of the applied tariff, but it should be kept in mind that there is not an ultimate fairness.
- **Additional Costs**: Weighing the contents of every waste container causes additional costs. This system should not be incorporated into the waste fee.
- **Fee Collection:** Collection of waste management fee should be considered independently from the "waste collection". Waste collection can be accomplished by a private sector, but the fee collection should be conducted by the public authority.
- **One Waste Management Fee:** Recyclable, hazardous, bulky wastes should be separately collected, but no extra separate fee should be charged for them. All the services conducted should be financed by one fee.
- **Household and Commercial Waste Fee:** Different services are given to households and commercial areas, therefore different waste fees should be applied to them.
- **Affordability:** The fee should be adjusted in such a way that people can afford it. But also it should be kept in mind that people's reluctance to pay the fee should not be confused with the affordability of the people.
- **Stopping the Service:** Stopping the collection of waste is not a solution, but it causes the illegal dumping of the wastes.

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- **Collection of Fee:** It is easier to collect the waste fee together with the fee of other services. Most of the time the waste fee is collected together with the electricity or water bill (ISWA & Abrelpe, 2012).

Who Should Collect the Waste Fee?

There is always a debate going on about the identification of the authority for the collection of the waste fee. The municipality and the private companies are the alternatives for the fee collection. According to the experiences in the past, it is suggested that the municipalities should collect the waste fee.

The disadvantages of the collection of the fee by the private organizations can be summarized as follows:

- Payment losses are higher when the waste fee is collected by the private organizations.
- The fee collected by the private organizations does not include the separated collection of the recyclable, hazardous, bulky wastes and the cleaning of the streets from littering as well as the public relation activities.
- It is also difficult for waste generator to have a waste management contract. It is not possible for each waste generator to have an affordable contract with the private sector.
- People can easily dispose waste "illegally" without paying fee. This is not so easy for the other services such as telephone, electricity, etc.
- The private organizations always have the tendency to stop the service to the people who do not make the due payments regularly. This causes the dumping of wastes illegally and the municipality has to interfere and remove these wastes.
- When the private organization has difficulty in collecting the waste fee, they concentrate their services on the commercial premises and the region in which there is no problem in the collection of the waste fee.
- Public sector such as municipality will have no influence on the waste management method.
- Administrative work of the municipality is not recognized and acknowledged by the public.
- More legislation will be necessary to reach the target.

The advantages of the collection of waste management fee by the regional authority have the following advantages:

- There will be fewer defaults of fee payments,
- Municipality has to finance the other public services such as cleaning the streets,
- Municipality will be sure that waste from each facility is collected,
- Municipality applies the same waste fee to all premises, even for those at remote areas,
- A uniform waste management system in the region is accomplished.

So, as a result it is more reasonable and effective to have the public authority such as the municipality to decide and collect the waste fee.

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FUTURE RESEARCH DIRECTIONS

The following topics can be investigated to minimize the use of natural resources, virgin materials and waste generation and encourage the recycling of wastes for the protection of the both natural resources and environment.

- Comparing the impact of the application of different types of fees at different social groups.
- Impact of recycling in the diversion of waste from the landfill. Comparing the amount of waste recycled with the amount of waste diverted from the landfill.
- Comparing the effect of recycling and the effect of application waste fee in the waste minimization at different social groups. Which is more effective?

CONCLUSION

The natural resources have been diminishing very fast by the careless usage of them. These natural resources are not limitless and they are becoming more scare because of the emissions and discharges of pollutant. The authorities apply fee for the services of supplying natural resources and treatment and discharge/disposal of wastes. Thus the Polluter Pays Principle is applied. The aim of the fee application is to minimize the waste generation. The fee model should be designed and the fee should be collected by the waste authorities. There are many fee models and many criteria to be considered in the design of the waste fee. The most important criterion in the designing of the waste fee is fairness, but it is not easy to satisfy everybody about the fairness of the model. It is also suggested to apply to a fee model based on the data which can be obtained easily and not change very often. The fee based on the weight/volume and the pollutant load of the waste generated encourages the people to generate less waste.

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KEY TERMS AND DEFINITIONS

Air Emission Fee: Fees imposed for the air emission permit.

Environmental Tax: Revenue rising instruments which are designed to fund environmental protection activities.

Government Charges: Charges imposed by governments on some products such as beverage containers, refrigerators, furniture, tires, fertilizers, motor oil, pesticides and solvents.

Ozone-Depleting Chemicals: Chemicals damaging the ozone layer.

Pollution Charge Fee: Fee based on the quantity of pollutants that are discharged into the environment.

Product Charge: Fee imposed on products that are believed to have harmful effects on environment.

Solid Waste Management Fee: Fee charged for the collection, disposal of municipal solid wastes.

User Charge: Fee paid in exchange for the use of natural resources or for the collection and/ or disposal of pollutants.

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Chapter 29
Water Quality Prediction Using Statistical Tool and Machine Learning Algorithm

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ABSTRACT

Water is the most valuable natural resource for all living things and the ecosystem. The quality of groundwater is changed due to change in ecosystem, industrialisation, and urbanisation, etc. In the study, 60 samples were taken and analysed for various physio-chemical parameters. The sampling locations were located using global positioning system (GPS) and were taken for two consecutive years for two different seasons, monsoon (Nov-Dec) and post-monsoon (Jan-Mar). In 2016-2017 and 2017-2018 pH, EC, and TDS were obtained in the field. Hardness and Chloride are determined using titration method. Nitrate and Sulphate were determined using Spectrophotometer. Machine learning techniques were used to train the data set and to predict the unknown values. The dominant elements of groundwater are as follows: Ca2, Mg2 for cation and Cl-, SO_4^2, NO_{3-} for anions. The regression value for the training data set was found to be 0.90596, and for the entire network, it was found to be 0.81729. The best performance was observed as 0.0022605 at epoch 223.

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1. INTRODUCTION

It is found that nearly one-third of the Global population is using groundwater for their drinking purpose. Groundwater is the main sources of water supply for local purposes in urban areas as same as in the rural areas in India. Tripathi et al. (2012) had studied that groundwater is an essential natural resource. Be conditioned on its utilization; it can be a renewable and non-renewable or a non-renewable facility. Talabi and Tijani (2013)convey that groundwater studies are an important issue in water quality research because which will directly affect the people due to pollution in various places. Due to pollution, there will be various kinds of disease like typhoid fever, paratyphoid fever, dysenteries, infectious hepatitis, schistosomiasis, Asiatic cholera, back pain, pneumonia, and nasal congestion will attack us severely. Ben et al. (2014)found that water is an important essential need in all humans' life for drinking and all another domestic purpose. In current scenario, up to a considerable extent, it is found that the life and majority of our financial action depend on population. The intemperate requirement on water facility by improving a population of the most developing district like Tirupur aggravate by the collision of environment change results in the drying up of exterior water and exhaustion of groundwater. Selvakumar et al. (2017) evaluated that it is one of the major need features in groundwater studies. The hydrochemical study divulges excellence of water that is a match for drinking, agriculture and industrial needs. Chemical research forms the basis of the explanation of the quality of water in connection to source, geology, use, and climate. Water being a fantastic solvent, it is mainly to know the geochemistry of dissolved voters and methods of announcing analytical facts. Mogaddam (2011) described that in huge groundwater basins, urbanization had created a developing demand for drinking water; while long histories of agricultural bustle have remain aquifers potentially at suffering from NO_3^-.Fehdi and Rouabhia (2014) analyzed that groundwater is one of the controlled aquifers. It is underground water soaked stratum formation that can cultivate a usable amount of water to a well. Aquifers are again classified into two: confined aquifer and unconfined aquifer. If the zone of saturation is overlapped between two impermeable layers, then it is termed as confined aquifer, and when impermeable strata are absent just above the saturated zone, it is termed as an unconfined aquifer.

Gampson et al. (2014) extended that for the purpose of healthy living safe drinking of water is essential in all human life. Groundwater is a selected source of water for human needs. Gnanachandrasamy et al. (2015) studied the groundwater has become the main source for domestic purposes, industrial and irrigation sectors of various countries. Millions of pumps by hand and profound bore wells have been released throughout India since 1970 to provide pure water than the water influenced by microbes. More or less, this water has some dissolved chemical constituents that are not acceptable by humans for drinking as it may cause bad taste and diseases also.

Malhotra et al. (2014) extended the hydrochemical computation of deep bore ground systems are more or less based on the presence of a high amount of files depending upon groundwater chemistry. Gampson et al. (2014)conveyed that various multivariate statistical proficiencies are widely applied to compute water standard through data reduction, types, and relationship. Although multivariate statistical techniques like principal elements analysis, discriminate analysis, cluster analysis and factor analysis are widely used to determine surface water and groundwater standard, to our knowledge, however, there have been limited attempts to demonstrate surface water standard parameters to incorporate into common linear mixed models to evaluating low and high flow hydrology and physicochemical surface water standard. Bharathi et al. (2017) investigated that a huge majority of groundwater standard issues are caused by contamination and over-exploitation. Mostly water standard issues are various to detect

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and hard to analyze. The solutions are commonly much branded, time-consuming is not always in effect. An altering picture is beginning to issue in many parts of our nation. Groundwater pollution is as such different to detect, since the problem may be not shown below the surface and also monitoring may be expensive, time-consuming and somewhat hit-or-miss by nature.

The primary objectives are to quantify groundwater sources, evaluate groundwater sources have changed over time, and provided tools need to forecast system response to future anthropogenic and environmental stress.

2. STUDY AREA

The area for this study is located at 11.10°N 77.33°E situated in the bank of the river, and total study area spreads over 5186.42 sq.km. The study was carried out in some bore wells from different areas in Tirupur district. The population density of Tirupur is 2479052. Tirupur district is an industrial district plays a vital role in agricultural also. The total area of cultivation is around 2,28,556 hectares. The climate in this study area is mostly tropical in nature, with temperature ranging from 22^0C to 35^0C throughout the year. Study area receives monsoon from June to August, which receives showers with reduced temperatures. Months of September to January will be post monsoon period of the study area which experiences moderate to cool climate with the peak temperature of 29^0C which can go down up to 20^0C; the Summer season will be from March to May during which the temperature shoots up to 35^0C with a hot and dry climate. The region is covered by red soil (50%), black soil (46.4%), and other soil (3.6%). Ordinary well and surface water are found to be major sources of irrigation compared to canal irrigation with water table available at a depth of 7m to 25m.

2.1. Sampling Procedure

Bore water samples from deep bore wells, and sampling of hand pumps was chosen based on the industrial unit along with several usage conventions. In brief, the 60 water samples from bore wells were collected randomly in polyethylene bottles for each season based on the prelude field survey done in several locations of Tirupur. Initially pumping was done for 10 minutes, and the water samples were taken for testing purposes. They were examined in the laboratories to find major ions by applying standard test methods. After 24 hours of collection, analysis of samples was carried out. Each parameter was found based on the standard test procedures while pH & EC were taken by using pH meter and EC meter, respectively. Total hardness and calcium hardness were calculated by EDTA titration method. Iron, Chromium, nitrate was calculated by the calorimeter. Silver Nitrate was used to find Chloride in titration method. Total solids (TS) and Total dissolved solids (TDS) were also computed. The tests were shown in Figure 1 & Figure 2.

The groundwater samples are analyzed by different parameters using the standards American Public Health Association. The test pH, EC and TDS are obtained by using pH meter, EC meter and TDS meter respectively. Water bath method is used to measure TSS. A titrimetric method is used for measuring Chloride, Total hardness, Calcium hardness and Magnesium hardness. Sulphate, Iron and Chromium are determined using Calorimeter. A spectrophotometer is used for determination of Nitrate.

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Figure 1. Field test for pH, EC, TDS and temperature

3. METHODOLOGY

3.1. Machine Learning

Machine learning is one of the most developing techniques which is expected to evolve in very near times. The soul of Artificial Intelligence lies in the utilization of machine learning depending on the inputs and outputs given to build functional relationships among data. Machine learning tools are used in various fields like weather forecasting, public health, communication systems, smart systems and many. The spirit of machine learning lies in applying various techniques like statistical approach, probabilistic approach and optimization techniques which help in finding the regularity of the training data set and to construct the linear relationship interdependent and noisy parameters. This makes things easy to make decisions which are difficult by traditional statistical approaches. Machine learning flowchart was shown in Figure 3.

Ni-Bin Chang et al. (2017) discussed that within the field of investigation, machine learning is a technique which can be used effectively to solve complex problems. In business terms, it is also called a prescient examination. Reasonable machine learning is tough knowing the fact that identifying the design or pattern is very hard and regularly sufficient data may not be accessible. Thus these machine learning programs are neglected to deliver.

3.2. Descriptive Statistics

Descriptive statistics Together with simple graphics analysis, they form the basis of virtually every quantitative analysis of data. The central tendency of a distribution is an estimate of the centre of a distribution of values. Measures of a central tendency include the mean, median and mode while measures of variability include the standard deviation (variation), the minimum and maximum values of the variables, kurtosis, and skewness.

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Figure 2. Laboratory test for hardness, chloride and iron

A mean is the simple mathematical average of a set of two or more members. The median is a simple measure of central tendency. The model is the number that occurs most often in a set of numbers. A measure of the range of values in a set of numbers. Standard deviation is a statistic used as a measure of the dispersion variation in a distribution, equal to the square root of the arithmetic mean of the squares of the deviations from the arithmetic mean. The standard deviation is a numerical value used to indicate how widely individuals in a group vary. If individual observations vary greatly from the group mean, the standard deviation is big and vice versa. A standard error is the standard deviation of the sampling

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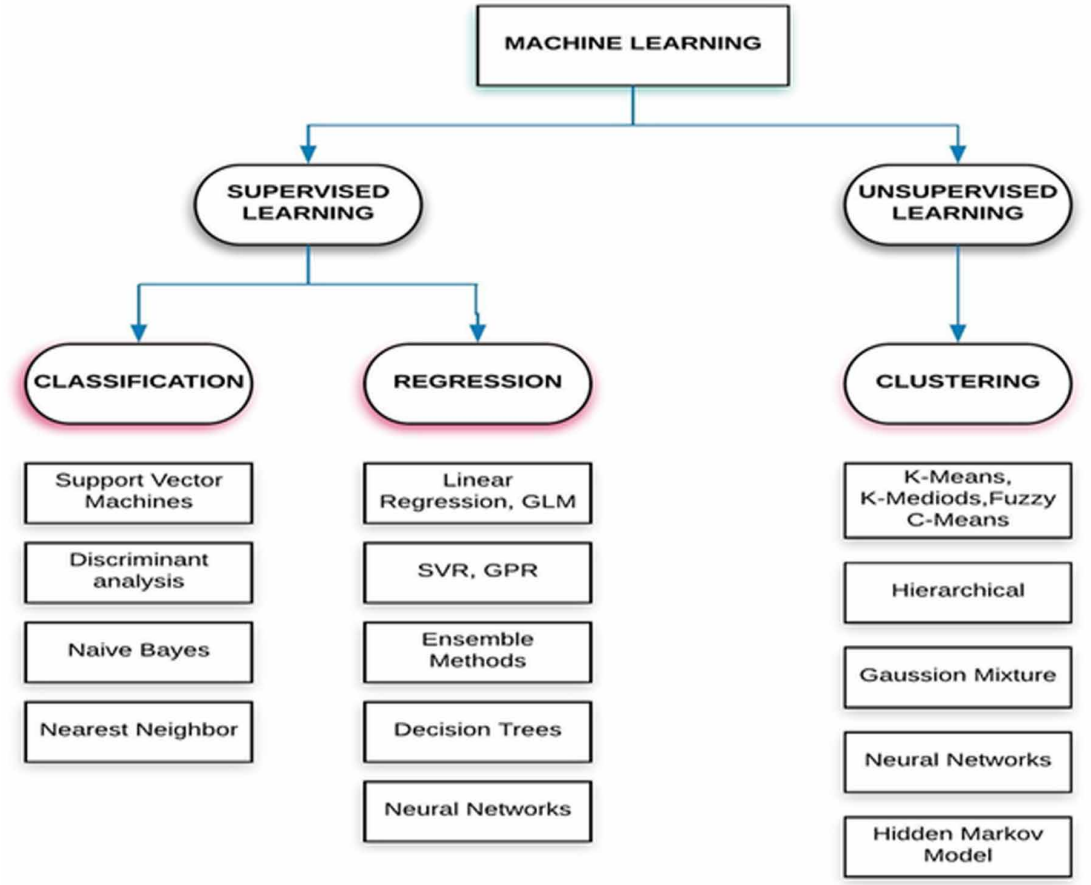
Figure 3. Machine learning flow chart



distribution of the statistic. The standard error is a statistical term that measures the accuracy with which a sample represents a population. In statistics, a sample means deviates from the actual means of a population. Skewness is asymmetry in a statistical distribution, in which the curve appears distorted or skewed either to the left or to the right. Skewness can be quantified to define the extent to which a distribution differs from a normal distribution. This situation is also called negative skewness. The variance is defined as, the average of the squared differences from the mean. In arithmetic, the range of a set of data is the difference between the largest and smallest values.

3.2. Neural Network Analysis

Artificial neural networks (ANNs) are the computing systems of Artificial Intelligence, which are truly inspired by biological neural networks which are similar to human brains. ANN works mainly depending on neurons in connections which are called artificial neurons. Each neuron will transfer the information from one node to another node. The architecture of ANN consists of three layers: input layer, hidden layer and output layer. The neurons in the hidden layer receive the data from the input layer to process and then it sends to the output layer. Figure 4 represents the architecture of a neural network opted for present work.

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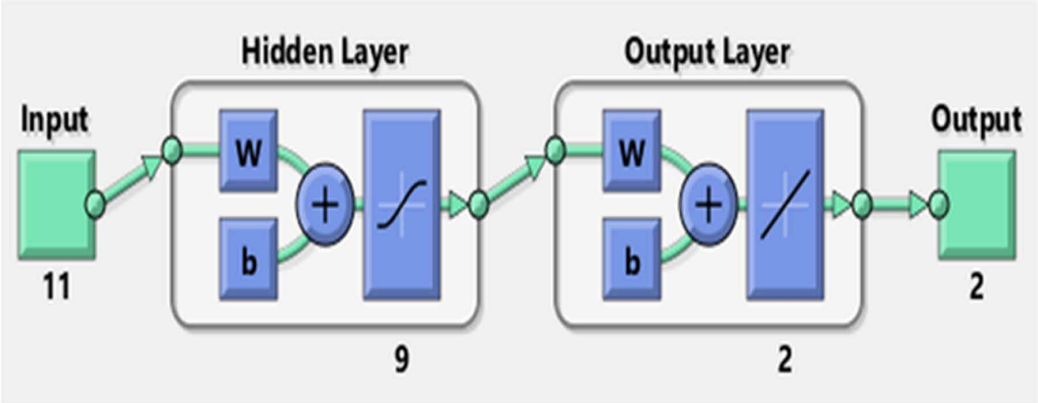
Figure 4. Matlab input and output circuit diagram



In general ANN applications, the signal at any connection is a real number, and the output is calculated by activation functions in hidden layers. The connection between artificial neurons is assigned with weights that adjust accordingly as the training process proceeds. Weight plays a vital role in increasing or decreasing the signal's strength at any connection. Artificial neurons will set a threshold number such that it passes the signal to the further neuron only when the aggregate value crosses the threshold number. Regression plot and best performance obtained were shown in Figure 5.

Initial normalization is very necessary and it mainly depends upon transfer function's operating range (1 to 0 or -1 to 1 or any other) in the neural network. The training efficiency can be increased if certain measures are taken on the inputs and outputs. Sometimes scaling of inputs and outputs prior to training will give better results, as they will fall within a particular range. Premnmx is a function which can be used to scale the information in a range -1 to 1. This scaled output values can be converted back into original targets by using a function named postmnmx. If training the data is done after using premnmx, then for every new input, preprocessing by using tramnmx function is mandatory with minimum and maximums which were obtained from the training dataset.

4. RESULTS AND DISCUSSIONS

Total of 60 groundwater samples was collected in the year 2016-2017 and 2017-2018 and referred for different parameter during monsoon seasons and Post- monsoon seasons respectively. In this analysis, two years data is attached and referred to the quality of water. Groundwater samples were collected using the standard procedure from deep bore wells settled at various area of the district during seasonal variation. Through the analysis, it is base that pH values are slightly acidic and basic for some samples rating from 4 to 9. For monsoon analysis in 2016, the 27 samples crossed the permissible limits, and in 2018, minimum samples are affected. In post-monsoon period in 2016-2017 for 27 samples, it is less than the permissible limits, and in present year one sample crossed the permissible limits. EC values range from 0 to 1.300 /cm. TDS and TSS value ranges from 0mg/l to 1200 mg/l in 2016 -2017 and 0 mg/l to 1600mg/l in present year for monsoon period. In post-monsoon season the value ranges from 0 mg/l to 1700 mg/l and 0mg/l to 1500 mg/l for different samples. There are no samples which crossed

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the permissible limits.36 samples are less than acceptable limits. Hardness in groundwater is established to be more and it exceeds the permissible limit in different samples. Geographical International System (GIS) is enforced to visualize the place of bore water standard in the study zone. Table 1 & Table 2 gives the statistics of water quality parameters for monsoon and post-monsoon respectively. The analysis was done for all the quality parameters, and it was shown in Figure 5.

Table 1. Descriptive statistics for Monsoon season

Statistics	Ph	Ec	Temp	Tds	Tss	Iron
Mean	7.49	1.421633	26.50333	643.1356	191.3333	2.471667
Standard Error	0.075864	0.114651	0.419341	45.2025	23.37784	0.243504
Median	7.4	1.2345	26.35	650	140	2
Mode	7.2	1.435	25.5	603	140	2.6
Standard Deviation	0.587641	0.88808	3.248205	347.207	181.084	1.886176
Sample Variance	0.345322	0.788686	10.55084	120552.7	32791.41	3.557658
Kurtosis	21.18362	-0.32944	-0.32393	-0.49901	11.70052	1.552115
Skewness	3.641356	0.649871	0.151316	0.340674	3.131432	1.37192
Range	4.4	3.664	13.3	1327	1050	8.3
Minimum	6.6	0.112	20.5	100	30	0.1
Maximum	11	3.776	33.8	1427	1080	8.4
Sum	449.4	85.298	1590.2	37945	11480	148.3
Count	60	60	60	60	60	60

Table 2. Descriptive statistics for Post monsoon

Statistics	Total Hardness	Calcium Hardness	Magnesium hardness	Chloride	Sulfate	Nitrate	Chromium
Mean	766.5667	321.75	453.8167	536.662	-1.15259	444.8333	0.3783
Standard Error	40.65953	30.6778	34.61159	53.43283	0.772127	37.36671	0.045704
Median	727.5	227.5	452.5	482.345	-1.962	420	0.28
Mode	825	125	330	269.91	-6.027	275	0.04
Standard Deviation	314.9474	237.6292	268.1003	413.8889	5.980868	289.4413	0.354024
Sample Variance	99191.84	56467.65	71877.75	171304.1	35.77078	83776.24	0.125333
Kurtosis	-0.41838	2.256717	0.046326	4.923221	8.302066	0.734857	1.149261
Skewness	0.331041	1.672181	0.553424	1.874544	2.423975	0.742612	1.293885
Range	1376	955	1121	2194.32	35.149	1415	1.42
Minimum	144	70	19	44.98	-10.342	15	0.01
Maximum	1520	1025	1140	2239.3	24.807	1430	1.43
Sum	45994	19305	27229	32199.72	-69.1553	26690	22.698
Count	60	60	60	60	60	60	60

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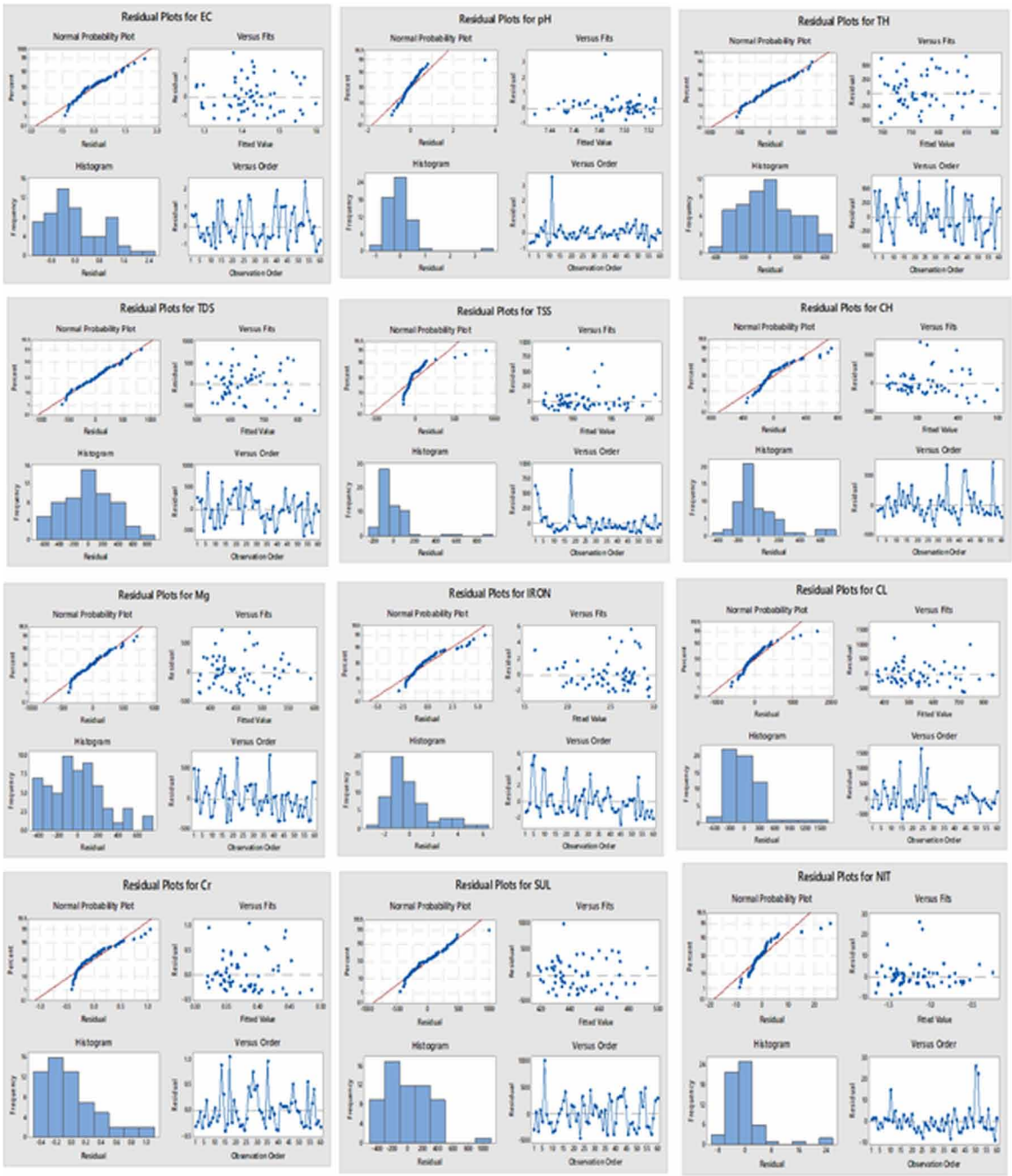
Figure 5. Descriptive analysis of several parameters



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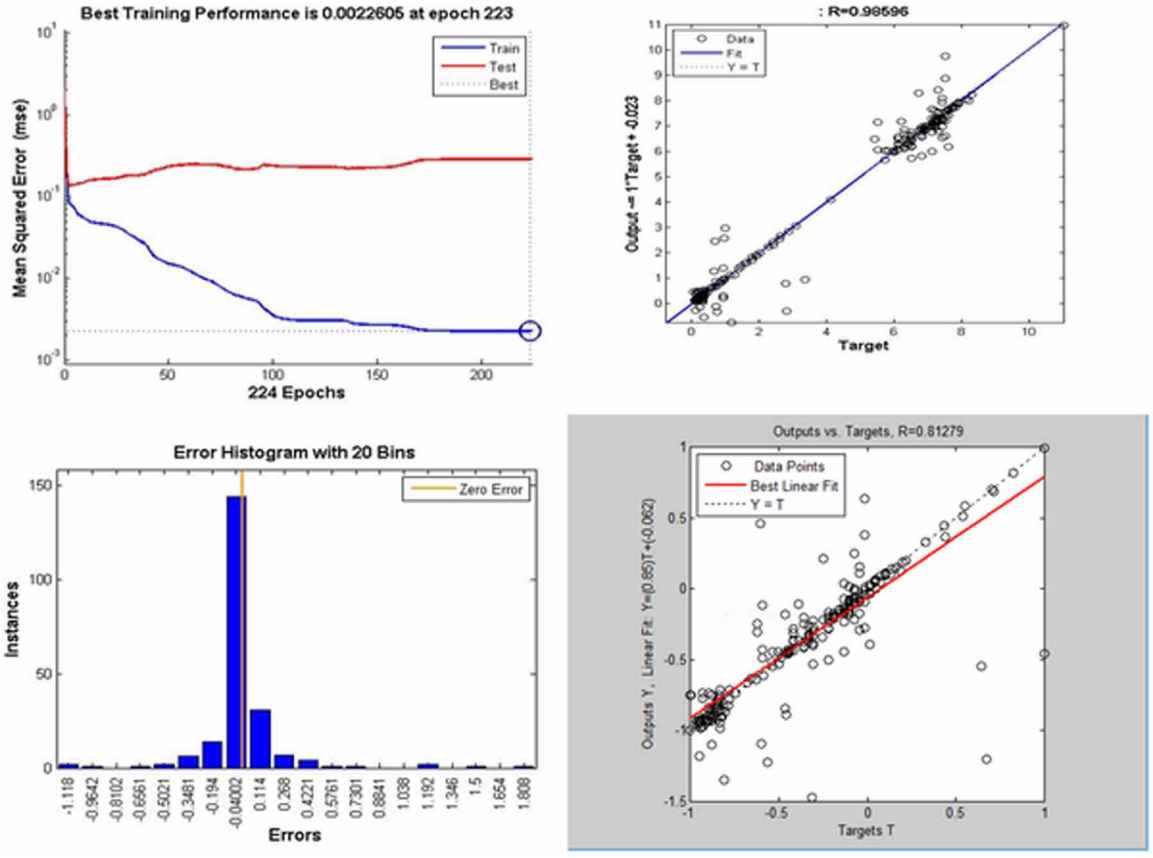
The dominant elements of groundwater are as follows: Ca_2, Mg_2 for cation and Cl^-, SO_4^{2}, NO_{3-} for anions. Deep bore well water is found to be good quality for drinking and agriculture purpose with less alkalinity and changing to high chromium hazard. Chloride value is limit in the post-monsoon and monsoon seasons. In 2016 – 2017 for monsoon the values are 0 to 900 which is under the permissible limits used for drinking and irrigation purposes and in post monsoon season the samples are under the limits. In 2017 to 2018 for monsoon and post-monsoon only 4 samples crossed the permissible limits and few samples under the acceptable limits. Values in Nitrate is about 90% of samples lies below the permissible limits, and only 10% of samples lies above the permissible limits. Comparing with the Sulphate, the values lies between the limits. Where the sulphate was below guidelines value for monsoon season and exceeded 45% for post monsoon and Nitrate exceeds about 5% in post monsoon compare to monsoon. And in monsoon Nitrate is good and lies between the permissible limits.

ANN technique has been applied to the data of investigations. The data was divided into 70% for training, 15% for validation and 15% for testing the network. Levenberg Marquardt algorithm was used for training. The regression value for the training data set was found to be 0.90596,and for the entire network, it was found to be 0.81729. The best performance was observed as 0.0022605 at epoch 223. The error histogram is obtained. The entire analysis using ANN was shown in Figure 6.

Figure 6. Best training performance graph



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5. RECOMMENDATIONS AND CONCLUSIONS

We concluded that this is our prime work to allow for a healthy environment and clean water for our future generation and let us provide our upcoming generation with a neat and clean environment. ANN was employed to train and develop the models for water quality. Regression value for the complete data was found to be 0.81729, and the best performance was observed at epoch 223. The calculated regression is very near to 1, indicating the high accuracy of the model. It is recommended that the water in this zone good and suitable for irrigation purposes and drinking purposes.

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Chapter 30
The Contribution of ICTs to Sustainable Urbanization and Health in Urban Areas in Cameroon

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ABSTRACT

The uncontrolled urbanization in African cities with inadequate access to urban domestic waste, housing and sanitation management services (DWHSMS) generates landscapes that become places of the spread of many pathologies leading to many public health problems. The city of Yaoundé (Cameroon) is not an exception in this situation which exposes an urban population to the most recurrent diseases. The situation become more complex in the fact that, the performance of the policies and the actions undertaken implied in developing countries, is not known in a precisely. The information sources are dispersed, old and not coordinated. ICT can, at the service of the great causes like the sustainable urbanization and/or environmental health, constitute the irreplaceable ones and essential decision-making tools. For this purpose, integrated and interoperable YUSIIP platform has proposed and deployed. The objective of this article is to present this Domestic platform and to show its contribution in (DWHSMS).

1. INTRODUCTION

Bad Domestic Waste, Housing, Sanitation Management Services (DWHSMS), and the absence of the application of law on the matter presents enormous consequences on health, the environment and the individuals living environment, particularly in the African cities, notably the town of Yaoundé, capital of

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Cameroon, concerned with our research tasks (Wéthé et al., 2002). The population of the city increases each year by 6% on average since 2001. This population growth appears by the increase in the domestic waste production, the proliferation of the shantytowns and the weakening safety systems, hygiene and sanitation. Each one of these factors can largely improve or degrade health in urban area and the city environment (economic and social situation, security and food quality, service of sanitary emergencies management, urban governance, etc.). According to the cases, they can also involve the proliferation of several fatal diseases as well as imbalances in ecosystems (Manegabe et al., 2017). The consequences of the dysfunction of their management systems on living environment and the natural ecosystem gain more and more in importance. They challenge all the actors implied to make suitable decisions and the proper authorities to make management of these factors the priority of their action.

Since about ten years, initiatives of the public authorities, private and public organizations, regional and local authorities and universities (Ngnikam et al., 2002; Fonkou et al., 2002) are being multiplied in Cameroon faced with the environmental degradation and urban area health. The informal sector, NGOs and associations joined the movement which aims at:

- **Domestic waste management:** The treatment and the valorization of domestic waste play a key role in the fight against the environmental pollution and the conservation of natural resources (Aloueimine et al., 2006);
- **The housing management:** The spontaneous and precarious shantytowns very populated cover more than 70% of urban space where the lack of basic services such water and the cleaning constitutes a vector of propagation of many pathologies which are posing multiple public health problems (the complication of paludism, respiratory infections acute, infections of the digestive system, etc.), as well as the environmental factors exposure to the health risks (Sy et al., 2011);
- **The sanitation management:** This management falls on the municipalities which must build and manage the autonomous drainage systems, main sources of diffuse pollution, not easily controllable (Wéthé et al., 2002), etc.

However, these initiatives of the public authorities, municipalities, private and public organizations, and NGOs and associations implied, faced with the degradation of the socio-sanitary and environmental conditions, encounter some problems related, on the one hand, on the organizational level, with the accelerated urbanization, the impoverishment of an important frank of the population, with a deficit in means and an insufficient dialogue between the various speakers, on the other hand, on the technical plan, public information on the influential factors on urban health and the academic research results, are very scattered and not always reliable, heterogeneous and difficult of access. The various methodological approaches and the development models of these systems were often unaware of the transverse dimension of the various processes, being limited to the computerization of some functions of the factors (Bagayoko et al., 2010). The risks related to these factors could wellness avoided if the data and knowledge were available (Ayissi & Moskolai, 2017). The lack of data exposes the population and the environment to the proliferation of several fatal diseases, the contamination by the pathogen and chemical substances (Corcoran et al., 2010). Moreover, urban area health would not be truly assured as a long time as the population will be kept out of urban waste management and. This population will continue to throw heterogeneous waste in the streets, drains, waterways, etc., and related risks to this waste could involve a delay on the economic plan through high mortality and morbidity rates which would be followed in the cities (UN- DESA, 2014).

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It's to contribute to the general problems of urban data control for a sustainable urbanization that we started, since 2002, research on the integration and interoperability mechanisms of the heterogeneous and incomplete information systems for decision-making in urban area in Cameroon. The setup of a Distributed Data warehouse (DDW), urban memory in Yaoundé, which is pressed on the technology of the data warehouses, Services Oriented Architectures (SOA), the urbanization of the information systems and Master Data Management (MDM) through the design and the development of Yaoundé Urban Systems Integrated and Interoperability Platform (in abbreviated form YUSIIP). The effectiveness of this mixed approach and the results of the capitalization of knowledge on urban environment through a unifying platform of multi-source data YUSIIP, from the point of view of the decision-making aid as regards management and the urban planning are already convincing (Ayissi & Moskolai, 2017; Kouamou al., 2008). The aim of this paper is to show the contribution of the DDW of YUSIIP in the problem of Domestic Waste, Housing and Sanitation Management Services (DWHSMS) in the particular case of Yaoundé town, the political Capital of the Republic of Cameroon. The multiple and varied health risks related to domestic waste, housing and sanitation management services in urban areas could be avoided if the data of different factors enumerated above would be available.

In the rest of this article, a state of the art relative on integration techniques of information systems and urban waste management systems is proposed in section 2, section 3 presents the general architecture of the YUSIIP platform. Then, in Section 4 a model of production of urban indicators is proposed, section 5 presents the results and discussions and finally a general conclusion and perspectives to finish the paper.

2. INTEGRATION OF INFORMATION SYSTEMS AND THE WASTE MANAGEMENT SYSTEMS

2.1. Integration Systems, Data Warehouse, Enterprise Architecture, Multi-Source Information Systems and the Master Data Management

The needs for urban stakeholders in the processes management of sustainable urbanization are varied (environment management, demography management, transport management, living environment management, etc.). They relate at the same time to the data, the figures which they seek to understand and the realization of the statistics and other exploitable relevant information, within the framework of decision-making, which it's operational nature, occasional or strategic. To solve these problems, several approaches are proposed that it's the integration of information systems, Enterprise Architecture, the construction of multi-source information systems and Master Data Management (MDM).

Integration is operation which consists of assembling the various parts of a system and to ensure their compatibility as well as the efficient operation of the complete system. The concept of integration can apply to various levels or objects: at the organizational unit level, processes, computer applications, software base and material. On the computer applications level which relates to the problems of the DWHSMS particularly (Reix, et al., 2016) one distinguishes two possible approaches to the problem. The priory integration which is matching to systems thought at the beginning of the construction of a single integrated information system or Management Information System (MIS), recovering the whole functional fields and various levels of piloting. The posterior integration which consists in arranging the relations between conceived systems in an independent way, to constitute a "unified" system or meta-system.

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Compared to a posterior integration, the recent solutions concern:

- EAI (Enterprise Application Integration) which consist of replacing the multiple links (footbridges) between applications by the construction of a platform centralized exchange ensuring the communication and the exchanges between these applications by diffusion messages (Avignon, Joguet, & Pezziardi, 2000);
- DW (Data warehouse) which are systems managing the data resulting from various applications and ensuring they are making up in accordance with common formats. These systems are especially used in the field of Decision Support Systems;
- The ERP (Enterprise Resource Planning) which are integrated information systems composed of modules, conceived in a coherent way and sharing a common database. The ERP are standardized, but adaptable systems which correspond to a logic of brutal urbanization, standard big bang consisting of replacing "small islands disparate and badly built" (old applications) by harmonized units, carefully connected to each other (modules). The harmonization concerns not only on the definition of the data, but also, in a major way, to a new design of the processes management. It's a unified and coherent information system making it possible to manage the various fields of the undertaking, and whose realization can combine several approaches (EAI, DDW, etc.);
- YUSIIP Project (Kouamou, Eteme, & Pettang, 2008) which the ambition is to contribute to the reach of the objectives for a sustainable urbanization in Cameroon implements the approach Data warehouse and identifies all the principal data which need urban managers and decision makers. First of all, the idea is to create an ideal model of data of which must lay out these urban stakeholders. It has been elaborated based on the principal processes suitable for environment management, demography, living environmental; such processes of Domestic waste, Housing, Sanitation and the pollution management Services, etc. This model is according to Bolognigni (2002) which allows the integration of data of the various information systems.

For the approach Enterprise Architecture "the metaphor of the city has been largely used in the field of information systems because of the similarity of the starting problems: How to remake, modernize? How to benefit from advanced technologies, without wiping the slate clean of the past, within limits of controlled costs while maintaining the life of the city during works? "(Longépé, 2003). It proposes to pass from a system existing to a new solution, the target system, by successive evolution (by definition of projects). It's a question of ensuring the evolution of the system for answering the evolution of requirements while improving its coherence and its effectiveness. In the framework of YUSIIP project, the setup objective of an operational platform starting from existing YUSIIP prototype is reached. Technological choices for the implementation of its architecture has been operated. Application architecture of the prototype has been described, by showing the various levels: the application zones (great functional units), the application quarter, the application block (programs, modules), then to guide the evolution of a situation where each block thus defined, according to the degree of accuracy (zone, quarter, block) corresponds to a unit within which data and treatments are strongly connected and having a coupling or weak connection with the other blocks. What constitutes "land use plan" or the YUSIIP guiding diagram and which organizes the platform while specifying: - the mission of each application, each block; - the regrouping of the blocks in coherent units; - the perimeter booked with the future applications to build; - the rules which the originators for the realization of the future applications must comply with. The urbanization of information systems thus seems a permanent concern aiming improving coherence of

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cuttings in applications, at increasing the effectiveness and the efficiency of the information system and, to limit the effects of technological proliferation. Thus, the urbanization and the integration of information systems pursue the same goal and seen two different moments from the same process of consistency and piloting of evolution of the information system (Reix, et al., 2016).

The construction of Multi-Source Information Systems (MSIS) addresses the problems: "how to optimize the city by the data and the uses?". Indeed, the urban planners and managers are working for several years to control the organization of territory, to improve coherence of interventions of many local and external actors (ministries, private and public organizations, Regional and Local Authorities, NGO and development assistance organizations, etc.), to ensure the well-being of populations and to coordinate development projects, made difficult because of multiplication of planning (Repetti & Prélaz-Droux, 2003). The recourse to communication and information technologies does not make it possible yet to completely apprehend the complexity of the processes of urban management and to improve the effectiveness of territorial management (computers, data bases, computer applications, ISDMA, GIS, SIRS, observatories, etc.) (Pettang et al., 1997; Prélaz-Droux & Musy, 1994). These monolithic tools are disparate and under exploited because of difficulties of insertion in institutional organizations, as well as the weak taking control by the stakeholders of urban management who are independent and have each one own destiny. With the optimization objectives of the city by the urban data (reuse, shares, co-production, publications, analyzes great volumes of data), of generations of a common strategic vision of the city which directly influences the actions of the actor's management and the co-operation with various partners, the urban reflection was then extended to the analysis of the management processes and the decision, with a partnership approach of Co-construction, as the technic resulting from company management.

The implementation of the platform YUSIIP identified two major challenges: firstly, SOA and the development of generic services do not solve the problems of surface heterogeneity and secondly the lack of a common data model for the data warehouse does not allow the normalization of the structure of semantic data models. Heterogeneity remains for the two cases, at the data level. (Ayissi, & Moskolai, 2017) propose to associate the approach of Master Data Management (MDM) by the setup of data repositories which will be coupled with the data warehouse, thus constituting a Distributed Data Warehouse (DDW). MDM is focusing on the rationalization management of data shared within an organization or between several organizations while managing in a unified and transverse way of heterogeneous data and dispersed in several not synchronized application systems.

2.2. Waste Management Systems

According to BRUNET Roger, waste is an "inevitable product of human activity, whose treatment is expensive and difficult, although it is useful (...)". Jean GOUHIER retorts that: "the study of waste makes it possible to understand the way in which people live and discharge their vital functions (consumption, food, health) and cultural (leisure, various activities), or professional. It's not divination: by studying dust bins, one can establish trends of behavior, based on the typologies carried out on the basis of content analysis of dust bins carried out over several years". In the literature, there does not exist a single definition. Researchers and professionals mobilize themselves and organize themselves more and more to take part directly in the management of the city and this since the economic transfers, policies and social which knew the urban companies in particular, in Africa at the beginning of the Nineties. Several works testify some.

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In their work, Morrissey and Browne (2004) examined the types of model systems currently used in the field of municipal waste management and highlighted some important gaps in these models. Based on their analyses, most of the municipal waste models identified in the literature are decision support models and seem to fit the objectives of this work. These models are mainly divided into three categories: those based on cost-benefit analysis, those based on life-cycle assessment and those based on multicriteria decision-making. Much of their work has focused on examining the models used to support decision-making in the area of waste management in an urban setting and highlighting some of the important gaps in these models.

In order to assess these systems on the point of view of sustainability, it's important to be based on reliable and relevant indicators. (Rigamonti et al., 2016) proposes thus the definition of a set of indicators for evaluation of the environmental and economic sustainability of the integrated management systems of domestic waste. The challenge consists to define simple but understanding indicators which can also be calculated by the administrators and the local managers of the waste management system and not only by the scientists or the experts.

In the literature, many studies have also concerned the behavioral study of recipients of waste management systems. The objective of the work of (Guerrero et al., 2013) was to determine the action and behavior of the recipients who play an important role in the waste management process and to analyze the influencing factors on the system. a period of more than thirty years. This study was conducted in urban areas in 22 developing countries on four continents. To evaluate the recipients, the authors used a combination of methods. Other works such as those of (Shekdar, 2009) have also worked on the subject and have identified the main stakeholders (people or organizations) who may be interested in waste management.

The heterogeneity of the cities and the recipients lead to requirements for the ICT systems deployed in waste management to collaborate, while being able to work autonomously, autonomous and resilient way. Moreover, it requires systems able to integrate the existing infrastructures and ICT. (Soto, et al., 2016) proposes a platform of intelligent city which should be an integration platform able to adapt to the regulations and policies of the cities which quickly change.

The result of these many research works and project that the problems related to the interoperability and the integration of urban waste management systems in the developing countries is not largely dealt. However, to have reliable and relevant indicators for strategic decision-making, it's important to federate the urban data in order to make them single. YUSIIP brings a solution to this problem.

3. GENERAL AND FUNCTIONAL ARCHITECTURES OF YUSIIP

In this section, general architecture and YUSIIP operations are presented and described. The general architecture of YUSIIP listed in the Figure 1 (a) shows that YUSIIP are a Multi-source Information System (MSIS), a platform of information exchanges between various organizations implied in urban management and a support of decision-making aid.

The YUSIIP platform is based primarily on a SOA (Services Oriented Architecture) architecture that promotes the use of standards in data exchange between heterogeneous information systems. It thus contributes to the development of an integrated system giving access generically to data coming from the different actors of urban management (individuals, organizations, municipalities, etc.). SOA streamlines service management, supports the division and distribution of consolidated data between heterogeneous

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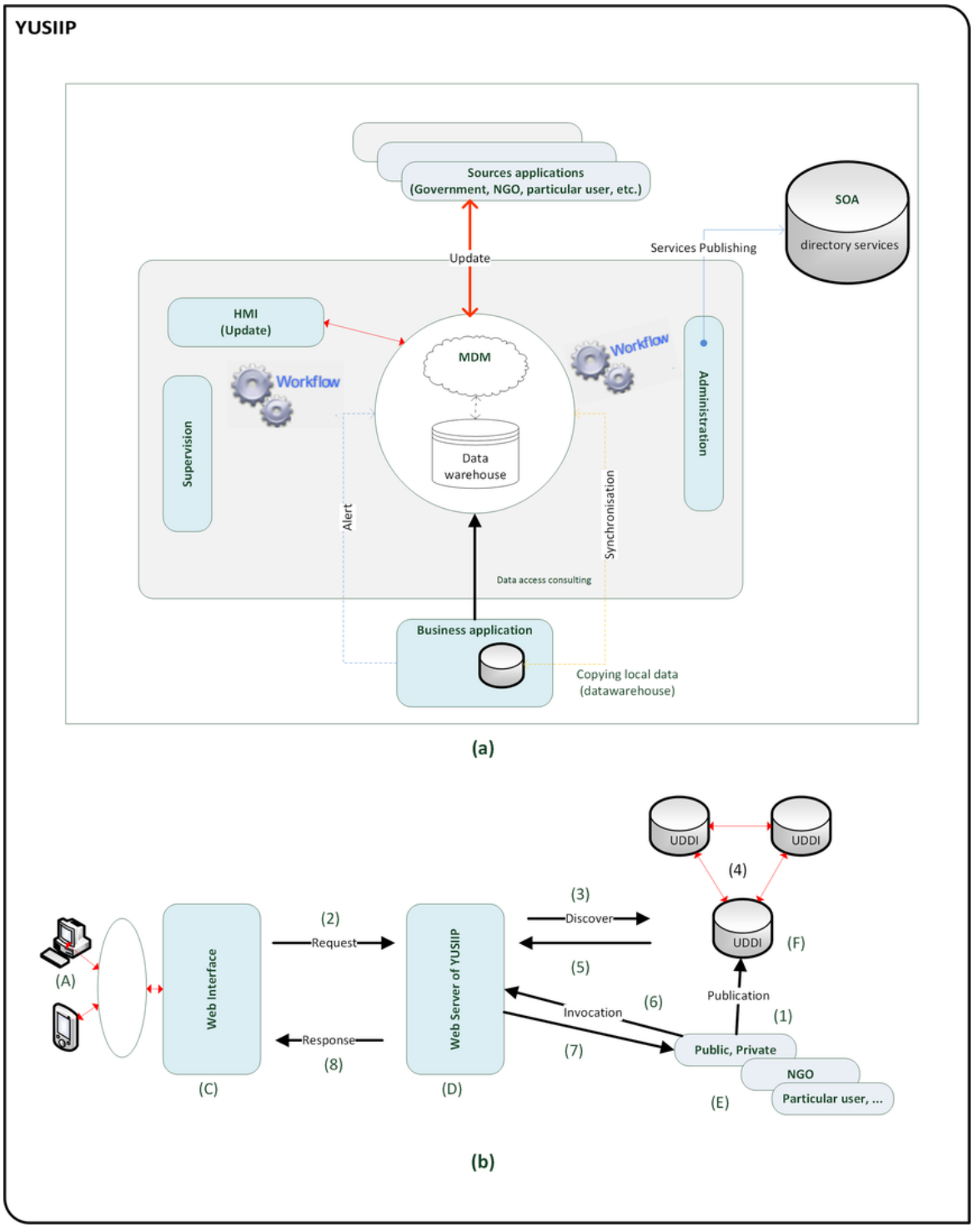
Figure 1. General architecture of YUSIIP platform



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applications via Data Services. Data from urban actors provides factual data or the characteristics of their data in the form of web services through (WSDL / XML / UDDI) complying with specific standard formats (1-thirds). These data formats ensure interoperability for the exchange of information between data providers and consumers (data users). Web services (2-tiers) that query the platform through its central repository (3-tiers). The YUSIIP platform implements a computer-aided software engineering (CASE) which builds the interactive system of decision-making aid (ISDMA), the data warehouse, and the relevant urban indicators progressively. Principle contributions within the choice of the CASE relates to the technical sides such as processes ETL ("Extract – Transform – Load"), OLAP technology (One Line Analytical Processing), the production of data bases of the concepts and the interfaces of visualization brute or incorporated data.

A data warehouse beginning from several disparate and heterogeneous data sources, which makes it possible to memorize perennially urban information and to refer to the sources existing data in order to facilitate their access and their reuse. According to (Inmon, 1994), data warehouse can be defined as "a collection of oriented subject data, integrated, not birds and historized, organized for the support of a process of decision-making aid". For decision-making applications that use heterogeneous data from a variety of sources, data warehouses are an interesting solution. Two storage spaces are distinguished: the data warehouse and the data smarts. The warehouse is perceived as a homogenous centralized storage space gathering useful data for analysis and decision-making, extracted from sources and able to be the subject of historical data. Smart is an extract from the warehouse, where the data is specifically prepared to facilitate their analysis and exploitation by users (decision-makers or managers). In order to provide an effective means for urban managers in their process of analyzing urban waste, housing and sanitation data, data from multiple and heterogeneous sources are integrated into a data warehouse.

To collect the needs of users of the YUSIIP platform, two main approaches have been proposed in this study:

1. The first approach concerns source-oriented collection. It is limited to identifying the needs of the data warehouse from all available data at the level of urban managers such as CIPRE, which since 1996 had been the statistical data on the direct recycling and recycling of plastic waste in Yaoundé. These data mainly concern statistics on: the amount of waste recovered, the geographical location of waste deposits, income, etc. For the management and production of these statistical data, CIPRE uses traditional calculation software (spreadsheets). Other urban managers also feed the data warehouse, such as HYSACAM, which specializes in the collection of household waste and dry and inert materials (glasses, metals, plastics, etc.). LAU undertakes studies and research on slums and sanitation, the INS (National Institute of Statistics) which produces general survey data on the living environment (information about neighborhoods, waste management, garbage cans, evacuations, etc.);
2. The second approach is a needs-driven collection that identifies the needs of users and stakeholders. Data are analyzed according to the relevance of user demand. These data come from information provided by urban managers such as CIPRE, HYSACAM, LAU and INS as well as the documents provided. The conceptual model for intelligent data retrieval in the warehouse in relation to the DWHSMS is shown in Figure 2. The model is composed of six tables: a "Waste Collect" and a set of tables (Organization, Waste, Quarter, City, and Time) connected by foreign keys. The Waste collection table contains information or measures relating to the description of the regular collection of solid waste, such as "Total quantity" and "Percentage of waste."

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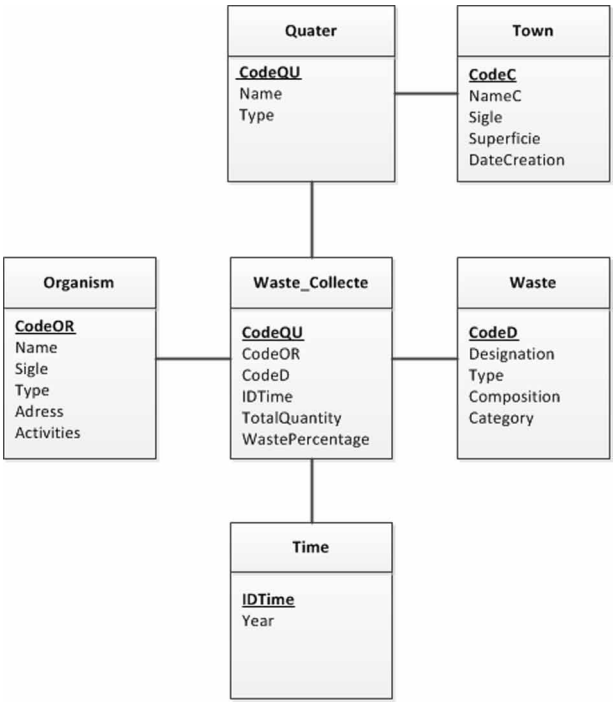
Figure 2. Conceptual model of data smart relating to urban waste



Our work has helped develop a solution for data management for the benefit of urban stakeholders to improve the quality of life in cities. Following the proposed Entities-Relations modeling (Figure 2), the multidimensional model consists of several tables, a "Waste Collect" and a set of size tables (Organism, Waste, Neighborhood, City, Time) each containing a primary key, and a set of entities. These size tables are interconnected by foreign keys. This type of dimension is particularly important for building a data warehouse based on a set of inter-linked data stores. For example, the Waste Collection table contains information or measures related to the description of regular solid waste collection, such as "Total Quantity" and "Percentage of Waste". It also contains information about the types of waste, the time, and code of the organization in charge of its management. Indeed, these conformal dimensions (multiplicity of foreign keys) have the same meaning in all the tables of facts with which they are related. Thus, these dimensions will ensure the consistency of all data warehouse by building a kind of link between data stores. This set of interrelated data is sometimes called decision bus. The above approach is a warehouse building approach for non-complex attribute data.

To provide semantic consistency of the data exchanged with the data warehouse solution, an integration of a Master Data Management (MDM) module has been proposed. This solution also makes it possible to set up a data repository as well as an adapted organization that will make it possible to manage the data in a transversal manner with the various sources of applications professions (Trigaux, 2009). The MDM solution centralizes data in a reference frame and propagates it between applications deployed within a single information system. It is therefore possible to apply a strategy for sharing information. The MDM integration provides the YUSIIP platform a better user interface (HIM) for data administration and all related governance functions: versioning, rights management, querying, validation, approval process up to date and interfaces with the integration data middleware. It is also an ideal solution considered as

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a repository of storage (Ayissi & Moskolai, 2017) and is complementary to the other two approaches (SOA, DW). MDM will enrich the data warehouse of a new layer by providing a unified, personalized and secure data retrieval environment in a meaningful way. In relation to the DW approach, MDM also focuses on unifying models and tools within the information system. To build a truly distributed data warehouse that takes heterogeneous data into account, SOA needs MDM to structure, standardize, and consolidate data from different sources. Similarly, MDM needs SOA to share and distribute consolidated data across heterogeneous applications. A sequencing of the various activities and functionalities of the YUSIIP platform for strategic management and decision making has also been presented in Figure 1(b).

Figure 1 (b) describes the operation of YUSIIP platform as it follows: (A) Various Equipment of connection (PDA, Smartphone, computers, etc.), (B) Average of network Internet connection, (C) Interfaces Web services which the users are reaching, (D) Waiter in which YUSIIP platforms are lodging, (E) Organizations being able to be in the private sector, public or even individuals, (F) Directory of Web services, (1) Once the Web service implemented, the provider service must publish the service in the register. This publication is done through the WSDL and the attribution of a UUID (Universal Unique ID) which makes it possible to identify each service in a single way, (2) When a user reaches the platform, it reaches the interface and a request is sent to the Web server where YUSIIP is lodging, (3) The research of the Web service will be done in our UUID register within the framework of a private register, (4) If it happens that the required service is not being present in our deprived directory then he will be researched in the public directories, service corresponding to the formulated request, (5) The answer (result) of the formulated request is returned to the Web server. This answer can be positive or negative; if it's positive, it will send the characteristics necessary to the use of the found services corresponding to request (details on the supplier, type of connection, address of the service, etc.), if it's negative then the service is not found and end of the process one passes directly to (8). (6) The Web server will thus establish a connection with the service in question. (7) If the service is available the exchange of messages (based on XML) can then start. (8) The answer is thus transmitted to the interface of the user.

4. SUGGESTION FOR A MODEL OF INDICATORS PRODUCTION

In this section, the data models (warehouse, stores) are supplemented by a necessary modeling of the treatments for the calculation of the indicators. In general, evaluation based on indicator systems extends to all domains (economy, urban development, etc.) by considering the recommendations of sustainable development. Indicators are used to show, measure or appreciate a given phenomenon. In the DWHSMS case, Figure 3 presents the model of production of the relevant indicators starting from urban phenomenon to appreciate.

The proposed model is articulated around several major axes namely: themes or subjects (examples: urban management, economic and social governance, environmental governance, etc.), factors or fields (examples: urban waste, housing, sanitation, pollution, etc.), problems relating to each field, observation variable ones and descriptive cards of relevant indicators. Its application to the DWHSMS (urban waste case) has structured information into a dashboard of indicators and statistics to understand certain areas and underlying issues. This availability of data makes it possible to solve existing problems and to anticipate others. The dashboard allows for the collection of generally dispersed data, providing a global view and better management of urban data.

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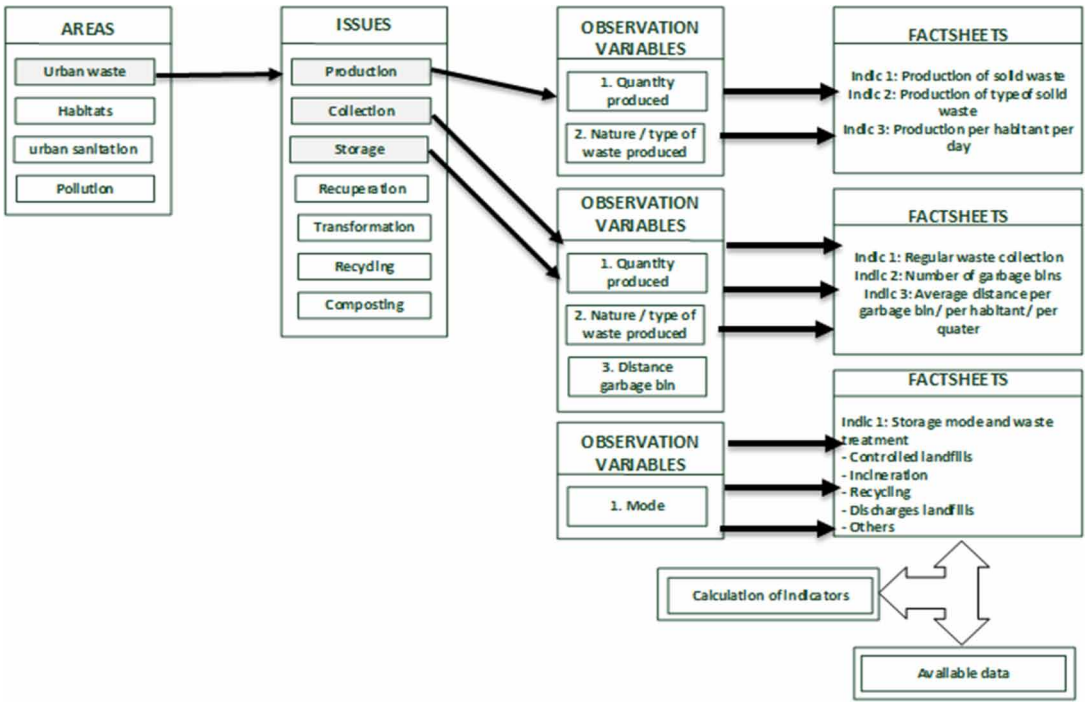
Figure 3. Generic model of production of the urban indicators, the DWHSMS case



5. RESULTS AND DISCUSSIONS

YUSIIP project contributes to building an overall vision of management and city planning in Yaoundé via the installation of a multi-source information system, making it possible to produce knowledge at the same time global (consolidated) and detailed. In this section, the YUSIIP contributions to the DWHSMS are presented and hold an overall discussion on the study of YUSIIP.

5.1. Contribution of YUSIIP Data Warehouse to the DWHSMS

The need for DWHSMS, sanitation, pollution, waste waters and the waterways is dictated by the sanitary and environmental imperatives in urban area. From this prospect, the exploitation of the YUSIIP Data Warehouse presents a real issue. According to the United Nations criteria for Sustainable Development Goals (SDGs), information on household waste management, housing and sanitation or the environment would contribute to the production of statistics, indicators that would make it possible to evaluate the city.

In other to help urban managers in decision-making to improve the quality of life in the urban area, some statistics and indicators of decision support are produced by the YUSIIP platform:

- **Urban Waste:** YUSIIP allows the data collect the characterization of domestic waste in the Yaoundé City and ensures the provision of this data for information and decision-making aid purpose;
- **Production of waste:** Waste is continuously generated, in increasing quantity with the development of lifestyles. They are heterogeneous and their quantitative composition varies according to

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space (city, quarter, household) and from time (year, month, week, day, and season/climate). For example, in Yaoundé (Cameroon), in 2005, the quantity of produced waste per habitant and per day was 0.85 Kg/hab/day. The average production of domestic waste was 0.6 Kg/hab/day in dry season whereas it was 0.98 Kg/hab/day in rain season. The production of waste also varies according to the living standard and the migration of the population (for example the tourist period). The geographical, climatic, economic and demographic factors are determining in the quantification of the generated waste in a city. Table of Figure 4 gives the evolution of quantity of collected waste to Yaoundé since 1996. Knowledge of the waste quantity produced in a given area is essential for the planning of a management system in order to envisage at the best dimension of the collect, installations of treatment and the storage center of waste (Aina et al., 2012). Moreover, the knowledge of quantity of produced waste could make it possible to predict the adequate strategies for a sustainable management of waste and environmental protection in urban area;

- **Physical Composition of waste:** Domestic waste constitutes a heterogeneous mixture of materials having very different chemical and physical properties. Table of Figure 5 gives the physical composition of waste in Yaoundé urban area.

The knowledge of this composition is essential because it makes it possible to determine the management mode of waste and to possibly promote the creation of the treatment and valorization channels. As indicated, the treatment and the valorization of domestic waste play a key role in the fight against pollution of the environment, the conservation of natural resources and energy saving. They can also slow down the global change of climate, caused by the emissions of greenhouse gases, which are responsible for the progressive warming of ground and which involves a global imbalance of natural ecosystems.

- **Chemical and Biological Composition of Waste:** Chemical and biological characterization of waste can contribute to highlighting the existence of harmful effects of pollutants recorded on human health and the environment of untreated waste, especially in urban area. The studies of WHO-Habitat (2010), Rajaganapathy et al. (2011) show for example that cadmium and lead are

Figure 4. Collected waste to Yaoundé since 1996

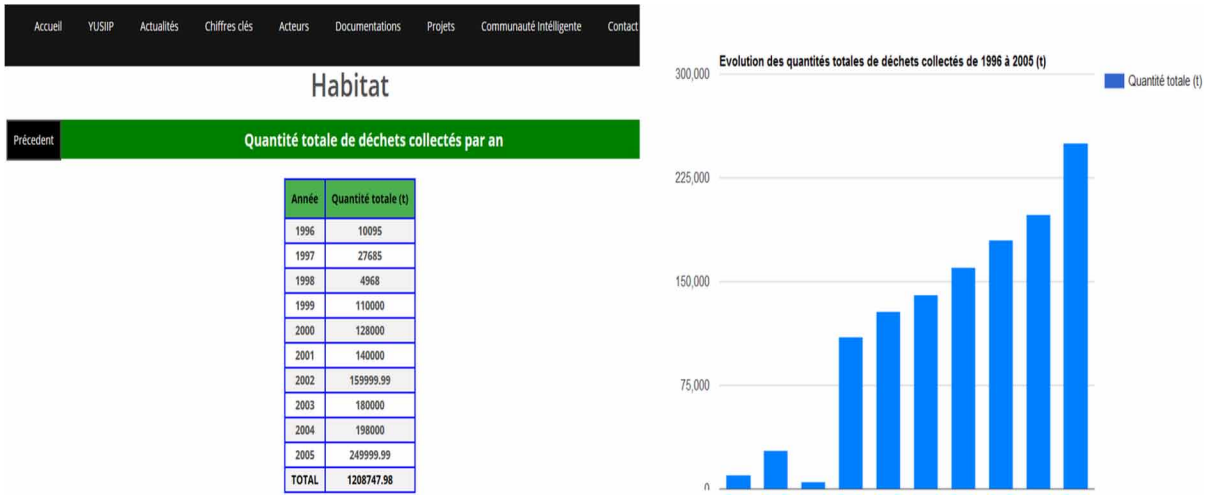

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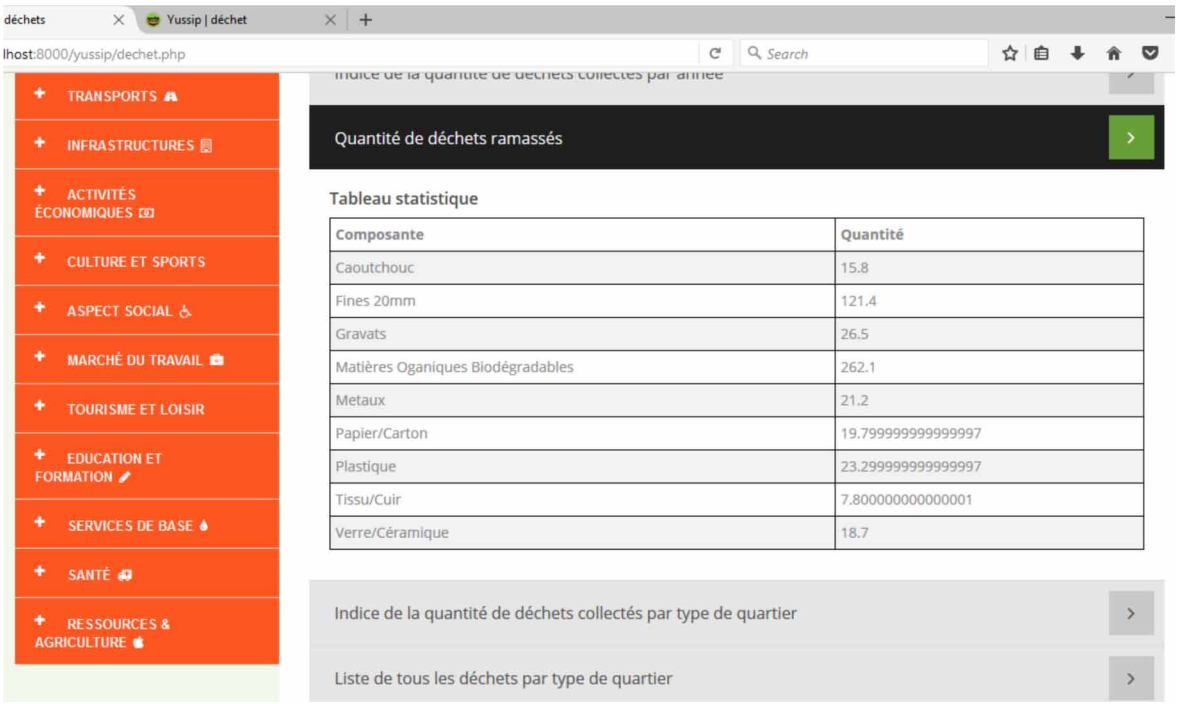
Figure 5. The physical composition of waste in Yaoundé urban area



carcinogenic substances, the manganese excess causes the cirrhosis of the liver, zinc is phytotoxic and is suspected of being carcinogenic for the man. In addition, in a Cameroonian society where the self-medication phenomenon is strongly widespread, the antibiotics used by the population against the bacterial infections, constitute another category of pollutants available in domestic waste. Indeed, these chemical substances are not absorbed in the host organism. Most of them turn over in the environment through the urine and the fecal matter (Czekalski et al., 2014; Samanta et al., 2012). The presence of these antimicrobials in the environment could lead to the dissemination of resistant bacteria in the ecosystems and would pose enormous problems on the man and the biodiversity in the cities.

5.2. Providing Data, Results of Studies on DWHSMS, a Real Issue

Domestic waste, planned and shantytowns, sanitation, waterways, groundwater, waste waters, etc., the studies in these fields are multiplied and it data collect is much developed. However, the data banks as well as the treatments and analysis results relating to it carried out by the researchers are not known from proper authorities. They also are not put at the disposal of managers, other researchers, expert trade or populations. YUSIIP can contribute to curing the lack of legibility and information pedagogy which can lay out the DWHSMS researchers. It collects, cleans and crosses supplements the existing data thanks to its CASE (computer-aided software engineering) set up. The data thus developed are diffused in the form of tables or of interactive cards, which gives accurate information about each Regional and Local Authorities (RLA) and by types of quarters (Figure 6).

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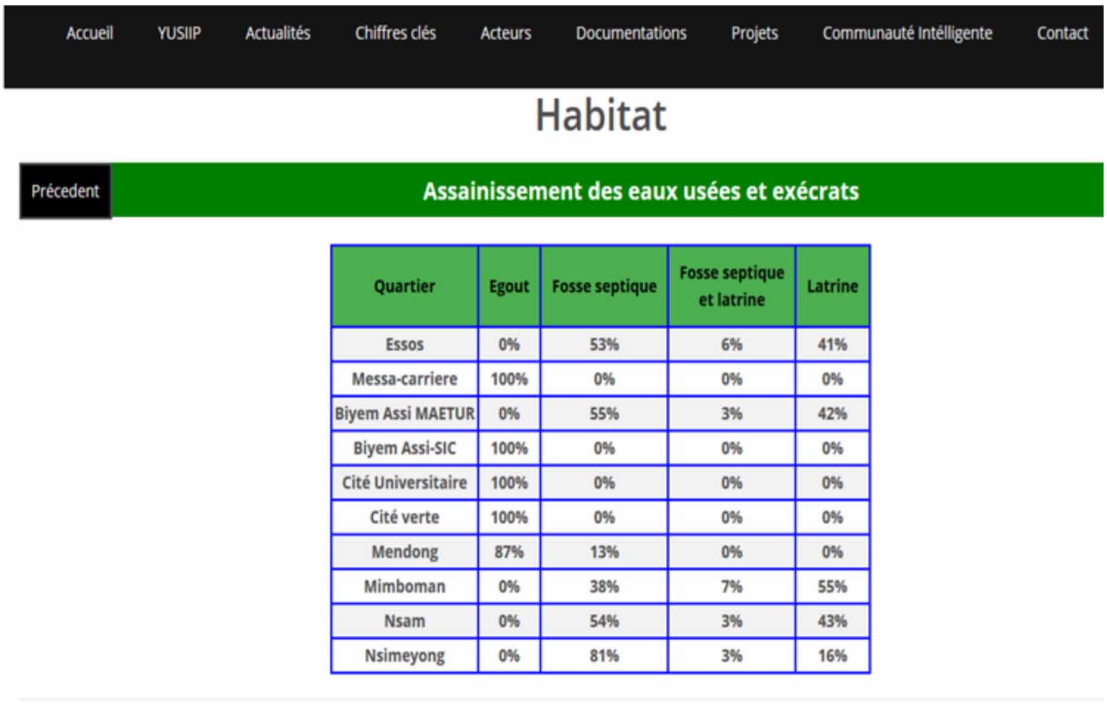
Figure 6. Results of studies on DWHSMS



Quartier	Egout	Fosse septique	Fosse septique et latrine	Latrine
Essos	0%	53%	6%	41%
Messa-carriere	100%	0%	0%	0%
Biyem Assi MAETUR	0%	55%	3%	42%
Biyem Assi-SIC	100%	0%	0%	0%
Cité Universitaire	100%	0%	0%	0%
Cité verte	100%	0%	0%	0%
Mendong	87%	13%	0%	0%
Mimboman	0%	38%	7%	55%
Nsam	0%	54%	3%	43%
Nsimeyong	0%	81%	3%	16%

Public education on the socio-sanitary and environmental risks on the DWHSMS in urban area:

- To conduct public awareness campaigns in keeping with waste and environment management. Thus the population which lives in the insalubrity and pollution of its environment would then be protected from pollutants coming from domestic waste;
- To educate populations on the dangers which waste would represent on health and environment.

5.3. Discussions

YUSIIP Project implements a strategy of the setting up of an efficient model of information systems oriented towards the decision-making aid and with the diagnostic, in order to promote a sustainable urbanization in Yaoundé (Cameroon). The platform can contribute to the piloting of management and urban planning in Yaoundé, i.e., to better concentrate efforts and resources towards the relevant urban problems thanks to reliable indicators; to contribute to the elaboration of the urban development models and the implementation of an information system adapted to the city is one of the objectives of our research project. This contribution aims to:

- Improve the processes of the factors influencing the urban development;
- Set up the means of improvement of the practices of urban development;
- Have indicators of piloting management and urban planning;
- Introduce the tools of the approach quality;
- Integrate the individuals and the populations into the process of the city management.

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Being particularly the DWHSMS, YUSIIP platform can contribute so that proper authorities in charge of domestic waste, housing and sanitation make to these factors, the priority of their action. Data control and knowledge goes:

- To contribute to controlling the urban waste management, without which there will be more loss in human lives, imbalances in the economy and the ecosystems, poverty and the delay in the development of Yaoundé compared with others of the same size cities;
- To contribute to the awareness of populations on the dangers which would present for example urban waste in health and environment. This awareness must pass obligatorily by the availability of data and knowledge on these influential factors in urban health, which constitute the required passage for sustainable management of urban areas.

However, YUSIIP data are still incomplete and the various cases of studies are not carried out in a systematic way. The task which consists in making available the produced data by the whole stakeholders, public and private organizations, social networks, connected objects imply that YUSIIP is integrated in a project of the city.

5.4. Prospects for Master Data Management

With technological advanced, and the view of computerization "proprietary", methodological approaches and models of different systems have often ignored the transverse dimension of urban processes. Today, with the need for interoperability of different systems for information exchange, enterprise architecture solutions alone have found their limits. Therefore, an enrichment of these solutions with the implementation of Service Oriented Architecture (SOA) and Reference Data Management (MDM) contributed to the integration of heterogeneous and sparse data. It is in this sense that the perspectives of the YUSIIP project to develop the data referential relate to:

- Produce continuously data which the availability will not be anachronistic any more in the absence of method and adapted means;
- Produce continuously data and reliable statistics.

6. CONCLUSION

African cities in general and those of Cameroon in particular face a waste management problem due on the one hand to the high population density in urban areas and on the other hand to the development of spontaneously inhabited neighborhoods. This situation is at the origin of the development of diseases such as cholera, malaria, typhoid, asthma, etc., which emanate from the pollution of the environment by waste of various kinds. It is therefore becoming important for cities and decentralized local authorities to take an interest in controlling urbanization and all that goes with it, in order to ensure the well-being of populations. Thus, this control of urbanization will integrate good waste management. However, the lack of DWHSMS data on the level of knowledge of the population of African cities, urban waste and its composition (physical, chemical, microbiological, etc.) expose the population and the environment to the proliferation of several deadly diseases, contamination by the pathogen and chemical substances.

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The multiple and varied risks associated with urban waste, in particular household waste in urban areas, could be avoided if the data listed above were available. Our previous work, which focused on the study of mechanisms for the integration and interoperability of heterogeneous and multi-source information systems, in a context of African cities, particularly Cameroonian cities, marked by a lack of resources (financial, personal, technical), insufficient dialogue between the various actors and scattered and not always reliable information, enabled the YUSIIP to be implemented. These results call for an integrated approach to sustainable organization, urban health, environment and poverty in urban development policies. The basic functions of the YUSIIP are to produce global knowledge about the city, to make available the data produced by all actors, public and private organizations, social networks, connected objects. In the case of DWHSMS, the YUSIIP's distributed data warehouse produces information on urban waste management, housing, sanitation and indicators, which would reduce the social, health and environmental risks of these factors. The distributed data warehouse could provide a basis for public education in urban waste management and environmental protection. The characterization of urban waste can help authorities to make waste management a priority for their action and to remove the dangers that waste would pose to health and the urban environment. In terms of DWHSMS research, our work is an opening for the implementation of an integrated and participatory waste management plan in Yaoundé. As a perspective we count:

- Intensify the collection of information on household waste, housing and sanitation through the promotion and/or strengthening of public-private-civil society partnerships for the enhancement of databases and the refreshing of the YUSIIP data warehouse;
- Integrate data on the behavior, practices and attitudes of the population of Yaoundé regarding household waste;
- Transform YUSIIP into a true open platform and services (OpenPaas) and application on DWHSMS management.

All this will help to reinvent the way urbanization is thought and urban waste is managed by national authorities, the city and local communities.

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Chapter 31
Advanced Nanomaterials for Water Engineering and Treatment:
Nano-Metal Oxides and Their Nanocomposites

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ABSTRACT

Loading of water with multifarious pollutants has dwindled the availability of quality fresh water and put questions on reliability and efficacy of conventional water treatment technologies. Also the quest for developing robust and cost-effective methods with minimum impact on environment had driven the focus of researchers and technologists on new technological developments. Nanotechnology – better referred as Aqua-nanotechnology in this regard provides scientists a new dimension to deal this big problem with small particles having application in 1) water treatment, 2) remediation, and 3) pollution prevention. This chapter will focus on fabrication and use of advance nanomaterials categorized as nanoadsorbents and nanoatalysts for these three main areas. A range of materials exploited in this regard are single and mixed metal oxides and their composites with polymer, clay, carbon based materials etc. while keeping focus on technological developments taken place over the period in regard with treating water and waste water.

INTRODUCTION

The importance of clean and safe water cannot be negated but a famous quote by Jacques Cousteau portrays the true reality about today's world approach that *We forget that the water cycle and the life cycle are one*. As per a report published by World Business Council for Sustainable Development (WBCSD) (Fry, 2005), there is a considerable increase in water consumption with an increase in the industrial

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revolution. All this development has no doubt made human life easy but on other hand has raised serious concerns over the sustainability of clean water as it caused limited share accounting for only 11% of water available for domestic consumption. Water pollution scenario is creating hype in the world and with its cross-border perspective water pollution is not an issue to be addressed and solved by some countries independently but it requires a consolidated approach to mitigate the pollution jinni. According to United Nations World Water Development report 2014, with depleting world water reservoirs and an anticipated rise of 55% in global water demand by 2050; an appreciable number of people are expected to have no access to clean water and improved sanitation (WWDR, 2014). With the development of new materials, chemicals, and technologies, the pollution scenario is getting worse. Also, the application of stringent laws and requirement of reduced levels of minimum contamination levels have put a question mark on the effectiveness of simple biological processes and conventional water treatment technologies (Zhou et al., 2002). Therefore, with the advent of technological innovations, there is a need to revolutionize methods for water treatment and remediation.

With its growing realm, Nanotechnology provides scientists a new dimension to deal with the ever rising problem of clean water availability (Bora et al., 2014; Qu et al., 2013). Also, the quest for developing robust new methods at lower cost, less energy, minimum use of chemicals and least impact on the environment, had driven the focus of environmentalist, water technologists, and engineers on nanotechnology revolution for rejuvenating the polluted fresh water reservoirs by implication of new materials and technologies. Already, the technology had put in a dramatic impact on water quality research and with its broad and diverse range of applications it offers various opportunities and challenges to further stimulate positively in this area of water engineering and treatment.

BACKGROUND

Access to safe and adequate water is the right of every individual living in this world but still 0.8 billion people according to WHO do not have access to quality drinking water and further 2.5 billion people lack access to improved sanitation. The industrial revolution in addition to bestowing us with amenities of life had also resulted in the production of diverse nature of new chemicals and materials which degradation is becoming a serious concern. Hence, loading of water with these diverse nature of pollutants including disinfectants and their byproducts, inorganic and organic chemicals, radionuclides and even resistant strains of microbes has not only limited the fresh water availability but has greatly impacted the water quality. All this resulted in inadequate drinking water, sanitation, and hygiene, which are estimated to cause more than 0.8 million diarrheal disease deaths per year and contribute substantially to several other diseases. Loading of the above-mentioned diverse range of pollutants and emerging of new contaminants also requires new treatment technologies to address the provision of safe water – the search lead to utilization of nanotechnology for water cleanup and remediation.

AQUA-NANOTECHNOLOGY

"Aqua-nanotechnology" has now been recognized as a branch of nanotechnology that deals with the application of nanomaterials for 1) water treatment, 2) remediation and 3) pollution prevention (Tratnyek et al., 2006). Nanotechnology-enabled treatment of water and wastewater provides the much needed

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technological revolution desired to facilitate the removal of a large range of contaminants in an easy, timely and affordable manner with much-improved treatment efficiency (Qu et al., 2013). This chapter addresses the development and implication of nanomaterials like metal and mixed metal oxides, polymer composites, clay composites, carbon-based composites etc. that ameliorated the water quality by promoting sustainable water management.

1. Nano Metal Oxides:

A variety of nano metal oxides (NMO) and their composites have been developed to treat water and wastewater for the removal of inorganic, organic and microbial impurities. Among these, titanium oxide, iron oxides, aluminum oxide, and zinc oxide are commonly used ones (Hua et al., 2012; Zhan et al., 2014).

Different synthetic approaches have been used to synthesize these NMO, among which co-precipitation, sol-gel and hydrothermal techniques (Rao, C. N. et al., 2006) have gained attraction because of their ease and low cost. These NMOs have been able to remove multiple contaminants simultaneously ranging from heavy metals and anions to dyes, pesticides, and microbes but in majority of cases their role as adsorbents is manipulated owing to their economic feasibility and ease of modification to enhance their selectivity and adsorption potential as well as considering (Bora et al., 2014).

Titanium dioxide, TiO_2, in anatase phase, had long been recognized as a material of choice for decontamination of water because of its structure and surface properties (Kumar et al., 2014) in addition to being low cost (Ghasemzadeh et al., 2014). Various heavy metals (Pb, Cu, Ni, Cd, Hg etc.) have been removed using TiO_2 showed adsorption capacities in the range of 7 to 166 mg/g mostly obeying pseudo-second order kinetics and Langmuir adsorption model (Ghasemi et al., 2012; Jin et al., 2015; Liang et al., 2000). The adsorption process was observed to be endothermic supported by pH in the range of 5-8 irrespective of the type of metal adsorbed (Ghasemi et al., 2012; Rashidi et al., 2010). At this pH electrostatic attraction between negatively charged TiO_2 NP and positively charged metal ions dominated promoting surface complexation reactions that support metal uptake (Jin et al., 2015). The adsorption process was dependent on crystalline phase both in the case of anions (F^{1-}) and cations (Pb^{2+}) uptake; pure anatase NPs are found more effective (Suriyaraj et al., 2014). Further, the removal efficacy was found to be independent of coexisting ions normally present in water i.e. Na; K, Ca, Mg; Al; Zn, Fe at tolerance levels of 5000; 2000; 1000 and 500 mg/L, respectively (Liang et al., 2000). The photocatalytic potential of these NMOs was exploited for removal/degradation of organic pollutants like dyes etc. (Farooq et al., 2009) and in some cases ensures complete mineralization of organic pollutants. The photocatalytic activity of TiO_2 was initiated by illumination, thereby transferring an electron to conduction band with the generation of a hole in valance band (Ba-Abbad et al., 2012) as shown in Figure 1a depicting the general photocatalysis mechanism. Because of its photocatalytic nature (Gautam et al., 2016; Hua et al., 2012) TiO_2 is found equally effective in degrading microbes and organic pollutant but the process is usually assisted by H_2O_2 or/and UV light (Ba-Abbad et al., 2012; Gautam et al., 2016) to activate TiO_2 to release photo-generated charges that then initiates the degradation (Gautam et al., 2016). This portrays major disadvantage of TiO_2 for its applicability in industrial settings (Abou-Gamra et al., 2015). In this regard few efforts were done to modify the TiO_2 structure to make it visible light responsive (VLR) by undergoing incorporation of other metals (Kaur, T. et al., 2016; Rauf et al., 2011), metal oxides (Wang, X. et al., 2006), metal salts (Hu, C. et al., 2006), non-metals (Long et al., 2011) or a combination of these (Wang, X. et al., 2006). This process led to the introduction of new states in the band gap of TiO_2

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resulting in overlapping of these states which consequently improve visible light absorption properties and charge transfer (Long et al., 2011). Enhanced adsorption capacities and degradation rates were observed for these VLR-TiO_2 nanomaterials (Kaur, T. et al., 2016).

Alumina, Al_2O_3, is another famous material used for water purification purpose as adsorbent because of its amphoteric nature (Szekeres et al., 1998). Enhanced toxicity of alumina and its mixed oxides nanoparticles as compared to their bulk counterparts was reported for algal as well as bacterial strains (Jiang, W. et al., 2009; Sadiq et al., 2011). The activity is affected by the size of NPs as indicated by the studies carried out on gram-negative bacteria i.e. *Pseudomonas* and *Enterobacter* (Riaz et al., 2016). The interaction of alumina NPs with bacterial strain led to changes in cell wall morphology causing cell deactivation and death of the organism (Jiang, W. et al., 2009). In addition to that alumina NPs underwent several other mechanisms that were proposed for the antimicrobial potential of metal oxide nanoparticles in general which are highlighted in Figure 2 (Dizaj et al., 2014). Nano-alumina is also used for scavenging of metals but with low adsorption capacities (Zhan et al., 2014). Efforts were put in to enhance the uptake of metal ions by undergoing modification (Li, J. et al., 2008) but results are not much encouraging except in some cases e.g. Cu^{2+} (167 mg/g) (Mahdavi et al., 2015; Stietiya et al., 2014). On another hand, high adsorption capacities were noticed in the case of dyes on unmodified nano Al_2O_3 (Zhan et al., 2014) while that of pesticides are determined by their nature and availability of positive sites on the adsorbent surface (Clausen et al., 2001).

Zinc oxide, ZnO, antimicrobial properties of its nanoparticles were exploited against various gram-positive and negative bacterial and fungal strains (Dobrucka et al., 2016; He et al., 2011; Yousef et al., 2012) and found to have highest toxicity when compared with their bulk counterparts (Yousef et al., 2012; Zhang, L. et al., 2007) and other metal oxides (Azam et al., 2012; Jiang, W. et al., 2009). The mode of action proposed is typical as for other NPs based on the release of metal ions, electrostatic interactions, generation of reactive oxygen species (ROS) and the collapse of the bacterial membrane as portrayed in Figure 2 (Dizaj et al., 2014). Antibacterial activity was affected by synthetic approach (Sirelkhatim et al., 2015) as well as water chemistry and showed an inverse dependence on particle size as it directly impacts the release of Zn^{2+} ions (Li et al., 2011; Zhang, L. et al., 2007). Some studies have also marked NP's concentration as a more dominating factor towards antimicrobial activity than the particle size. Moreover, stabilizing agents can augment the activity by directly affecting agglomeration, but no direct impact on the type of stabilizing agents was observed (Zhang, L. et al., 2007).

Figure 1. Photocatalytic degradation mechanism of pollutants on a) MONP b) ZnO-TiO_2 nanocomposite c) ZnO-α-Fe_2O_3 Nanocomposite for degradation of 2,4-D (Chen, J. et al., 2016; Homaeigohar et al., 2014; Lee et al., 2016; Maya-Treviño et al., 2014; Umar et al., 2013)

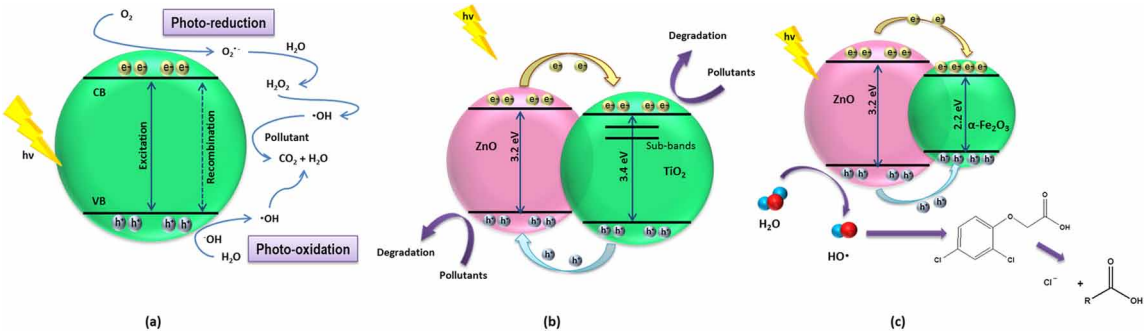

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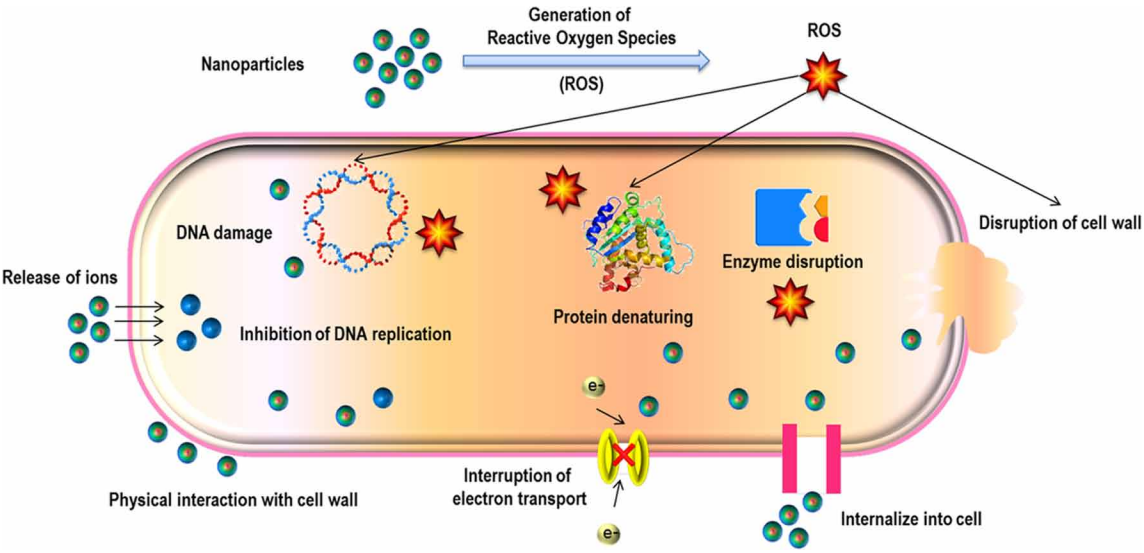
Figure 2. Different mechanisms responsible for antimicrobial activity of metal oxide nanoparticles (Dizaj et al., 2014)



ZnO system has the advantage of being not UV-assisted (Dobrucka et al., 2016) however use of it can enhance the photocatalytic potential to a considerable extent (Sirelkhatim et al., 2015). High degradation/ removal rates for various dyes (Zhan et al., 2014), pesticides (Khan, S. et al., 2015), organometallics (Olushola et al., 2014), pharmaceutical compounds (Han et al., 2012) and other organic aliphatic and aromatic contaminants (Anju et al., 2012; Shinde et al., 2011) were noticed both in absence and presence of irradiation on treatment with ZnO NP/ thin films/ nanowires/ nanoneedles. The reaction displayed dependence on calcination temperature, irradiation time, pH and ZnO dosage (Hayat et al., 2011), defects formation (Meng et al., 2015), particle size and structure/morphology (Wang, H. et al., 2007; Yang, J. L. et al., 2004). Correspondingly, photocatalytic degradation efficiency of anions like CN^- (Bagabas et al., 2013) and PO_4^{3-} (Elkady et al., 2016) was greatly impacted by the morphology of ZnO. In case of metal adsorption, overall low adsorption capacities were observed for Ni^{2+}, Pb^{2+} and As^{5+} (Mahdavi et al., 2012; Venkatesham et al., 2013; Zhan et al., 2014) while for Cd^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} higher removal rates were noticed (Mahdavi et al., 2012; Rafiq et al., 2014; Sheela et al., 2012) which were even greater than the ones shown by iron and copper oxides (Mahdavi et al., 2012) but lower than that of MgO (Rafiq et al., 2014). For Nobel metals, three times improved removal efficacy was observed for nano ZnO as compared to nano TiO_2 (Park et al., 2003).

Oxides of iron, magnetite (Fe_3O_4), maghemite (γ- Fe_2O_3), hematite (α-Fe_2O_3) and goethite (α-FeOOH) because of their low toxicity, unique magnetic properties and biocompatible nature have always remained the material of choice for water treatment (Teja et al., 2009; Xu, P. et al., 2012). Rapid fluoride adsorption had been assisted by nano γ-Fe_2O_3 but with low adsorption capacity (Jayarathna et al., 2015). The use of mixed iron oxides helped in increasing the uptake capacity but system took much longer time to achieve equilibrium (Mohapatra et al., 2011). Chemical and electrostatic interactions together with ligand exchange reactions between an anion and OH^- or water on adsorbent surface played their role in the removal of anions (Mohapatra et al., 2011). The uptake as a general protocol depends on upon the initial pH, adsorbent dose, temperature and initial adsorbate concentration and presence of co-ions like

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SO_4^{2-} and Cl^{-1} (Mohapatra et al., 2011; Nalbandian et al., 2016). In the case of α-Fe_2O_3 nanofiber, indirect independence of CrO_4^{2-} removal was observed on the diameter of nanofiber which was attributed to change in the surface area solely because of physical nature of adsorption (Nalbandian et al., 2016). In the case of heavy metals, fast removal of on nano γ-Fe_2O_3 was facilitated by the presence of reactive sites on surface hence enabling the system to reach equilibrium in short time (Hu, J. et al., 2006). Contrarily, nano-Fe_3O_4 took a longer time to achieve equilibrium (Giraldo et al., 2013; Mahdavi et al., 2012) probably due to differences in surface area and particle size. Introducing functionalization to Fe_3O_4 had greatly reduced the time to achieve equilibrium and with better adsorption capacity that increased with increase in the concentration of functionalizing moiety (Huang et al., 2009). The uptake efficacy though dependent on cation nature, pH, temperature etc. (Giraldo et al., 2013) but dramatic change in adsorption were observed with change in particle size (Xiao et al., 2015) surface sites, porosity and ionic strength (Giraldo et al., 2013). In contrary to previous studies Cheng *et.al.* showed no effect of a change in ionic strength on adsorption of Arsenic (Cheng et al., 2016). Studies on the effect of competing ions like HCO_3^{1-}, SO_4^{-2}, F^{1-}, Cl^{1-} and NO_3^{1-} indicated no effect on adsorption while HPO_4^{2-} and SiO_3^{2-} impacted to somewhat extent (Cheng et al., 2016). Similar studies performed pointed out that the effect of coexisting ions (i.e. sulphate, phosphate, nitrate, silicate) on removal efficacy vary with change in pH (Tuutijärvi et al., 2012).

The surface adsorption of IONP was more effective and rapid for hydroxyl containing dyes like bromocresol green than the ones that don't have OH group e.g. methyl red (Saha et al., 2011). Complete and fast removal of such dyes was achieved by use of hematite hollow nanofibers (Gao, Q. et al., 2015) and γ-Fe_2O_3 owing to chemisorption (Khan, M. et al., 2016). Simply changing the pH to alkaline media effectively desorbed these IONP ensuring their reuse (Saha et al., 2011). In the case of phenol, the mineralization efficacy depended on the generation of OH radicles and presence of other organic pollutants which suppressed the degradation process (Wang, W. et al., 2013). The process can be speeded up by use of UV irradiation and controlling its irradiation time and laser energy (Bardajee et al., 2013; Gondal et al., 2009).

IONP have proved themselves as effective antimicrobial agents as well against different microbial strains (Ismail et al., 2015). They operate in similar way as other NMO (Figure 2) i.e. on basis on reactive oxygen species generated that later interact with DNA and protein of bacteria leading to damage of cell (Tran et al., 2010) but the activity level achieved by Fe_2O_3 was less than ZnO and CuO NPs (Azam et al., 2012). Gram negative bacteria were more resistant to IONP than gram positive owing to differences in the cell wall, cell physiology and degree of contact (Azam et al., 2012). Positively and negatively charged surface modified Fe_3O_4 NP depicted dissimilar response to bacterial toxicity since different surface charges interacted with the bacterial cell differently; order of toxicity observed was positively charged > bare Fe_3O_4 > negatively charged. Moreover, surface properties of NMO are more decisive in determining antimicrobial activity than the properties of the core itself (Javanbakht et al., 2016).

Nano-Mixed metal oxides (NMMO) of iron, aluminum, titanium and zinc have also been exploited for water treatment. Several methods have been used for their synthesis which includes sol-gel, co-precipitation, wet chemical synthesis, microemulsion etc. Unique properties resulted from the combination of these materials (Kapoor et al., 2004). Among these, photocatalytic activity is one of the most exploited property in water treatment. This in the case of NMMOs helps in reducing electron-hole pair recombination which portrays the major disadvantage of NMO. In addition to that such combinations promote the generation of OH● and ROS thereby enhancing the photocatalysis process. A model system of ZnO-TiO_2 and ZnO-α-Fe_2O_3 is presented in Figure 1 b and c. which are produced by a combination of

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two NMOs (Chen, J. et al., 2016; Homaeigohar et al., 2014; Lee et al., 2016; Maya-Treviño et al., 2014). The introduction of ZnO into TiO_2 promoted sub-bands production along with generation of defects resulting in a decrease in energy gap and better response to UV illumination (Chen, J. et al., 2016). Hence, owing to these attributes much higher and faster dye degradation was achieved by these NMMO systems when compared to pure NMO. Various combinations used in this aspect are ZnO/TiO_2, γ-Fe_2O_3/SiO_2, Al_2O_3/TiO_2, ZnO/Fe_2O_3, WO_3/TiO_2, ZnO/Fe_3O_4, ZnO/SnO_2, CeO_2/TiO_2, SnO_2/TiO_2, ZrO_2/TiO_2 CuO/ZnO etc. Factors like the type of dopant, doped or molar concentration, irradiation time, precipitation agent during synthesis, sintering temperature, crystallite size, pollutant type, counter ions etc. determined the degradation efficacy in these cases. The change in molar concentration considerably affected the band gap, phase change, purity, morphology, crystallite size (Cun et al., 2002; Hameed et al., 2009; Wang, J. et al., 2009). In the case of mixed metal oxides of IONP presence of competitive ions like heavy metals considerably altered the uptake of dyes depending upon radii and charge they carry. In addition to that low concentrations of humic acid promoted adsorption process because of enhancement in the available surface area but in excess amounts they obstructed the adsorption process by blocking the passage of adsorbate (Chen, D. et al., 2016).

Defluoridation achieved by use of MgO/γ-Al_2O_3 was higher than $/\gamma$-Al_2O_3 and was slightly affected by the presence of counter-ions (Nazari et al., 2015) while in the case of Al_2O_3/Fe_3O_4 NMMO, the presence of other ions had no impact on removal efficacy (Chai et al., 2013). The electrostatic interactions which demarked the main role in adsorption process were affected by the presence of competing ions in order phosphate > carbonate >> sulphate > nitrate > chloride (Azari et al., 2015). TiO_2 doped IONP when used as an adsorbent, the equilibrium was achieved within 5 min for As^{3+} uptake even in dark while for As^{5+} UV illumination was required to remove it from the water. As^{3+} adsorption was predicted to take place by oxidation to As^{5+} which then adsorbed on to the NMMO surface (Yu, L. et al., 2013).

Triple metal combinations were also evaluated by many researchers in the search for having effective and efficient photocatalysts, adsorbents and antimicrobial agents with promising results (Motlagh et al., 2015).

2. Polymer Composites

Metal matrix polymer nanocomposites are usually synthesized by two main techniques

1. *In situ* synthesis, and
2. Direct compounding (Zhang, Q. et al., 2013; Zhao et al., 2011).

Incorporation of these MONP into polymer matrix have not only increased the surface area, reactivity and mechanical strength but also inherent in them the unique combination of properties of both inorganic nanoparticles and organic polymer matrix making them fit for meeting the water treatment process requirements i.e. antifouling, photocatalytic, flux enhancement, hydrophilicity etc. (Baghbanzadeh et al., 2016; Jeon et al., 2010; Zhang, Q. et al., 2013). Further, it facilitates to overcome separation issues of NP (Zhao et al., 2011). Many inorganic materials have been used as inorganic fillers to prepare these polymeric hybrids e.g. metal NP (Palza, 2015), MONP (Baghbanzadeh et al., 2016), metal carbonates (Rong et al., 2006) etc. but here in this chapter the scope will just focus on the ones prepared using MONP.

The addition of metal oxides advocated hydrophilic character of the polymeric material thereby promoting antifouling properties. Moreover, modifications using magnetic or superparamagnetic MONP

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ensured easy separation and recovery of the adsorbent by application of low-gradient magnetic field (Qu et al., 2013). Highest and fastest recovery achieved in the case of core-shell magnetic nanorods based polymer composites was ~ 25s (Venkateswarlu et al., 2015). Optimization of nano Fe_3O_4 in Polyethersulfone (PES) - nano Fe_3O_4 membrane facilitated in achieving desirable pore size, roughness, porosity, contact angle, water flux and rejection capacity. Using high weight % of IONP put a negative impact on water flux by suppressing microvoids growth and enhancing film skin thickness; the best results were achieved for 10 and 15 wt.% doping (Alam et al., 2013). Likewise, doping of Al_2O_3 into PES, having application as membrane bioreactors, led to decrease in de-ionized water permeation with an increase in polymer ratio while the opposite effect was observed with the rise in NP concentration (Maximous et al., 2009). Correspondingly, varying the amount of SiO_2 NP (30 nm) in PES potentially impacted water flux, hydrophilicity and antifouling abilities of the membrane and hence this can be tailored to achieve desirable properties (Shen et al., 2011).

Magnetic capturing of Cu^{2+} was achieved by controlled coating of polyethylenimine (PEI) onto Fe_3O_4 NP. Increase in PEI coated amount enhanced the uptake which was facilitated by the presence of amino nitrogens in the structure of PEI; this enabled manipulating the adsorbents' colloidal properties to achieve maximum adsorption even at ultra-trace levels of free Cu^{2+} ions selectively (Goon et al., 2010). Contrary to this, uptake capacity increased (341.43 – 489.12 mg/g) with decrease in PVA content (4.55 – 1.43%) in case of PVA/ SiO_2 NC fibers modified by mercapto groups with maximum adsorption reaching to 504.89 mg/g in just 40 min. Higher affinity for Pb^{2+} was detected in hybrid polymers prepared by unmodified or amino functionalized Fe_3O_4 NP and nanorods followed by other metals like Cd^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+} and As^{3+} (Badruddoza et al., 2013; Ge et al., 2012; Venkateswarlu et al., 2015). Contrarily, better uptake was achieved in the case of Fe_3O_4 NP/carboxymethyl-β-cyclodextrin; attributed to the presence of –COOH and –OH functional groups in adsorbent (Badruddoza et al., 2013). Uptake was slightly affected by the presence of monovalent ions but in the case of divalent strong competition was observed (Ge et al., 2012). Additionally, increase in ionic strength can cause decreases in ions removal (Badruddoza et al., 2013). Ion exchange properties of Fe_3O_4/polypyrrole core-shell NC were exploited for Cr^{6+} that replaced doped Cl^- with chromate ions (Bhaumik et al., 2011). On another hand, Pb^{2+} uptake was expedited by improving porosity and surface roughness of Polyethersulfone /hydrous manganese dioxide (PES/HMO) NC membranes achieved by increasing HMO:PES ratio (Gohari et al., 2013). Type of MONO doped, particle distribution with respect to depth, the amount of doping and dopant to polymer ratio considerably affects the behavior and properties of the composite membranes (Maximous, N. et al., 2010). Desorption of metals like Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} from polymer composites was attained through Na_2-EDTA, HNO_3, H_3PO_4 and HCl solutions depending on the polymer system, metal adsorbed and leaching agent nature (Badruddoza et al., 2013; Gohari et al., 2013; Venkateswarlu et al., 2015). Relating these polymer composite systems with activated carbon showed comparable removal efficiencies for Pb^{2+}, little less for Cr^{3+} and much lower for Cd^{2+} (Maximous, N. N. et al., 2010).

High fluoride adsorption capacities were also reported within 60 and 120 min for the magnetically modified polyacrylonitrile and polyaniline hybrids, respectively. Desorption studies performed indicated irreversible nature of adsorption process in former case 85% desorption was achieved for polyaniline NC at pH 12 (Jokar et al., 2014; Nouri et al., 2014). Dye adsorption on to Fe_2O_3/Polyacrylonitrile NC occurred as a result of electrostatic attraction between positively charged IONO and negatively charged dye molecule. The uptake capacity depended on the synthetic approach used with maximum adsorption achieved for the hydrothermally grown nanoparticles i.e. 50.08 mg/g (Patel et al., 2016). Mixed metal

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oxide polymer (Fe_3O_4/Cu_2O/PANI) NC with different morphologies i.e. flower-like, microsphere with ordered nanosheet and porous dandelion were synthesized by altering aniline/Cu^{2+} ratio and used for dyes and oil adsorption. The high uptake capacity was achieved due to porous structure and in the case of dyes combined effects of electrostatic interactions, coordination of dyes anionic group with metal ions and van der Waals forces. The prepared materials were selective for anionic dyes as cationic dyes face repulsive interactions between positively charged dyes groups and metal ions (Cao, J. et al., 2014). Complete mineralization of phenol was attained under visible light by optimizing the aniline/TiO_2 concentration during *in situ* synthesis of TiO_2-PANI NC. The photocatalyst maintained the activity till 5 recycles and performed much better than neat TiO_2 (Li, X. et al., 2008).

3. Chitosan and Clay Based Nanocomposites

Chitosan is a natural low-cost polymer having excellent chelation properties and easy modification protocols making it suitable for water purification purposes (Ngah et al., 2011; Reddy et al., 2013). The presence of amine groups facilities adsorption of cations, anions or polar molecules by chelation, electrostatic interactions, dipole interactions, van der Waals forces etc. (Rangel-Mendez et al., 2010). Certain disadvantages of these biopolymers i.e. agglomeration, denaturing, separation inefficiency and inadequacy to be used in packed columns limit their applications. Provision of support or modification helps in overcoming these disadvantages but lowers the uptake potential and intraparticle diffusion of these bio-composites (Ngah et al., 2011; Rangel-Mendez et al., 2010; Tanhaei et al., 2015; Zhang, J. et al., 2011).

Using IONP as additives in Chitosan NC enhances chemical stability and provide ion selectivity (Tanhaei et al., 2015). The usual procedure of making these NC is to grow a layer of chitosan on NP making core-shell structure (Figure 3a (Reddy et al., 2013)) that not only prevents agglomeration of chitosan but also increase number of free amino groups (Fan et al., 2011; Zhang, J. et al., 2011). In other studies, hydrogen bonding of MONP with these amino groups and availability of free O-H with partial positive charge was suggested (Shrifian-Esfahni et al., 2015). In the case of Arsenic removal, these magnetically active chitosan materials showed higher selectivity for As^{5+} than As^{5+} but the process was highly pH dependent (Wang, J. et al., 2014). Beads prepared by dispersing of FeOOH NP in chitosan chelates with arsenic either by forming a covalent bond with amine group or iron (Hasan et al., 2014) as contrary to Fe_3O_4/chitosan NC where –OH group on adsorbent surface interacted with arsenic (Wang, J. et al., 2014). Besides, NC of chitosan with single metal dopant e.g. Al_2O_3 (Gandhi et al., 2010), TiO_2 (Miller et al., 2010), CuO (Elwakeel et al., 2015) or with mixed metal oxides like Al_2O_3- TiO_2 (Yamani et al., 2012), Fe-Mn binary oxide (Qi et al., 2015) had been used for heavy metal removal. On comparative account, the bimetallic NC had better adsorption potential than the pure systems (Yamani et al., 2012). The presence of counter ions presents in water impacted differently on the metal uptake. For example As^{5+} uptake was hindered by HPO_4^{2-}, HCO_3^{1-} and SiO_3^{2-} ; not affected by SO_4^{2-} and enhanced by Ca^{2+} and Mg^{2+} ions (Qi et al., 2015) while that of Cr^{6+} was reduced by presence of all the co-ions employed in the experiment i.e. NaCl, Na_2SO_4, $NaNO_3$, $CaSO_4$ and $MgSO_4$ (Gandhi et al., 2010). Effective separation was achieved in the case of these NC but employing ultrasound radiation ensured much faster separation (Liu, X. et al., 2008). These nanocomposites offered the advantage of reuse owing to reversible nature of metal and magnetic chitosan NC interaction hence, the simple weak acid treatment made these adsorbent workable up to 6 cycles (Fan et al., 2011).

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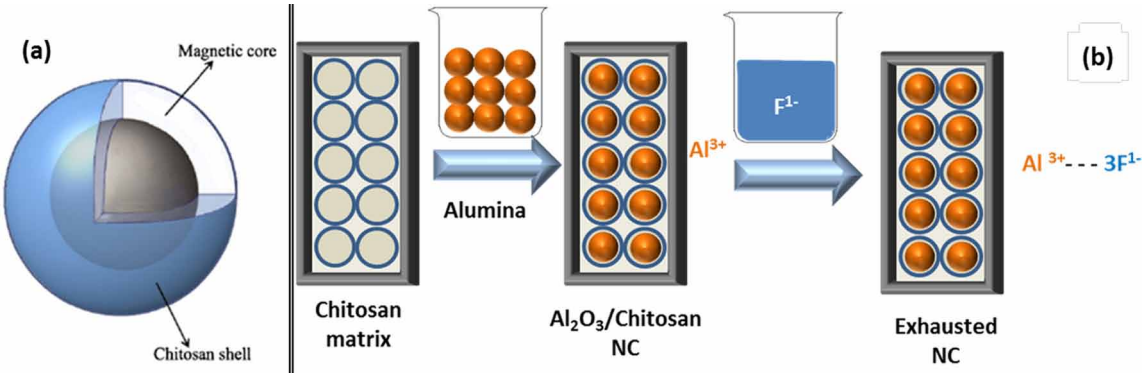
Figure 3. a) Magnetic core chitosan shell (Reddy et al., 2013) b) Mechanism of F^{-1} adsorption on Al_2O_3/ Chitosan NC (- - - shows electrostatic adsorption and complexation) (Viswanathan et al., 2010)



Fluoride removal onto Al_2O_3/chitosan composite was directed by 1) electrostatic attraction between Al^{3+} and F^{1-} and 2) complexation of F^{1-} with positively charged surface as shown in Figure 3b (Viswanathan et al., 2010). However, dyes adsorption on to MONP/chitosan was suggested to be chemisorption in which amino groups on the surface of chitosan NC bind to negatively charged groups of dyes (Salehi et al., 2010; Zhang, J. et al., 2011). Magnetic chitosan NC promoted dye removal as well through spontaneous and endo- or exo-thermic process obeying Langmuir adsorption model and pseudo-second-order kinetic model (Cao, C. et al., 2014; Fan, Zhang, Li, et al., 2012; Fan, Zhang, Luo, et al., 2012; Reddy et al., 2013). The selectivity for a specific dye uptake can be enhanced by using the molecular imprinting technique (Fan, Zhang, Li, et al., 2012). Synergistic effects of mixed metal oxides and chitosan were also exploited to achieve better removal percentage of acidic dyes (Jiang, H. et al., 2013; Zhu, H. et al., 2012). Higher uptake i.e. 216 mg/ g was achieved for Remazol Red 198 in 60min at room temperature by using O-carboxymethylchitosan-N-lauryl doped with γ-Fe_2O_3 NP (Demarchi et al., 2015). Faster (< 20min) and even higher removal were achieved for methyl orange by using Fe_3O_4/Al_2O_3/chitosan and γ-Fe_2O_3/chitosan NC i.e. 416 mg/g and 779 mg/g (Obeid et al., 2013; Tanhaei et al., 2015). Factors like chitosan amount, MONP wt. %, solidifying solutions type and concentration, UV light, adsorbent structure, dye nature etc. affected the degradation efficacy of the chitosan NC (Haldorai et al., 2013; Li, Q. et al., 2008; Zubieta et al., 2008). In the case of dyes as well co-ions present in the water and wastewater like Cl^{1-}, SO_4^{2-} and HCO_3^{1-} affected uptake capacity negatively (Salehi et al., 2010). Concurrently, multifunctional nature of these hybrid materials had been investigated for simultaneous uptake of heavy metal, bactericidal activities and photocatalytic properties and results obtained were encouraging (Haldorai et al., 2013, 2014; Zhang, X. et al., 2011). Also, studies carried out on actual wastewater samples showed effective cleanup by the MONP and chitosan NC (Zhang, X. et al., 2011).

Even better results are obtained by introduction of layer by layer system (i.e. TiO_2/ chitosan supported on glass) that achieved 32 times faster decolourisation rate as compared to single layer system (TiO_2) owing to collective role played by multiple effects of photocatalysis, adsorption in sub-layers and charge-transfer process (Nawi et al., 2012). The rate of degradation strongly depends on the TiO_2 content and number of layers as increase in these parameters led to increasing in film thickness, mobility, and diffusion of dye molecules, penetration of light source and growth in crystallite size of TiO_2 (Nawi et al., 2012; Zainal et al., 2009).

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Antimicrobial applications of chitosan against many fungal, bacterial and viral strains are well researched. This broad-spectrum nature, higher bacteriostatic and bactericidal activities and lower toxicity to mammalian cells make it a material of choice. The mode of action is based on interaction with the cell membrane and chelating action (Rabea et al., 2003). With the incorporation of NP, the bactericidal effects of NC are amplified owing to multifarious mechanisms that hamper bacterial growth and promote cell inactivation (Haldorai et al., 2013; Shrifian-Esfahni et al., 2015). The viable bacterial count results showed 99% and 93% *E. coli* inactivation by CuO and MgO impregnated chitosan, respectively as compared to 7% for pristine chitosan (Haldorai et al., 2013, 2014). Likewise, Lower MIC values were observed in the case of susperparamagnetic IONP/chitosan NC *vs* superparamagnetic IONP i.e. 40 µg/mL compared to 70 µg/mL for *P. aeruginosa* and 45 µg/mL compared to 90 µg/mL for *E. coli* respectively (Shrifian-Esfahni et al., 2015).

Clays, another natural source, are hydrous aluminosilicates that act as a natural scavenger of pollutants (Bhattacharyya et al., 2008). Modifications of clays either through intecalation, acid activation, functionalization, incorporation of dopants, the formation of hybrid structures etc. had been practiced for improving their properties (Bhattacharyya et al., 2008). Montmorillonite, bentonite, kaolinite, sepionite, halloysite and zeolite are the common clay minerals that have been used as fillers for preparing NC materials (Motshekga et al., 2013). Dispersing MONP into the clay structure reduce agglomeration and settles the particles on the surface or inside the pores of clay thereby enhancing surface area (Yuan et al., 2009).

Antimicrobial potential of clays is enhanced by harnessing them with the MONP ones making these hybrid materials extremely useful. Comparative account of undoped and doped bentonite against *E. coli* and *E. faecalis* showed that pristine bentonite had no effect on the bacterial growth; ZnO-bentonite showed inhibition zone in the range of 5-9mm and Ag/ZnO-bentonite (6-11mm) had activity comparable to Ag/bentonite (8-11mm) (Motshekga et al., 2013).

Different clays like bentonite, sepiolite, montmorillonite were doped with Fe_3O_4 and utilized for adsorption of heavy metals. 15.3 mg of Cr^{6+} /g of Fe_3O_4/monmarillonite was removed owing to the electrostatic interaction that led to its reduction to Cr^{3+}; the adsorption depended on upon the synthetic approach used to prepare adsorbent (Yuan et al., 2009). Much higher uptake of Cr^{6+} (161.29mg/g) was achieved on $MgFe_2O_4$ /bentonite composite and with easy regeneration using 0.1N NaOH (Kaur, M., Singh, et al., 2015). On another hand, Fe_3O_4 impregnation in bentonite resulted in low uptake capacity (18.76 mg/g) for Co^{2+} (Hashemian et al., 2015). Higher uptakes for As^{3+} i.e. 50.35 mg/g were observed when sepiolite was used instead with good effectiveness on real ground water samples as well. The fast adsorption of As^{3+} into NC was facilitated by the highly porous structure of clay that promoted easy access to iron oxide to result in As(III) – Fe(III) complexes and partial oxidation of As^{3+} to As^{5+} as outlined in Figure 4. The presence of F^{-1} and PO_4^{3-} as counter-ions impact the removal of As (III) to some extent because of competition posed by the similarity in structure and dissolution constants (Tian et al., 2015). Quick uptake of heavy metals (i.e. 2 min) was achieved using Fe_3O_4/talc NC leading to adsorption capacities in order of Pb^{2+} (74.62 mg/g) > Ni^{2+} (33.33 mg/g) > Cu^{2+} (21.05 mg/g) as calculated using Langmuir model (Kalantari et al., 2014).

MONP were supported on different aluminosilicate for evaluating their catalytic degradation pattern towards organic contaminants (Khatamian 2012). In general, the supports provided better degradation potential compared to unsupported ones by augmenting the radicle attack on organic moiety. Moreover, changing its size to nanoscale further enhanced the degradation rate. The type of support also impacted considerably as it not only determines the morphology of NC but also facilitates the binding of adsorbate to its surface.

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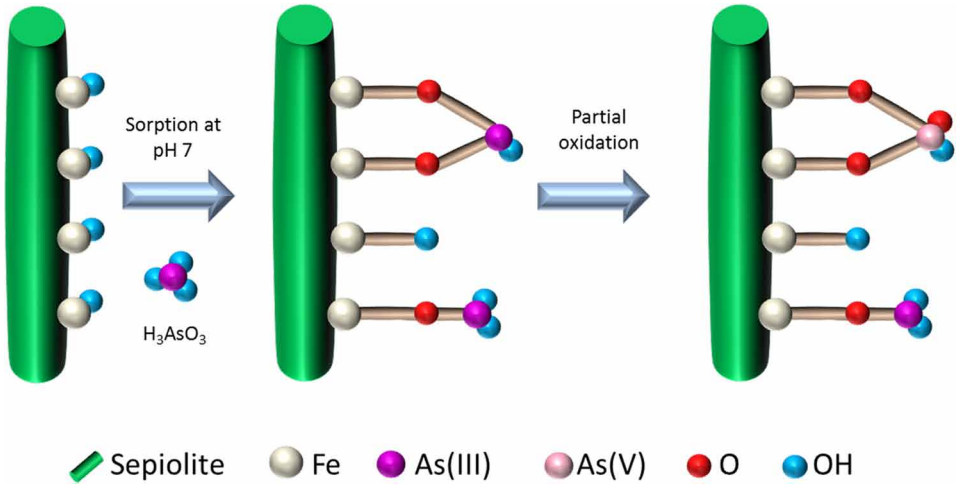
Figure 4. Proposed mechanism of As^{3+} adsorption on Fe_3O_4/ sepiolite nanofibers (Tian et al., 2015)



Among the three type of supports i.e. HZSM-5, clinoptilolite and zeolite HY, the best results were obtained with HZMS-5 because it promoted finely dispersed structure, enhanced hydrophobicity, high adsorption capacity, and delocalization of electrons generated . Reduction in pore size and surface area of support was observed with incorporation of ZnO NP in nanoclinoptilolite or HZSM-5 (Khatamian et al. 2012) while the opposite behavior was observed when Fe_2O_3 NP was doped in montmorillonite (Hristodor et al., 2011) probably due to the differences in synthetic approach used. Also, increase in MONP loading reduced the rate of degradation owing to aggregate formation and surface masking led to a reduction in active sites or due to $OH^{\cdot}$ trapping). Changing the type and concentration of electron scavenging agents e.g. H_2O_2 and $KBrO_3$ influenced degradation rates by controlling $OH^{\cdot}$ availability and electron - hole combination (Hristodor et al., 2011). Incorporating metal ions like Fe^{3+}, Ni^{2+}, La^{2+}, Y^{3+} etc. into TiO_2/Zeolite NC had also played their role in reducing the electron – hole recombination and introducing defects in MONP crystal structure thereby enhancing catalytic degradation rate even higher than the undoped TiO_2/ZSM-5 NC (Khatamian et al., 2012). Further investigation into the mechanism of degradation points out that the pore size of zeolites is usually less than 1nm while the size of organic molecules e.g. dyes is greater than that hence adsorption into the porous structure is not probable just surface interactions of MONP or zeolite play their role in adsorbing these molecules. The size of these molecules sterically hinders adsorption of more molecules on NC surface, therefore, the researchers claim that dye degradation does not take place on the surface of NC directly rather due to $OH^{\cdot}$ generated on the surface of catalyst and holes as well (Wang, C.-C. et al., 2008). Further insight into the adsorption potential of these NC led to important findings i.e. Fe_3O_4 NC with bentonite had a really high affinity (1600 mg/g) for methylene blue which is 2 to 3 times higher than the normal bentonite (Hashem, 2012).

4. Carbon-Based Composite

Graphene (GR), Graphene oxide (GO) and reduced graphene oxide (rGO) are known to be a good adsorbent and used in many water treatment studies (Cohen-Tanugi et al., 2012; Gao, W. et al., 2011; Kemp et al., 2013). Modification of GR or GO were carried out to exploit its properties for water remediation by using metal oxides (Upadhyay et al., 2014). Such incorporation not only averts the possibility of

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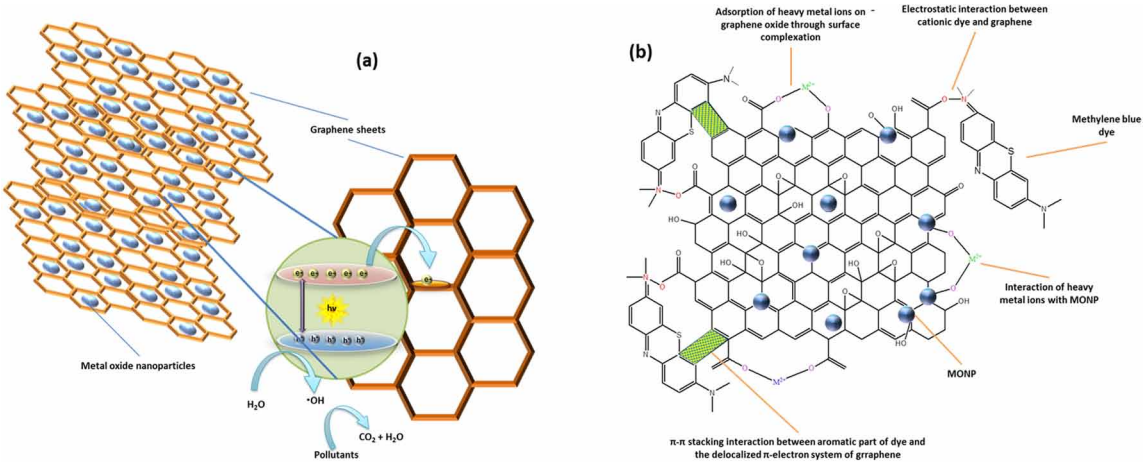
Figure 5. Metal oxide-graphene composites a) Photocatalytic activity based on percolation mechanism showing electron transfer from metal oxide's conduction band to graphene b) various interactions operative in adsorption of pollutants i.e. heavy metal ions and dye molecules (Upadhyay et al., 2014)



electron-hole recombination and metal leaching but also promotes pollutants' removal by π-π stacking. The arrangement also favors the appearance of new valence bands by promoting hybridization. Therefore, owing to these properties the photocatalytic activity and adsorption of this graphene-based MONP composites have been investigated and exploited for enhanced removal of organic moieties and heavy metals. Figure 5 gives an insight into photocatalytic mechanism operating in these composites and various mechanisms leading to adsorption of pollutants from water (Upadhyay et al., 2014).

TiO_2 doped GO NC membranes were found 100% effective in filtering dye molecules at low concentrations (Xu, C. et al., 2013). Much improved uptake capacity (83.26 mg/g) was achieved by using sheets of reduced GO (rGO) with TiO_2 incorporation which was even higher than its nanotubes (75.36 mg/g), pure sheets of GR (48.73mg/g) and tubular titanate (36.51mg/g) (Nguyen-Phan et al., 2012). Use of $ZnTiO_3$ in modifying rGO resulted in improved methylene blue degradation when assisted with visible light irradiation in comparison to $ZnTiO_3$. The adsorption occurred as a result of π- the π interaction between dye and GO that manipulated with structural changes of the composite, for this reason, less uptake was noticed in the case of the cubic structure as compared to hexagonal one (Gayathri et al., 2015). Fe_3O_4/GO magnetically active material had been exploited as a multipurpose water purification material that achieved 97% dye degradation, 77.67% bacterial cell lysis and 69 mg/g Pb (II) adsorption capacity that remains viable up to 5 cycles (Santhosh et al., 2014). The NC was also effective in removal of both anionic (33.66 mg/g) and cationic dyes (13 – 173 mg/g) (Ai et al., 2011; Meral et al., 2014; Sun et al., 2011; Yao et al., 2012), p-chloroaniline (43.86 mg/g) and aniline (375.94 mg/g). Simultaneous removal of Cd^{2+}, methylene blue, and orange G was carried out by using Fe_3O_4-GO leading to reduction in adsorption capacity from 91.92, 64.23, 20.85 to 59.69, 58.08, 20.48 mg/g, respectively as the matrix changed from ultrapure water to tap water owing to presence of interfering ions (Deng et al., 2013).

Fe_3O_4/GO exhibited better adsorption properties for the metals under study at all the pH values following the order Pb(II) > Cu(II) > Cd(II) when compared with MWCNT and powdered activated carbon (AC). Experiments also suggested a decrease in each metal uptake in the multi-component system as compared to the single component system though overall metal adsorption capacity was enhanced in the

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former case (Hur et al., 2015). Yoon *et.al.* advocated that conversion of GO to rGO was a facile step as a comparison of $As^{3+/5+}$ adsorption on to Fe_3O_4 NP modified GO and rGO displayed a compatible affinity with both the composite materials. Insight into adsorption mechanism suggested that electrostatic interaction played important role in binding As^{5+} to the adsorbent while surface complexation governed As^{3+} attachment (Yoon et al., 2016). Modification of GO with mixed metal oxide NP (Fe_3O_4 and MnO_2) was tried for sorption of $As^{3+/5+}$ but led to the removal of only 14.04 and 12.22 mg/g, respectively (Luo, X. et al., 2012). Metal adsorption on Fe_3O_4/GO NC depends on the nature of ions and level of affinity with Fe to form an inner or outer shell complex (Tayyebi et al., 2015). In case of double core GR structures containing iron core, Fe_2O_3 inner shell and outer shell of Si-S-O compound the adsorption mechanism was due to synergetic effects of surface complexation and single layer adsorption which is different from the pure GR in which only the later phenomenon plays its role (Zhu, J. et al., 2011). The dispersion of mesoporous Fe_2O_3/TiO_2 nanoparticles on reduced GO helped in enhancing the number of active sites ensuring attainment of equilibrium in 15 min and 99.5 mg As^{5+} and 77.7 mg As^{3+} uptake per gram of adsorbent at neutral pH while maintaining the same sorption up to 4 cycles. The order of interfering anions in this case follows: phosphate > sulphate > nitrate > chloride > fluoride (Babu et al., 2016).

In the case of nanocomposites doping with MONP gained attention and showed considerably high activity as compared to the pristine MONP or Graphene-based compounds (Cao et al., 2013). Diverse nature of bacterial strains was used as a model to determine the effect of these NC using TiO_2, ZnO, and Fe_3O_4 as dopants (Bykkam et al., 2015; Dědková et al., 2015; Upadhyay et al., 2014; Wang, Y.-W. et al., 2014). The usual mechanism responsible for the antimicrobial activity was through the generation of ROS and release of anions (Chang et al., 2015; Wang, Y.-W. et al., 2014). GO role was proposed as the main agent that either proliferates in bacterial cells or caused slicing off a cell resulting in oozing of cell contents (Upadhyay et al., 2014). Factors like weight % of MONP, ROS amount produced, time of irradiation, the viability of microorganisms and production of extracellular protein by microorganisms impacts the antimicrobial potential of these nanocomposites. Among these, the first four are related to each other as Wt.% and time of irradiation directly affects the ROS generation which should be more than the bacterial colonies growth so that bacteria do not have ample time to divide themselves. As far as protein generation is concerned, it is expected to block MONP active sites by adhering onto their surface hence causing a decrease in their activity (Dědková et al., 2015). In addition to that activity was also affected by changing the loading of GR as the excess of it can also hamper the availability of MONP active sites (Cao et al., 2013). Further, the presence of anions e.g. HCO_3^{1-} and HPO_4^{2-} considerably hampered the activity by capturing the holes, reacting with OH●, blocking the active sites of MONP surface by adsorbing on its surface and absorption of exciting light. The same impact but with less intensity was observed for SO_4^{2-} and NO_3^{1-} ions. The presence of Cl^{1-} ions on contrary either had no impact on the activity or assisted the antimicrobial activity by propagating formation of Cl●, a disinfectant. The cations i.e. Na^{1+} and K^{1+} occurrence did not influence on the viable count of bacteria (Chang et al., 2015).

Carbon nanotubes (CNT), single walled (SWCNT) and double walled (MWCNT), properties have been exploited for the water purification with and without modifications (Ong et al., 2010; Rao, G. P. et al., 2007; Upadhyayula et al., 2009). The potential of MWCNT for dye adsorption in absence and presence of light irradiation was accessed by using methyl orange as test contaminant. MWNT synthesized by chemical vapor deposition showed better adsorption capacity (35.4–64.7 mg/g) as compared to the commercial one (25 mg/g) (Yan et al., 2011; Yao et al., 2011). Structural modification of CNT by MONP doping complements the degradation potential of NC (Ahmad et al., 2014; Behnam et al., 2013). Removal efficacy rose in order CNT < MO < MO/CNT and irradiated > non-irradiated systems

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together with noticeable change in light absorption properties (Ahmad et al., 2014; Saleh et al., 2012) that facilitated enhanced photocatalytic, sonocatalytic and sonophotocatalytic activity as compared to the single component systems (Ahmad et al., 2014). Such systems also accelerated the degradation of contaminant (e.g. diazinone) to less toxic product (i.e. 2-isopropyl-6-methyl-4-pyrimidinol) (Behnam et al., 2013). Varying the amount of either CNT or the dopant directly influenced the uptake potential of NC. Gain in CNT loading from 1-20 wt. % led to increasing in surface area from 49.6 -135.5m^2/g facilitating boost in COD reduction from initial value of 627 to 43 mg/L (Ahmad et al., 2014). The process was governed by slip-induce surface diffusion that assists electron trapping and photon absorption (Nguyen et al., 2016). Also, synergistic effects, enhanced by the homogeneity of the composite, promoted effective charge transfer that impacted the degradation or adsorption potential (Miranda et al., 2014).

Higher uptake potential of modified CNT was also noticed in the case of heavy metals adsorption. Independent studies carried out on NMO/ CNT exhibited improved removal % for metal ions when compared with CNT, charcoal and pure NPs (Chen et al., 2009; Gupta et al., 2011). The studies indicated dependence on agitation time and pH in case of batch studies while on bed thickness subject to column studies (Gupta et al., 2011). The composites were selectively adsorbed Pb^{2+} in mixed systems irrespective of dopant used (Gupta et al., 2011; Peng, Luan, Di, et al., 2005). Ca^{2+} and Mg^{2+} always present in water significantly enhanced the As^{5+} adsorption from 10 to 81.9 and 78.8 mg/g on to CeO_2-CNT owing to the formation of ternary surface complex reaction (Peng, Luan, Ding, et al., 2005). Cd^{2+} removal was aided with MnO_2 doped o-MWCNT (acid oxidized) prepared at different pH and compared with unmodified MWCNT and o-MWCNT; the order followed was MnO_2/o-MWCNT (pH5) > MnO_2/o-MWCNT (pH3) > MnO_2/o-MWCNT (pH7) > o-MWCNT > MnO_2/o-MWCNT (pH1) > raw MWCNT. The reason was attributed to 1) increase in surface roughness with pH, 2) enhancement in uniformity and thinness of MnO_2 layer deposited with an increase in pH and 3) increase in MnO_2 loading with pH that hinders available area for adsorption (Luo, C. et al., 2013). The introduction of 20-30 nm thick diamine functionalized SiO_2 homogeneous layer onto MWCNT was able to remove Pb(II) > Cu(II) > Zn(II) > Ni(II) in larger amounts as compared to SiO_2@MWCNT, o-MWCNT and MWCNT. The intraparticle diffusion model predicts the adsorption process to occur in three stages i.e. adsorption onto the exterior surface of NC, adsorption into the interior surface of pores and diffusion resistance leading to attainment of equilibrium (Yang, W. et al., 2013). Antibacterial activity of TiO_2/CNT thin films (5-30nm) depended on CNT:TiO_2 and annealing temperature that altered the photocatalytic performance owing to indirect impact on the formation of carbonaceous bonds between the CNT and MO (Akhavan et al., 2010)

Carbon encapsulated magnetic nanoparticles (CEMNPs) has emerged as a new class of nano adsorbent consisting of metallic cores completely covered in carbon coatings that are 1-5 nm thick (Pyrzyńska et al., 2010). The magnetic core helps in easy separation and carbon shell ensures effective adsorption (Zhang, D. et al., 2010). Comparative account of these CEMNPs with activated carbon and CNT promoted better uptake of Cu^{2+} and Cd^{2+} i.e. 30-60% *vs.* < 20% owing to differences in surface charge densities of these materials (Pyrzyńska et al., 2010). It was also determined that limiting step in CNMEPs is film diffusion in contrast to intraparticle diffusion (Bystrzejewski et al., 2011). The adsorption capacities reported for these nanoparticles for Cu^{2+}, $Cd^{2+,}$ and Co^{2+} fall in the range of 1.23 – 3.21 mg/g (Bystrzejewski et al., 2009; Pyrzyńska et al., 2010) while for Cr^{6+} it is 0.63 mg/g (Zhang, D. et al., 2010). These NP effectively decontaminated water by adsorbing phenols, phthalates, sulfonamides, tetracyclines and quinolones antibiotics based on hydrogen bonding, π-π and hydrophobic interactions. The adsorption phenomena and uptake of certain compounds were affected by the amount of oxygen-containing species and surface graphitized carbon which can be varied by changing the temperature during synthesis of CNMEP (Niu et al., 2011).

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NP impregnated activated charcoal (AC) helps is solving water treatment issues by enhancing the properties of activated charcoal. Incorporation of magnetic nanoparticles assisted in the fast and easy separation of adsorbate making them useful for water purification applications (Fayazi et al., 2015). The addition of these enhanced the basicity as well as adsorption potential of modified charcoal in comparison to pure one. Utilization of these NC in micro-filter membrane system led to 85.3, 80 and 79.6% removal of dissolved organic compounds, turbidity and UV_{254}, respectively, in addition to longer removal operation when compared with other micro-filter systems (Kim et al., 2013). Clustering of $MgFe_2O_4$ into AC structure formed 40-50 nm sized nanocomposite that effectively adsorbed Cr^{6+} through the spontaneous and exothermic process leading to increasing in q_e from 500 (NC) to 333 mg/g (unmodified charcoal) at room temperature. NaOH treatment helped in 80% desorption but with 5% reduction in removal efficiency (Kaur, M., Kaur, et al., 2015). Dyes removal efficacy varies by changing the amount of loading of MONP into AC. The reason can be attributed to resulting differences in particle sizes, surface morphology, and photocatalytic effects. Experiments had also shown a considerable decrease in degradation percentage for the same adsorbent or photocatalyst by changing the systems' exposure mode from UV light to fluorescent lamp (Hu et al., 2011). The efficiency of ZnO/AC NC system for dye adsorption depended on the size of charcoal particles, irradiation time, H_2O_2 amount (Yu, X. et al., 2015) and sonication time (Jamshidi et al., 2016).

In addition to these, there is various nanomaterial i.e. hybrid nanomaterials are used for the water treatment and purification. In this regard NMO-clay-polymer composites, NMO-polymer-CNT, NMO-Chitosan-Graphene oxide, NMO-chitosan-activated carbon etc. have been exploited and some of them proved to have good qualities needed for water purification purposes (Jeon et al., 2010; Larraza et al., 2012; Liu, L. F. et al., 2010; Ray et al., 2015).

CONCLUSION

The water pollution scenario arising from the flow of omnifarious contaminants led to evolution and need of aqua-nanotechnology that through its broad spectrum approach gives rise to various possibilities to solve this problem. In this regard metal oxide nanomaterials had gained attention but owing to their agglomeration and separation issues led researchers and technologist to opt for their nanocomposites. These include composites with carbon-based materials (carbon nanotubes, graphene etc.), natural and synthetic polymers, clays (including zeolite). Efforts were put into synthesizing the materials with high adsorption capacities, photocatalytic potential and recyclable, in essence, to make the water purification procedure fast, cost-effective and environmentally friendly. Among this variety of nanomaterials, the choice of best nanomaterial to be used always depends on the nature and concentration of a contaminant to be removed and matrix composition which needs to be treated in addition to cost involvement. The magnetic clay based composites offer advantages including the combination of materials available owing to its natural source and magnetic nature that makes the material cost effective. In addition, it offers easy separation and multifunctional nature that enables adsorption of heavy metals, decontamination from microbial impurities and photocatalytic degradation of organic pollutants hence offering a single solution to this wide scoped water pollution problem.

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Chapter 32
Geopolymer Sourced with Fly Ash and Industrial Aluminum Waste for Sustainable Materials

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ABSTRACT

Geopolymer is alumino-silicate material which can apply for many applications due to that geopolymers have several attractive properties of high strength, low permeability, high acid resistance, hazardous materials, and immobilization of toxic materials. This chapter presents synthesis of the dense and the porous structures of geopolymer by using fly ash and industrial waste as the raw materials. Aluminum hydroxide waste (Al-waste) and fly ash (FA) were used to synthesis the dense geopolymers for cement materials. The Al-waste based geopolymer influenced the geopolymer strength, when sodium hydroxide (NaOH) concentration was changed at different curing temperatures. As preliminary microwave oven was exposed in the lower NaOH paste of geopolymer, the successful synthesis of geopolymer cement was obtained. In addition, porous fly ash geopolymers was achieved using a household microwave oven. The geopolymer paste was cured within 1 min by using a microwave oven at different output power. Porous geopolymers were formed immediately as ued at 850 W power of the microwave oven.

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INTRODUCTION

Geopolymers are known as sustainable materials with eco-friendly process, since these simply can use wastes for raw materials, and have excellent mechanical properties (Kumar & Kumar, 2011; Nazari & Sanjayan, 2015). Usually, the geopolymer materials are activated in a high alkali solution (Davidovits, 2008) because alumino silicate geopolymers consist of tetrahedral AlO_4 and SiO_4 units that occur easily in a polycondensed polymer framework in high-alkali conditions (Davidovits, 1991). In geopolymer materials prepared at low temperatures with high alkali solutions, generally alumino-silicate materials such as slag (Karakoç et al., 2014), metakaolin (Rovnaník, 2010a), and fly ash (Ryu, Lee, Koh, & Chung, 2013) were mixed with alkaline solution. For example, sodium or potassium hydroxide is necessary for dissolving silicon and aluminium atoms from raw materials of natural minerals or industrial waste. The silicate alkaline solution includes:

- A binder,
- Alkaline activator, and
- A dispersant or plasticizer (Abdullah, Jamaludin, et al., 2012a; Nazari, Bagheri, & Riahi, 2011; Somna, Jaturapitakkul, Kajitvichyanukul, & Chindaprasirt, 2011).

The basic forms of the chemical structure have silicon-aluminate 3D structures with cross-linked chain bonds together in the geopolymer matrix (Songpiriyakij, Kubprasit, Jaturapitakkul, & Chindaprasirt, 2010). The condensation reaction of geopolymers proceeded greatly at room temperature (Puertas, Martínez-Ramírez, Alonso, & Vázquez, 2000). At elevated temperatures of 40–95 °C, geopolymerization is improved in the strength of specimens (Bakharev, 2005; Chindaprasirt, Chareerat, & Sirivivatnanon, 2007; Panias, Giannopoulou, & Perraki, 2007; Swanepoel & Strydom, 2002). Dense geopolymer materials having apparent density higher than 1 g/cm^3 were applied for construction materials (Andini et al., 2008). Several reports described the use of metakaolin and fly ash as starting materials in geopolymerization (Duxson, Fernández-Jiménez, Lukey, et al., 2007; Komnitsas & Zaharaki, 2007). Moreover, industrial wastes of various types were used to synthesize geopolymers materials such as:

- Aluminum slag,
- Grey cast iron slag, and
- Blast furnace slag.

Among them, the use of etching surface waste, aluminum hydroxide, is interesting in the raw material for geopolymers. The Al-waste has high aluminum contents, making it suitable for the synthesis of better Al-source of geopolymers. Therefore, it is extremely attractive to investigate the geopolymerization of fly ash and Al-waste as a sustainable source for cement substitute materials.

In contrast, foam geopolymers were synthesized in high- or low-temperature processing conditions for widely diverse applications such as in carriers of catalyzer, adsorbents, sensors, hot gas filters, solid–liquid separation processes, and thermal insulators (López, Sugita, & Kobayashi, 2014a; Strozi Cilla, Raymundo Morelli, & Colombo, 2014; Studart, Gonzenbach, Tervoort, & Gauckler, 2006; H. Wang, Li, Wang, & Yan, 2015). In high-temperature processing, the raw materials and foaming agents (aluminium powder or hydrogen peroxide) were mixed with silica fume in situ foaming techniques. After geopolymerization, the geopolymer sample was sintered at 1000-1200 °C to produce in the high strength of

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porous geopolymer (Abdullah, Jamaludin, et al., 2012b). Moreover, a low temperature process achieved geopolymerization in an alkaline environment with a foaming agent for the decomposed into the water and oxygen. In this case, aluminium and silicon in fumed silica also initiated the release of hydrogen gas, leading to a porous structure. Porous geopolymer was cured in a conventional oven at 40-70 ºC for 24–48 h in a long curing period (Böke, Birch, Nyale, & Petrik, 2015; Masi, Rickard, Vickers, Bignozzi, & van Riessen, 2014; Rickard, Vickers, & van Riessen, 2013; Somaratna, Ravikumar, & Neithalath, 2010; Vaou & Panias, 2010). Heat curing was applied to improve the reaction and the strength of geopolymer materials. Recently, microwave energy was used for innovative tool in the chemical reactions, thereby creating an inverse temperature profile (Gubb et al., 2011). The benefits of microwave heating also include instantaneous, very rapid heat-up time, and easy to control (Chindaprasirt, Rattanasak, & Taebuanhuad, 2013). The application of microwave oven cure for dense geopolymers prepared from FA and Al-waste was introduced (Onutai, Jiemsirilers, Thavorniti, & Kobayashi, 2015).

Background

As a construction materials, the portland cement and concrete are mostly essential and widely used in the world. The demand of using cement and concrete has continuously increased and tend to grow up in the future (Chindaprasirt et al., 2007). In the estimation, the usage of cement was approximately 2540 million tons (Mt) in 2006. The cement production in 2050 will be estimated around 3680 Mt to 4830 Mt (Hasanbeigi, Price, & Lin, 2012). In this circumstance, many problems are occurred in the cement industry of environmental fields. The greenhouse gases have been liberated into the atmosphere for production process such emitting and becomes the main problem of the global warming, by carbon dioxide emission during the production processes (Flower & Sanjayan, 2007). The amount of carbon dioxide is released into the atmosphere with approximately 0.8 tons/ 1tons in the cement industry (Alaa M. Rashad, 2011; Heath, Paine, & McManus, 2014; Pangdaeng, Phoo-ngernkham, Sata, & Chindaprasirt, 2014). In order to reduce the emission in the cement processes, many efforts have been paid to find the other cementitious materials to replace cement (Davidovits, 1994; Rovnaník, 2010a). Therefore, development of sustainable material is needed for cement and concrete.

In 1950s, Victor Glukhovsky et al. developed alkali activated systems containing calcium silicate hydrated and alumino-silicate phases, which were used to build a tall building. These alkaline alumino-silicate cementatious systems are called “soil silicate” (Komnitsas & Zaharaki, 2007). After 1972, Joseph Davidovits (Davidovits, 1982, 1984; Davidovits, 2008) reported another form of cementitious materials using silicon and aluminum activated in a high alkali solution. The new materials are called “Geopolymer”. The gepolymers are inorganic polymers having three dimensional alumino-silicates in the cementitious materials (Chindaprasirt et al., 2007; Cioffi, Maffucci, & Santoro, 2003; Davidovits, 1991). These materials have frame work of sialate and having silica-alumina networking in the molecular framework. Moreover, geopolymer materials are easily applied for coating and adhesive layers as binder for fiber composites, waste encapsulation (Davidovits, 2008). In addition, cement materials for concrete were proposal for geopolymers produced by condensation reaction. The polymeric process of alumino-silicate and alkali activators is one of other options for alternative green cement. This is due to reduction of approximately 80% of CO_2 emission to the atmosphere as compared with process for the cement. Moreover, geopolymer has an advantage in the production at low temperature and low pressure by using alumino-silicate sources. Also, it can be prepared from natural source in nature and industry such as metakaolin, fly ash, blast furnace slag etc. with a strong alkaline solution (Abdulkareem, Mustafa

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Al Bakri, Kamarudin, Khairul Nizar, & Saif, 2014b; Rovnaník, 2010b). Geopolymers have excellent properties such as high mechanical properties, low shrinkage, fire resistance and durability (Duxson, Fernández-Jiménez, Provis et al., 2007). Summarized geopolymer sourced from waste materials for many applications:

- As concrete and cement (Pavithra et al., 2016),
- Composites (Roviello, Ricciotti, Ferone, Colangelo, & Tarallo, 2015),
- Immobilisation of toxic and radioactive waste (Xu & Van Deventer, 2002),
- Adsorbent for heavy metal ion (Li, Wang, & Zhu, 2006) and
- Fire resistant and protection matrix (Sakkas, Panias, Nomikos, & Sofianos, 2014).

In general chemical structure of geopolymer, sialate (silicon-oxo-aluminate) segments are main chemical framework (Figure 1). This consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all oxygen atoms. Alkali cations or positive ions such as Na^+, K^+ and Ca^{++} are charged-balanced of the negative charge of Al^{3+} in IV-fold coordination (Davidovits, 1994). A polymeric structure of (poly) sialate formed constitutes the main building blocks of geopolymeric structure and the empirical formula of polysialates is displayed asfollow (Hanjitsuwan et al., 2014a): M_n $[(-Si-O_2)_z-Al-O_2-]_n$, wH_2O, where M is monovalent cation such as sodium or potassium, n is degree of polycondensation, z is amount of $Si-O_2$ (1, 2, 3 or higher) and w is amount of water.

It is common that geopolymerization can start from room temperature containing silica and alumina unit to be oligomers (dimer, trimer) which provide the actual unit structures of the three dimensional macromolecular edifice. The geopolymerization stages can be supposed into three stages:

1. Deconstruction,
2. Polymerization and
3. Stabilization (Blackstock, Neill, & Mcintosh, 2012; Muñiz-Villarreal et al., 2011; Yao, Zhang, Zhu, & Chen, 2009).

In geopolymer, the polymerized sialates are linkaged together by the type of sialate (Si-O-Al) and siloxo (Si-O-Si). The chemical structure of polysialate geopolymers includes the classified of polysialates, which are separated into four elementary units according to terms of the Si/Al atomic ratio as followed (Davidovits, 1982, 1984; Davidovits, 1994):

1. For the units, first is sialate and poly(sialate) at Si:Al = 1. These have -Si-O-Al-O- included in the chain and ring polymers from the polycondensation reaction of monomer, ortho-sialate $(OH)_3$-Si-O-Al-$(OH)_3$.
2. In the second unit, sialate- siloxo and poly(sialate- siloxo) at Si:Al = 2, (-Si-O-Al-O-Si-O-) are the chain and ring polymer from the result of condensation between ortho-silicic acid $Si(OH)_4$. These chains have three isomorphs as a linear, mono-siloxo-sialate and 3 cycles.
3. In the third unit, sialate- disiloxo and poly(sialate- disiloxo) at Si:Al = 3, (-Si-O-Al-O-Si-O-Si-O-) are described from the result of condensation reaction between two ortho-silicic acid $Si(OH)_4$. The sialate units are corresponded to form six isomorphs: 2 linear, 2 branched and 2 cycles.
4. Finally for fourth unit, sialate link and poly(sialate- multisiloxo) unit at Si:Al > 3 which are chains from bridge Si-O-Al between two poly(siloxonate), poly(silanol) or poly(sialate) chains.

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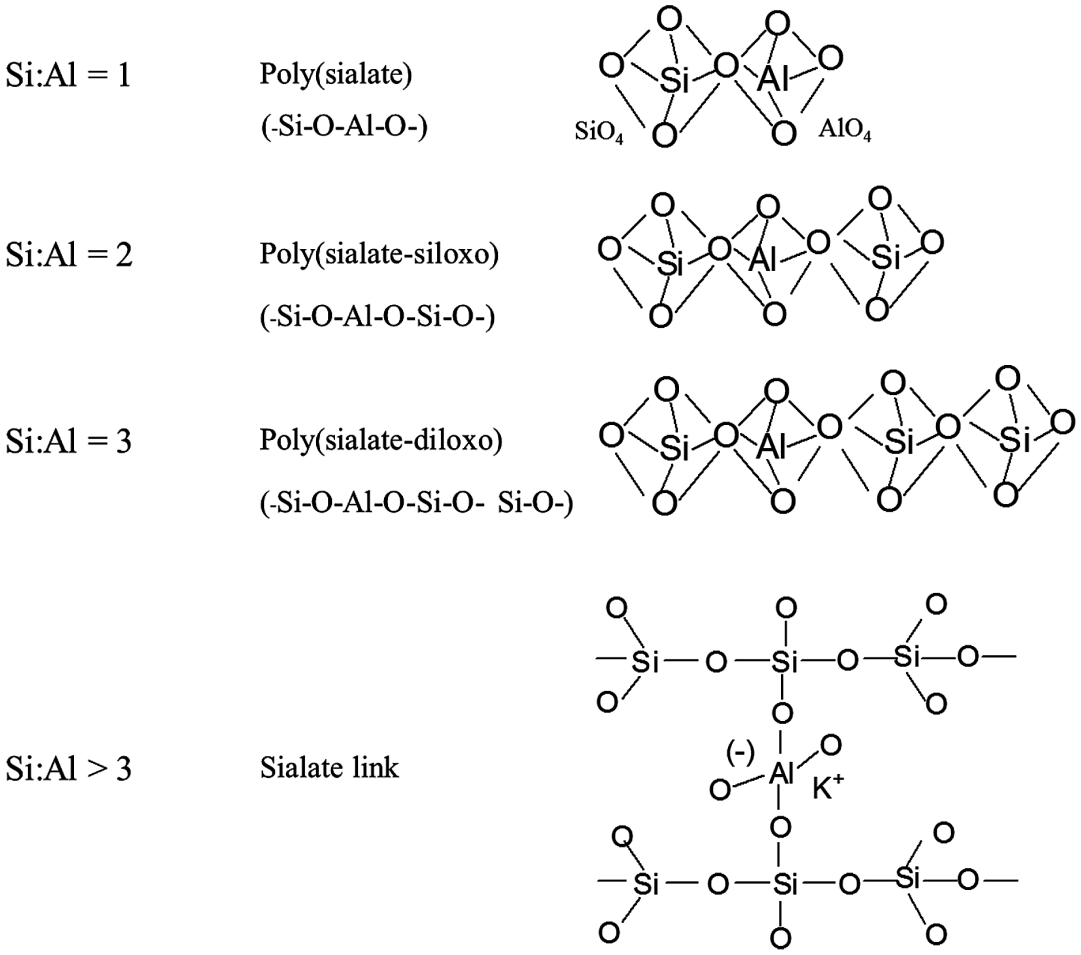
Figure 1. Chemical structure of polysialates



The geopolymerization process involves:

1. Deconstruction,
2. Polymerization and
3. Stabilization (Yao et al., 2009; Zhang, Zhu, Zhou, & Wang, 2016).

In the deconstruction process, leaching of the solid alumino-silicate materials by alkaline hydrolysis produces aluminate and silicate species (Comrie & Kriven, 2006). The dissolution of the solid particles of the source for geopolymerization occurs at the surface. In high pH alkali solutions, the Si-O-Si, Al-O-Al and Al-O-Si of aluminosilicate source are dissolved (Somna et al., 2011). The alkali metal cations from the activated solution play important role in the geopolymerization and balance out the charge of the aluminium in form of four-fold coordination with oxygen (Lecomte et al., 2006). Then, the polymerization process occurs in the solution. The neighbouring reactive groups formed as Si-O-Na and O-H-Al and small silicate molecules from the alkali silicate thereafter undergo condensation reaction with the liberation of alkali hydroxide to form the preliminary unit for the geopolymerization.

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In the stabilization, the application of mild heat typically between room temperature up to 90 °C causes formation of the preliminary units in the terms of polycondensation. This can form rigid chains or nets of oxygen bonded aluminate and silicate tetrahedral which are similar to cement chemical structure. The higher "curing" temperature produces stronger geopolymer cements as each of the hydroxyl groups in these macromolecules are capable of condensing with one from a neighbouring molecule. It is theoretically possible for any one silicon to be bonded via an oxygen bond and to four neighbouring silicon or aluminium sites. As a result, very rigid polymer network is formed.

Several reports describe the use of metakaolin and fly ash as starting materials in geopolymerization. Moreover, industrial wastes of various types are used to synthesize geopolymer materials. For example, in cement and concrete, Pavithra et al.(Pavithra et al., 2016) developed the geopolymer concrete with fly ash. Moreover, Yeonho et al. (Park, Abolmaali, Kim, & Ghahremannejad, 2016) studied the feasibility of geopolymer concrete to which crumb rubber from recycled tires. Geopolymer cement and concrete showed low shrinkage after drying, less cracks and high strength. Therefore, the production cost of the geopolymer cement and concrete could be in 10-30% cheaper than Portland cement production.

In the adsorption of heavy metal application, geopolymer can be used as the materials for absorbing heavy metal from waste water. In recent years, fly ash based geopolymer was used for Cu and Pb removal from an aqueous solution. The absorption capacity was reached to 92 mg/g and 80 mg/g of Cu and Pb, respectively (Al-Zboon, Al-Harahsheh, & Hani, 2011; S. Wang, Li, & Zhu, 2007). Moreover, the geopolymer not only absorbed heavy metal but also could absorbed dye from waste water. The absorption capacity of fly ash based geopolymer demonstrated approximately 0.12 mmol/g (Li et al., 2006). Geopolymer adsorbents were prepared from silica and metakaolin in different Al and Si components (López et al., 2014a; López, Sugita, Takaya, & Kobayashi, 2014b) and applied for removal of metal ions, Cs^{+} and Pb^{2+}, from other heavy metal ions mixture (López, Sugita, Takaya, & Kobayashi, 2014c). In the application for immobilization heavy metal and radioactive waste, geopolymer was used to immobilize, stabilize and adsorb low amount of radioactive waste in pure and mixed form (Van Jaarsveld, Van Deventer, & Lorenzen, 1997). The results indicated that the fly ash based geopolymer had high property to immobilize lead ion (Lee et al., 2016). Geopolymers acted as the binder to convert semi solid waste to adhesive solid and also immobilized hazardous waste by locking in the three dimensional framework. Moreover, the geopolymer materials could be apply for composites materials, hybrid composite materials for geopolymer and epoxy melamine resins were designed to produce a novel material showing high compatibility between the organic and inorganic phases. In the applications, requiring high temperature resistance is for kitchen tools and plates, coatings and flooring (Roviello et al., 2015). In addition, the geopolymer materials can be used for fire protection possessing excellent physicochemical, thermal and mechanical properties. So, fire resistant geopolymers were developed by the potassium based geopolymers (K-geopolymer) prepared with mixing ferronickel (FeNi) slag, doped with pure alumina (Sakkas et al., 2014).

UTILIZATION OF ALUMINIUM WASTE BASED GEOPOLYMER

Since geopolymers consist of aluminum-silica framework in the chemical structure, the source of Al becomes important especially in cases of waste reuse. Every year, aluminum consumption is increasing for many applications such as anodizing processes for producing decorative and protective films on aluminum and alloys. After etching step, Al-waste in gibbsite phase ($Al(OH)_3$) is wasted: typically

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about 360 tons/year from various industries is discarded in landfills (Álvarez-Ayuso, 2009; Colonetti, Hobold Kammer, & De Noni Junior, 2014; Ribeiro & Labrincha, 2008). Consumption of fossil fuels in power plants for energy production is increasing, leaving fly ash waste. About 3 million tons/year of such industrial waste are produced by large and small power plants. These wastes should be regenerated to produce novel materials. If people can recycle this, then such material becomes sustainable products that provide environmental, social, and economic benefits. Especially, as renewable resources of both aluminum hydroxide waste and fly ash, these seem to be applicable for reuse in concrete materials. Therefore, approximately 13,500 million tons of Portland cement are manufactured annually using processes that incorporate high heating energy of 1400–1600 °C for calcining raw materials (Detphan & Chindaprasirt, 2009).

Aluminum hydroxide waste (Al-waste) from the aluminum frame industry and fly ash (FA) from power plant were used as the raw materials of geopolymers. Their chemical compositions are presented in Table 1 and Figure 2 shows SEM micrograph of the raw materials for a) Al-waste and b) FA. The Al-waste particles were irregularly shaped, with diameter of about 100 μm. The particle distribution of the Al-waste was 40–110 μm. In contrast, the FA contained spherical particles with about 40 μm diameter in the fine powder. The laser-scattered particle distribution of fly ash showed that the powder size was 0.2–130 μm. Geopolymerization was conducted for Al-waste and FA, when the wastes were mixed with aqueous NaOH solutions of 5, 10, and 15 M concentrations. Al-waste were used for 0, 10, 20, 40, and 60 wt% for the Al-waste at different NaOH concentrations. After geopolymerization precess, the geopolymer bulk were cured at room temperature, 60 °C and 80 °C for 24 h.

As mentioned, geopolymerization in alkaline solution is known to increase the mechanical property of the resultant geopolymers. The properties depended strongly upon silicate and aluminum ratios and on the curing temperature (Görhan & Kürklü, 2014; Hanjitsuwan et al., 2014b; Nazari et al., 2011; Somna et al., 2011). It is important for the present study to examine the dependence of the curing temperature and the NaOH concentration. The flexural strength and compressive strength for each specimen was observed in geopolymers prepared using different aluminium hydroxide contents and NaOH concentrations. Actually,

Table 1. Chemical composition of fly ash and aluminum hydroxide waste

Chemical Compound	Fly Ash (%)	Aluminum Waste (%)
SiO_2	31.94	0.18
Al_2O_3	18.37	63.28
Fe_2O_3	17.39	-
CaO	19.84	0.01
MgO	1.86	0.31
SO_3	5.13	< 0.01
Na_2O	1.20	-
K_2O	3.05	0.05
MnO	0.07	2.05
P_2O_5	0.16	0.01
TiO_2	0.40	0.01
L.O.I	1.47	34.02

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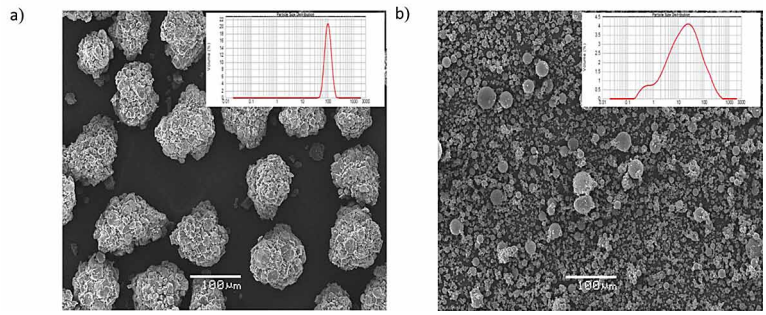
Figure 2. SEM micrograph of a) Aluminum hydroxide waste and b) Fly ash with particle size distribution



a tendency was seen by which the geopolymer strength increased as the NaOH concentration increased. For the flexural strength (Figure 4a), the high strength in 40 wt% of the Al-waste contents was obtained in 5, 10 and 15 M of NaOH concentration. This might be because of the fact that the higher concentrations of NaOH are able to dissolve both silica and alumina in a homogeneous slurry paste. Especially, high strength appeared at 80 °C, meaning that the curing temperature affected the geopolymer strength. After curing at higher temperature, increased bulk strength for the 40 wt% of Al-waste was observed with the maximum flexural strength of 6.05 MPa. A similar temperature tendency was also apparent for compressive strength (Figure 3b). The high compressive strength of 40 MPa was obtained for 40 wt% of Al-waste used in 10 M of NaOH concentration at 80 °C. As a result, slurry containing high alkaline solution was preferred for the condensation reaction to form Si–O and Al–O in the geopolymers. As reported (Görhan & Kürklü, 2014), this preference was mainly attributable to the excellent dissolution of silica and alumina components in the slurry. Therefore, high temperatures enhanced the geopolymerization in the Si–O–Al formation by the condensation. Regarding to development of compressive strength in Portland cement pastes and concrete specimens, the strength increased with increased curing temperature (Chindaprasirt et al., 2007; Somna et al., 2011). However, when the NaOH concentration was 15 M, the compressive strength started to drop. Excess NaOH was the cause of the compressive strength decrease attributable to the alumino-silicate gel precipitation at the early stage (Somna et al., 2011). On the other hand, the temperature was higher than 80 °C, water in the geopolymer slurry was evaporated to produce a porous structure (López et al., 2014a). In addition, the mass loss was capable of forming cracks in the geopolymer matrix because of the thermal shrinkage (Abdulkareem, Mustafa Al Bakri, Kamarudin, Khairul Nizar, & Saif, 2014a). The apparent bulk density of the geopolymer specimens increased when increasing the amount of the Al-waste to 40 wt%. However, as the Al-waste was added with 60 wt%, the apparent bulk density decreased. As seen in Figure 4, the micro CT-x ray technique showed the interior structure of geopolymer matrix in different amounts of the Al-waste. These geopolymers were prepared in the 40 wt% of the Al-waste at 80 °C with 10 M NaOH concentration. The inside geopolymer exhibited numerous cracks and pores for Figure 4a in the no addition of the Al-waste. In cases Figure 4b and 4d for 20 and 60 wt% of the Al-waste contents, the inside structures had fewer cracks, but round pores existed in these geopolymers morphological structure. In contrast, a denser structure was observed in the 40 wt% of the Al-waste (Figure 4c). Especially, in Figure 6d for 60 wt% the Al-waste, many pores were visible in the geopolymer. This result suggests that excess Al-waste caused the decrease of the geopolymer strength.

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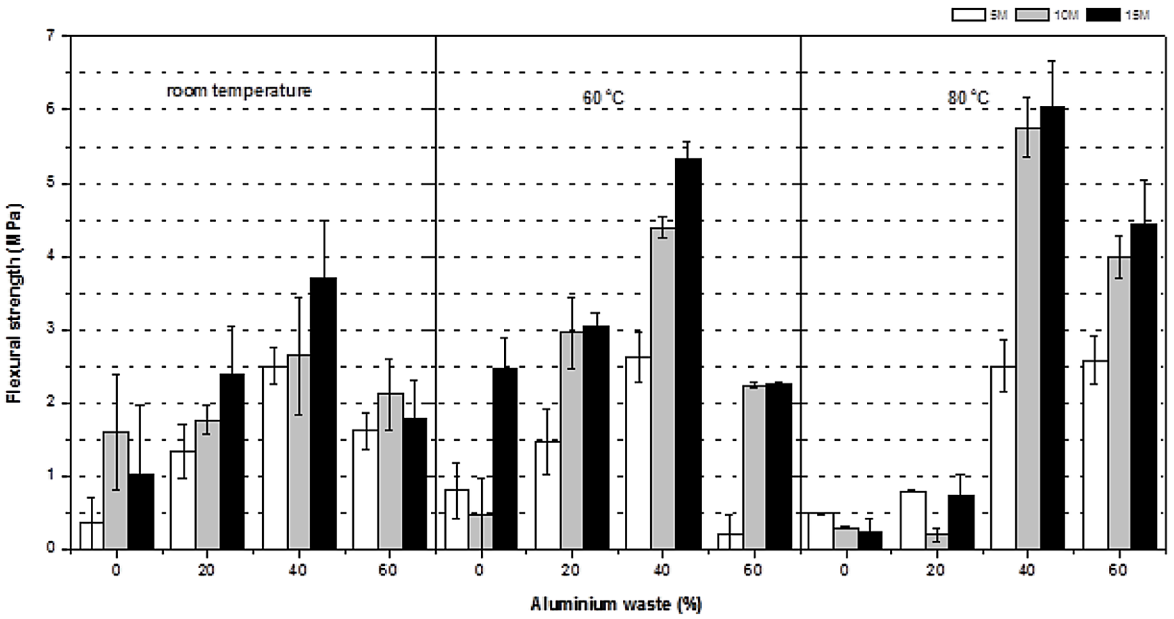
Figure 3. Comparision of a) flexural strength and b) compressive strength of geopolymer paste at age of 7 days

a)



b)

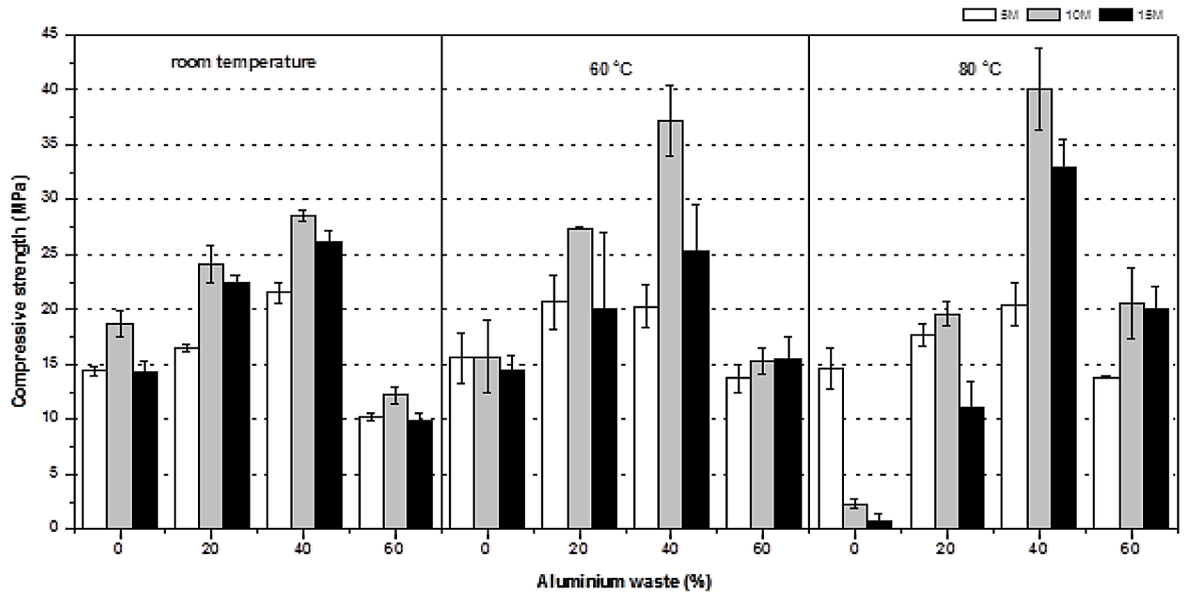


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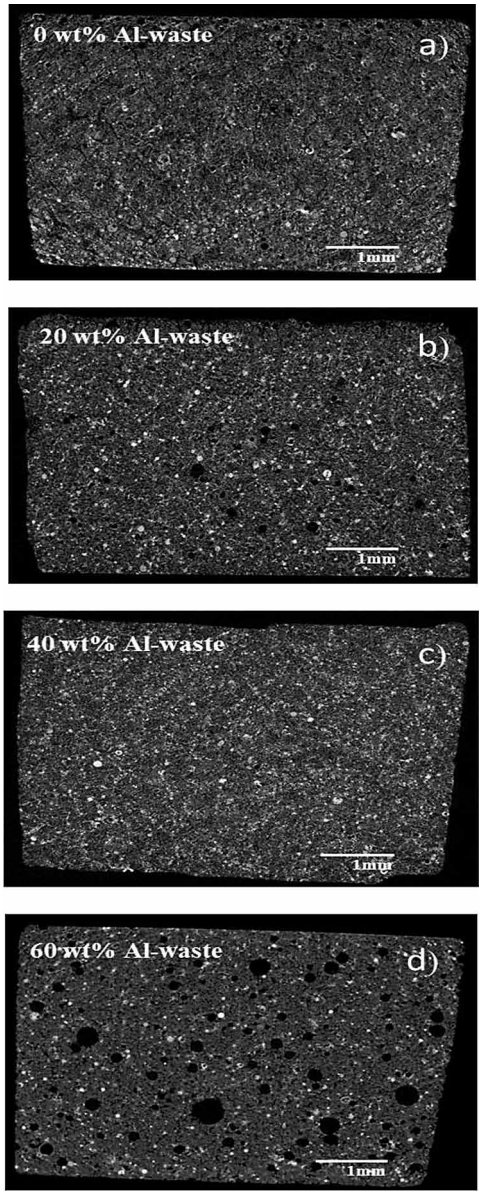
Figure 4. X-ray CT images of geopolymer sepecimens with different amounts of Al-waste on structure of geopolymer specimens: a) 0 wt %, b) 20 wt %, c) 40 wt % and d) 60 wt % Al-waste with 10 M NaOH and cured at 80 °C for 24h



FLY ASH BASED GEOPOLYMERS

Fly ash is one of source material for geopolymer (Table 2) and is generally by-product obtained from industrial processes. Fly ash is commonly composed of a fine powder consisting mostly of spherical glassy particles (Figure 2) and is produced in coal fired power stations. Fly ash has pozzalonic properties and for example reacts with lime to form cementitious compounds. It is known as a supplementary cementitious materials (Pangdaeng et al., 2014). So the mechanical property of fly ash based geopoly-

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mers were improved. The use of dense fly ash based geopolymer concrete led to many improvements in overall concrete performance. Some key benefits are included: reduced water content, improved workability, reduced segregation, low heat of hydration, improved finishing, lower drying shrinkage, increased durability, improved long term strength, good carbonation protection, improved resistance to sulfate attack and improved resistance to alkali silica reactivity as listed below.

Moreover, the improvement porous structure of fly ash based geopolymers also was reported for application as shown in Table 3. Moreover, for example, the porous structure of geopolymer materials was observed when microwave method was used as heating source (Onutai, Jiemsirilers, Thavorniti, & Kobayashi, 2016). Fly ash was obtained from Mae Moh Power Plant in Lamphang, Thailand for used as a raw materials. For geopolymerization, sodium hydroxide solutions and sodium silicate solutions were used as activators. The solid fraction in geopolymer mixture was 65 wt%. The ratio of Na_2SiO_3/NaOH solution and SiO_2/Al_2O_3 were fixed at 2.5 and 2.69 at 2-15 M NaOH, respectively. The geopolymer paste was cured by heating in a microwave oven at the different power setting (200-850 W) for 1 min. During microwave heating, the geopolymers temperature were detected by using an infrared thermal scanner as presented in Figure 5. The temperature development was the function of microwave power and sodium hydroxide concentrations. The specimen temperature increased with an increasing incident power and sodium hydroxide concentration. The temperature reached to 65-130 ^oC within 1 min. The aqueous paste of fly ash and sodium silicate contained different NaOH concentrations of 2 M-15 M was cured in the household microwave oven and then the geopolymer paste adsorbed microwave energy. The microwave heating occurred depending upon the NaOH concentration due to the dipolar polarization and ionic conduction mechanisms. Polar molecules such as water produce heat because the water absorbs microwaves as a result of the polarization induced by the external oscillating electric field (Vollmer, 2004). Therefore, the conduction mechanism from charged particles such as Na^+ and OH^- can oscillate back and forth under electric force producing an electric current to heats up neighboring materials through molecular collisions of charged species (Anwar et al., 2015; Vollmer, 2004). Moreover, the heat of geopolymers are increased during geopolymerization as a fact that the geopolymerization process is exothermic chemical reaction (Davidovits, 1991; Jumrat, Chatveera, & Rattanadecho, 2011). When the geopolymer paste was processed to the solid geopolymer, microwave heating was able to achieve higher temperatures in a very short time depending on the NaOH concentration. During the process, the volume of geopolymer specimen are immediately increased. Consequently, the water was vaporized easily at temperatures higher than 100 ^oC. Vaporization of the water might influence the morphology of the geopolymers. Bubbles from evaporation of water were fixed inside the geopolymer sample along with the general heat curing process, producing a porous geopolymer structure (Hanjitsuwan et al., 2014a).

The porous geopolymer morphology in the microstructure was compared in each sample synthesized in a conventional oven at 80 ^oC, with household microwave at 200 W and 850 W power for 1 min (Figure 6). The morphological analysis elucidated that the microstructural changes occurred with heating and curing at 80 ^oC and microwave curing. All samples showed that the ash particles remained in the geopolymer matrix. During the dense morphology of the matrix was created, the rough surface of the geopolymers was observed for the paste having 10 M and 15 M NaOH concentrations. At 850 W of microwave curing, the tendency was extremely effective at higher NaOH concentrations, as depicted in Figures. 6i) and 6l). In the geopolymers cured with 15 M of NaOH concentration, the apparent density was increased markedly when the microwave was operated at 500-850 W. The values of apparent bulk density showed about 0.9 g/cm^3 for the 15 M NaOH concentration at 500-850 W, while these were 1.4-1.5 g/cm^3 for the 2 M and 5 M NaOH concentrations. When the NaOH concentration was increased, the

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Table 2. Summarized synthesis dense fly ash based geopolymer

Raw Material	Conditions	Compressive Strength	References
Fly ash (paste)	NaOH solution = 10 M Na_2SiO_3/NaOH ratio = 1.5 Curing temp. at 65 °C for 48 h	35.0 MPa at 2 days	(Chindaprasirt, Jaturapitakkul, Chalee, & Rattanasak, 2009)
Fly ash (paste)	NaOH solution = 14 M Curing temp. at 25 °C	15.0 MPa at 7 days 25.5 MPa at 60 days	(Somna et al., 2011)
Fly ash (paste)	NaOH solution = 18 M Na_2SiO_3/NaOH ratio = 0.67 Curing temp. at 40 °C for 24 h	56.0 MPa at 7 days	(Hanjitsuwan et al., 2014a)
Fly ash (paste)	NaOH solution = 9 M Na_2SiO_3/NaOH ratio = 1 Curing temp. at 60 °C for 24 h	53.0 MPa at 91 days	(Jang & Lee, 2016)
Fly ash (mortar)	NaOH solution = 10 M Na_2SiO_3/NaOH ratio = 0.67 Curing temp. at 60 °C for 72 h	52.0 MPa at 7 days	(Chindaprasirt et al., 2007)
Fly ash (mortar)	NaOH solution = 6 M Na_2SiO_3/NaOH ratio = 2 Curing temp. at 85 °C for 24 h	22.0 MPa at 7 days	(Görhan & Kürklü, 2014)
Fly ash (paste) (mortar) (lightweight concrete)	NaOH solution = 12 M Na_2SiO_3/NaOH ratio = 1 Curing temp. at 40 °C for 24 h NaOH solution = 12 M Na_2SiO_3/NaOH ratio = 1 Curing temp. at 40 °C for 24 h NaOH solution = 12 M Na_2SiO_3/NaOH ratio = 1 Curing temp. at 40 °C for 24 h	44.0 MPa at 28 days 47.0 MPa at 28 days 18.0 MPa at 28 days	(Abdulkareem et al., 2014b)
Fly ash (paste) Fly ash-rice husk and bark ash (paste)	NaOH solution = 18 M Na_2SiO_3/NaOH ratio = 2.5 Curing temp. at 25 °C FA:RHBA = 40:60 NaOH solution = 18 M Na_2SiO_3/NaOH ratio = 2.5 Curing temp. at 60 °C for 24 h	17.0 MPa at 7 days 34.0 MPa at 28 days 49.2 MPa at 7 days 56.0 MPa at 28 days	(Songpiriyakij et al., 2010)
Fly ash-sawdust (paste)	FA:Sawdust = 80:20 NaOH solution = 10 M Na_2SiO_3/NaOH ratio = 8 Curing temp. at 40 °C for 24 h	55.0 MPa at 14 days	(Duan, Yan, Zhou, & Luo, 2016)
Fly ash (paste) Fly ash-metakaolin (paste)	NaOH solution = 10 M Na_2SiO_3/NaOH ratio = 1.6 Curing temp. at 20 °C FA:MK = 80:20 NaOH solution = 10 M Na_2SiO_3/NaOH ratio = 1.6 Curing temp. at 20 °C	57.0 MPa at 28 days 80.0 MPa at 28 days	(Duan, Yan, & Zhou, 2016)
Fly ash-silica fume (concrete)	NaOH solution = 14 M Na_2SiO_3/NaOH ratio = 1 Curing temp. at 100 °C for 72 h	73.0 MPa at 28 days	(Okoye, Durgaprasad, & Singh, 2016)

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Table 3. Summarized synthesis porous fly ash based geopolymer

Raw Material	Method	Conditions	References
Fly ash	added aluminium powder = 1.5-5.0 wt%	NaOH solution = 8 M Na_2SiO_3/NaOH ratio = 2.5	(Sanjayan, Nazari, Chen, & Nguyen, 2015)
Fly ash	added aluminium powder = 0.06-0.12 wt%	NaOH solution = 2.8-3.2 g. Curing temp. at 80 °C for 12 h	(Hlaváček, Šmilauer, Škvára, Kopecký, & Šulc, 2015)
Fly ash	added sodium hypochlorite = 0.40-0.60 wt%	NaOH: FA= 0.20 wt% Curing temp. at 60 °C for 24 h and 80 °C for 48 h	(Böke et al., 2015)
Fly ash-metakaolin	gel casting	KOH solution = 15 M K_2SiO_3/KOH ratio = 2 Curing temp. at 80 °C for 5 h	(Strozi Cilla, Colombo, & Raymundo Morelli, 2014)
Fly ash	added superplasticizer = 2 volume%	NaOH solution = 12 M Na_2SiO_3/NaOH ratio = 2.5 Curing temp. at 60 °C for 24 h	(Abdullah, Hussin, et al., 2012)
Fly ash	added sheet glass powder = 8 wt% added surfactant solution = 10 wt %	NaOH solution = 10 wt% Curing temp. = 105 °C for 12 h Sintering = 1050 °C for 2 h	(Zhao et al., 2010)

Figure 5. Temperature profile of geopolymers in different power of microwave 1 min and pictures of the obtained geopolymer at 850 W

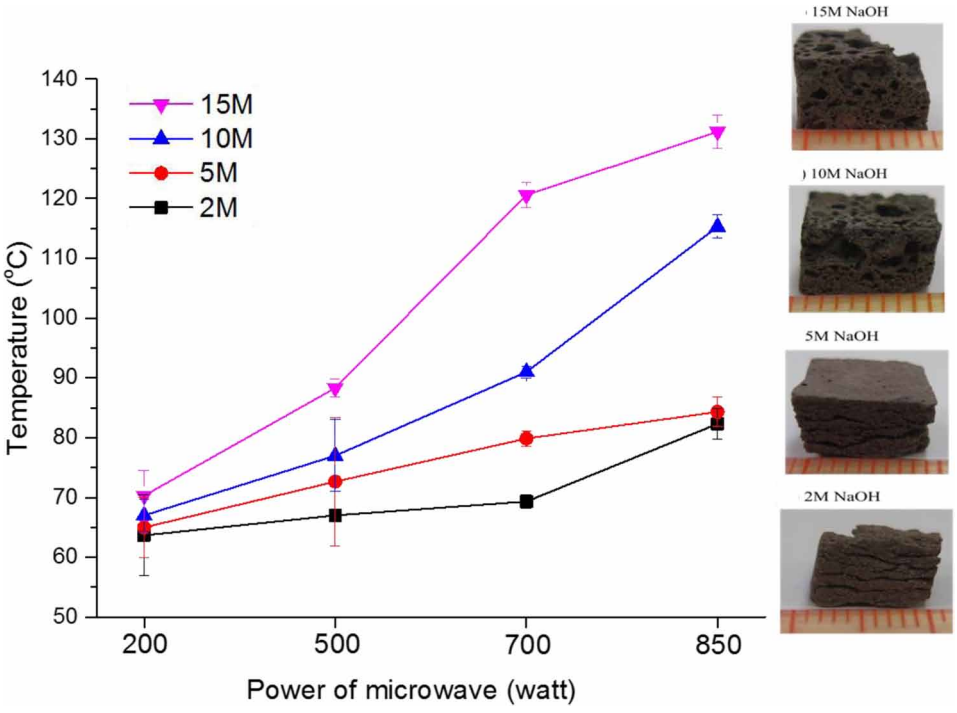

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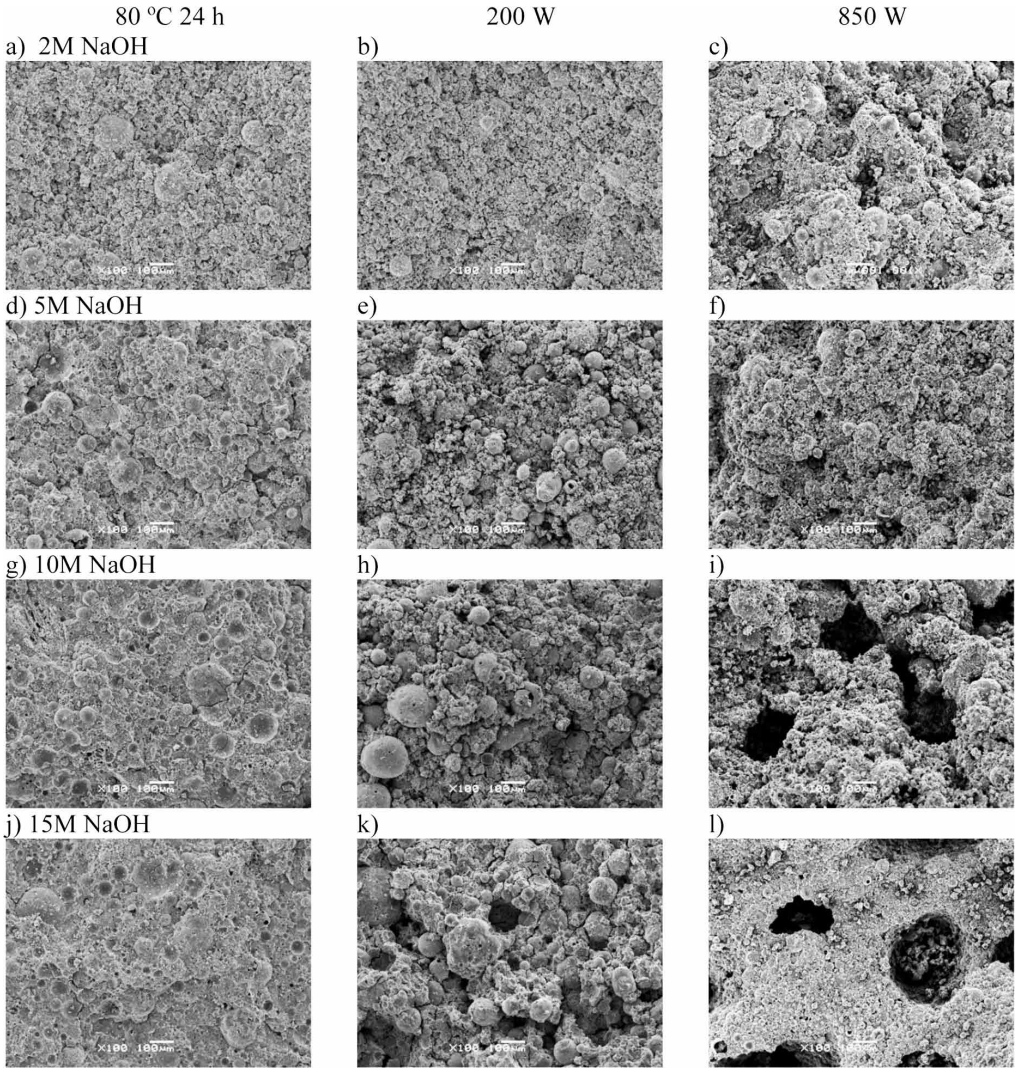
Figure 6. Microstructure of geopolymer sample synthesized by curing at 80 °C 24 h and using microwave radiation at power 200 and 850 W for 1 min



strong alkali rapidly increased the interior temperature, especially in 10 M and 15 M materials at 700 and 850 W. Therefore, the bubbles of the water evaporation seemed to be increased in the bulk porous structure, thereby decreasing the apparent density.

CONCLUSION

In this chapter authors conclude the reuse fly ash and industrial wastes, Al-waste, for producing geopolymers which are sustainable and green materials. In their waste materials, geopolymers were synthesized from fly ash and aluminium waste with different proportions of raw materials for alternative cement. Moreover, when different NaOH concentration and different curing temperature was changed, effect of

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the alkali was described. Fly ash based geopolymer and synthesis porous geopolymer using microwave radiation from household microwave were also reviewed. The results showed that porous geopolymer was produced at 10 or 15 M NaOH with 850 W of microwave radiation power, due to that the high power of microwave radiation increased the slurry temperature and affected water evaporation in the geopolymer paste. The bulk and porous geopolymers were successfully produced by using FA and Al-wastes.

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KEY TERMS AND DEFINITIONS

Apparent Density: The mass per unit volume (or the weight per unit volume) of a material, taking into consideration any voids.

Compressive Strength: The maximum compressive stress that, under a gradually applied load, a given solid material can sustain without fracture.

Hazardous Materials: Any item or agent (biological, chemical, radiological, and/or physical), which has the potential to cause harm to humans, animals, or the environment, either by itself or through interaction with other factors.

Industrial Waste: The waste produced by industrial activity which includes any material that is rendered useless during a manufacturing process such as that of factories, industries, mills, and mining operations.

Mechanical Property: A property that involves a relationship between stress and strain or a reaction to an applied force.

Sustainable Materials: Materials used throughout our consumer and industrial economy that can be produced in required volumes without depleting non-renewable resources and without disrupting the established steady-state equilibrium of the environment and key natural resource systems.

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Chapter 33
Removal of Emerging Contaminants from Water and Wastewater Using Nanofiltration Technology

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ABSTRACT

Conventional water/wastewater treatment methods are incapable of removing the majority of Emerging Contaminants (ECs) and a large amount of them and their metabolites are ultimately released to the aquatic environment or drinking water distribution networks. Recently, nanofiltration, a high pressure membrane filtration process, has shown to be superior to other conventional filtration methods, in terms of effluent quality, easy operation and maintenance procedures, low cost, and small required operational space. This chapter provides a comprehensive overview of the most relevant works available in literature reporting the use of nanofiltration for the removal of emerging contaminants from water and wastewater. The fundamental knowledge of nanofiltration such as separation mechanisms, characterization of nanofiltration membranes, and predictive modeling has also been introduced. The literature review has shown that nanofiltration is a promising tool to treat ECs in environmental cleaning and water purification processes.

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1. INTRODUCTION

Emerging contaminants (ECs) can be broadly defined as any synthetic or naturally occurring chemicals but cause known or suspected adverse ecological and(or) human health effects. This ever-increasing contaminants pose potential environmental and health threat to the living organism (Bolong, Ismail, Salim, & Matsuura, 2009). In some cases, due to low concentration emerging contaminants have likely existed for a long time, which may not be detected until new analytical methods are developed. Hence, some ECs are not necessarily new chemicals, which are from municipal, agricultural, and industrial wastewater sources and pathways (Petrović, Gonzalez, & Barceló, 2003).

There are two reasons why emerging contaminants are of continued concern for the health and safety of consuming public. The first one is the trace level of most ECs with concentration at μg/L or ng/L, and broad range of physiochemical characteristics, which make both detection and elimination extremely difficult (Richardson & Ternes, 2005); And the second one is the adverse health and environmental effects of ECs even at a low concentration. Some intermediate metabolites or transforming products of ECs (especially for endocrine disrupting chemicals) exhibit biologically active effect as well (Diamanti-Kandarakis et al., 2009).

The main issue of ECs is nonexistence of limiting regulations, especially for new compounds, by-products, pharmaceuticals as related to the water and wastewater treatment industry. The first Contaminant Candidate List (CCL) was created in 1998 by United States Environmental Protection Agency (US EPA) for contaminants that are currently not subject to any proposed or promulgated national primary drinking water regulations. Even through many efforts have been devoted, there is limited number of contaminants with Maximum Contaminant Level (MCL) regulated by US EPA.

The main groups of ECs are described in Table 1.

Table 1. Main group of emerging contaminants, definitions and examples

Group	Definition	Examples	Environmental Risks	Comments
Pesticides	Any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (by US EPA)	Atrazine, Diuron, Alachlor, Diazinon	Probable human carcinogen, endocrine disrupting potential	Dominant group in the list of persistent organic pollutants (Berg, Hagmeyer, & Gimbel, 1997)
Disinfection by-products (DBPs)	The byproducts formed by the reaction between disinfectants and naturally-occurring materials	Trihalomethanes, Haloacetic acids	Increased risk of cancer and liver, kidney, or central nervous system problems	
Endocrine disrupting chemicals (EDCs)	The chemicals which can interfere with body's endocrine system	Estrone, Estriol, Testosterone, Progesterone	Developmental, reproductive, neurological, and immune effects in both humans and wildlife	Certain fish and wildlife are easy to be affected.
Pharmaceutically Active Compounds (PhACs)	Pharmaceutical residues and their metabolites	Ibuprofen, Diclofenac, Diatrizoateb	Inherent potential for a wide range of physiological effects	Potential for induction of proliferation of antibiotic resistance (Van Wyk, 2015)

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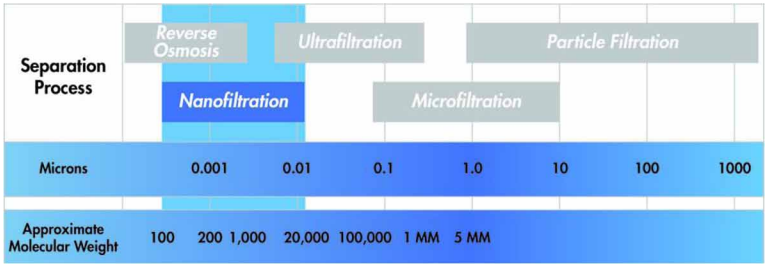
As most ECs are small organic molecules, most conventional water treatment processes exhibit ineffective removal of emerging contaminants. Given the variety of emerging contaminants, advanced water treatment methods should be suitable for this purpose. The ability to reject small organic contaminants makes nanofiltration membranes almost a nature choice for emerging contaminants. Compared with other membrane system (e.g., microfiltration, ultrafiltration and reverse osmosis), nanofiltration show remarkable potential for the removal of small organic contaminants (Figure 1), since the molecular weight cut-off values of most nanofiltration membranes are in the range of 200 to 300 Da, which coincides with the molecular weight of many ECs of concern.

Nanofiltration, defined as process between ultrafiltration and reverse osmosis, however is a controversial technology. The origin of nanofiltration can be traced back to 1960s, even before the term of nanofiltration was coined at the second half of 1980s (Loeb, Titelman, Korngold, & Freiman, 1997). In the beginning, the nanofiltration was categorized as open reverse osmosis or loose ultrafiltration. By the early 1970s, a full series of first-generation cellulose acetate membrane has been developed by Loeb and Sourirajan (Strathmann, Scheible, & Baker, 1971). The cellulose acetate was the standard material for nanofiltration until the composite nanofiltration was developed (Pepper, 1988). This breakthrough significantly enhanced the performance and popularity of nanofiltration, making nanofiltration membranes widely available. In the last decade, majority of studies on nanofiltration moved to chemically stable nanofiltration membranes. Many pH/solvent stable membranes were developed and commercially available (Musale & Kumar, 2000; Toh, Lim, & Livingston, 2007).

Nanofiltration membranes have been shown to be able to remove turbidity, microorganisms and hardness, as well as a fraction of the dissolved salts, which is similar with reverse osmosis. The initial application of nanofiltration in water industry was pretreatment of desalination process with significantly lower operating pressure, which brings energy-efficient advantages. However it is the high rejection of charged or uncharged organic compounds that makes nanofiltration membranes the suitable option to remove emerging contaminants. Even though the reverse osmosis membrane shows higher rejection of low molecular weight compounds, the lower operation pressure brings nanofiltration excellent efficiency. The use of NF to replace RO shows reduced energy costs and reduced volumes of toxic pollutants for the water treatment. For a typical nanofiltration membrane, the rejection of a divalent ion is above 95%, while the rejection of a monovalent ion can be anywhere between 20 and 80% with 600 - 100 PSI working pressure. For example, NF270 is a commercially available nanofiltration membrane with pure water permeability of 13.5 (L m^{-2} h^{-1} bar^{-1}) (Schaep, Vandecasteele, Mohammad, & Bowen, 2001).

In this chapter, the fundamental of nanofiltration will be introduced in second section, while the application of emerging contaminant removal will be discussed in third and fourth section.

Figure 1. Filtration membrane spectrum
(www.axeonwater.com).



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2. FUNDAMENTAL OF NANOFILTRATION

As discussed in the first section, nanofiltration as a pressure-driven membrane has been studied for over 40 years. In this section, the fundamental of nanofiltration will be focused, and the material, the preparation, characterization and predictive models of the nanofiltration will be covered as well.

2.1. Materials and Preparation of Nanofiltration Membranes

There are three major groups of nanofiltration: asymmetric membranes, composite membranes and ceramic membranes. The first two belongs to the polymeric membranes. But the asymmetric membranes can be prepared via one step, the phase inversion method. The classical cellulose acetate membranes are the most important member of this group. Composite membranes are composed of porous nonselective supporting layer coated with a thin-film layer. This multilayer approach offers much more flexibility and control of the synthesis, which makes thin film composite nanofiltration more competitive over asymmetric membrane (Matsuura, 2001; Petersen, 1993; Song, Liu, & Sun, 2005). The membranes based on ceramics are the hot spot especially in the last decade. It has shown higher resistance against organic solvent and high pressure (Benhui, 1996).

2.1.1 Phase Inversion

Phase inversion is the process of controlled polymer transformation from a liquid into a solid state. Immersion precipitation is definitely the most popular method to prepare asymmetric membranes (Mulder, 1996). Since the casting solution of polymer and solvent is immersed into a non-solvent bath (coagulation bath) in typical immersion precipitation, the morphology and the performance of the membrane depends on thermodynamics as well as kinetics. Therefore the resulting membranes can be controlled by the composition of the casting solution, the type of polymer, coagulation medium and post treatment (if any) (Kawakami, Mikawa, & Nagaoka, 1996; Paulsen, Shojaie, & Krantz, 1994).

Even through the asymmetric membranes have been studied for decades, the general quantitative model for formation of asymmetric membrane by immersion precipitation is still under investigation. Based on the previous researches, some qualitative conclusions can be drawn as follows (Schäfer, Fane, & Waite, 2005):

- More charged group in polymer can lead to higher hydrophilic polymer, which would increase water flux of the membranes and alter the salt rejection (Dias, Rosa, & de Pinho, 1998; Stamatialis, Dias, & de Pinho, 1999).
- Increased polymer concentration of casting solution can lead to increased thickness and lower fluxes (Mulder, 1996).
- High interaction between the non-solvent and solvent often produces high porosity of the membrane by addition of additives and increased temperature of coagulation bath (in certain range) (Yeow, Liu, & Li, 2004).

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2.1.2 Interfacial Polymerization

The interfacial polymerization has become a very successful and useful method to synthesize the composite nanofiltration membrane, since the concept of interfacial polymerization was first introduced in 1966 (Zimmermann, 1966). Due to better performance of composite membranes over asymmetric ones, many progresses have been made on the preparation of novel composite membranes in the last decade. Among the commonly used monomers, the cross-linked aromatic polyamide composite membrane produced by interfacial polymerization of phenylenediamine (MPD) and trimesoyl chloride (TMC) is still most successful in the present.

Compared with phase inversion, interfacial polymerization brings us more flexible optimization, which makes the research on interfacial polymerization more systemic. The hydrophilicity of polymer is still an important factor on membrane performance. Triamine 3,5-diamino-N-(4-aminophenyl) benzamide (DABA) monomer was used with m-phenylenediamine (MPD) and trimesoyl chloride (TMC) to improve the water flux of membranes, by more hydrophilic (giving rise to lower contact angles), smoother and thinner surface (H. Wang, Li, Zhang, & Zhang, 2010). Membranes with high resistance against chlorine (one of the common disinfectants used in water and wastewater treatment) were also prepared with 1,3-cyclohexanebis(methylamine) (CHMA) in water with TMC in hexane (Buch, Mohan, & Reddy, 2008). Besides the researches in polymer, many studies were performed on porous supports of composite membranes. By using novel support polymers, several thermally/solvent stable composite membranes were synthesized. For example, a thermal stable composite membrane by polymerization of piperazine (PIP) and TMC on poly (phthalazinone ether amide) (PPEA) membrane can function effectively at 80 °C (C. Wu, Zhang, Yang, & Jian, 2009).

Another important development in composite membrane is the addition of nanoscale particles into film of membranes, which is named as thin film nanocomposite (TFN) membrane. By incorporating of titanium oxide (TiO_2), this hybrid thin film composite show photocatalytically destructive capability on microorganisms, which can be used to solve biofouling problem (Kim, Kwak, Sohn, & Park, 2003). Surface modification of TiO_2 can also increase water flux up to 2-fold compared with the pure polyamide membrane with negligible rejection loss (Rajaeian, Rahimpour, Tade, & Liu, 2013). Multiwall carbon nanotubes (MWNTs)/polyester thin film nanocomposite membranes showed superior high water flux due to the high hydrophilic property (H. Wu, Tang, & Wu, 2010). Similar research with Metal–organic frameworks to yield high flux membrane (3-fold increase in permeance) was performed on polyamide (PA) thin film (Sorribas, Gorgojo, Téllez, Coronas, & Livingston, 2013).

2.1.3 Ceramic Membranes

Ceramic based membranes are a unique class of nanofiltration membranes due to inorganic components. Ceramic membrane shows higher chemical, structural and thermal stability over polymeric membranes. Even though it only holds a small membrane market share, many progresses of ceramic membranes were made, especially in solvent-resistant nanofiltration membrane area (Hendrix & Vankelecom, 2013). Similar to polymeric membranes, support materials are still required for membranes based on ceramic. The difference is mesoporous intermediate layer is usually chosen as support. Al, Si, Ti or Zr oxides can be used to build ceramic membranes (Guizard, Ayral, & Julbe, 2002).

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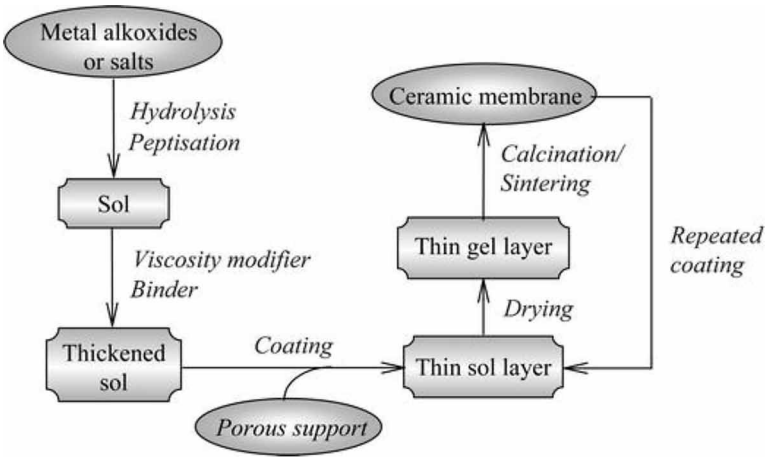
Figure 2. Flow diagram for the preparation of microporous or mesoporous membranes via sol–gel techniques
(Hong & Elimelech, 1997).



The general procedure to prepare active layer of ceramic membrane is sol-gel method, which involves converting colloidal solution into a gelatinous substance (Hsieh, 1996). The general procedure for ceramic membranes is shown in Figure 2.

2.2 Characterization of Nanofiltration Membrane

In this section, characterization for nanofiltration membranes will be divided into performance parameters, morphology parameters, as well as charge parameters to discuss (Artuğ & Hapke, 2006).

For performance, retention of the membrane and permeability coefficient are the most important parameters. By definition, the retention can be calculated with Equation 1:

$$R = \frac{c_f - c_p}{c_f} \tag{1}$$

in which c_f represents the concentration of the feed and c_p represents the concentration of permeate. The permeability is characterized by permeability coefficient (L_p), which is calculated by the slope of plotting the water flux as a function of the pressure.

For morphology, pore size, porosity, surface roughness and hydrophobicity are important parameters. Gas adsorption is usually the first choice to study the pore characteristics of solid materials (Schull, 1948), but for nanofiltration membrane with nanometer range pores (for example, the average pore diameter of NF90 is only 0.68 nm) this method is not accurate any more. Same issue occurs when permporometry is used to measure small pores, which produces same inaccurate results with gas adsorption (Cao, Meijernik, Brinkman, & Burggraaf, 1993). Microscopic techniques, especially atomic force microscopy (AFM) are very suitable for nanofiltration membranes. High resolution images of many commercial membranes were achieved by AFM. Even though several emerging technics or methods were applied to measure the pore size distribution, AFM and SEM are still preferred for the measurement (Otero et al., 2008).

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Hydrophobicity is another essential morphology parameter, which is often characterized by contact angle (defined in Equation 2):

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{2}$$

in which γ_{SV} and γ_{LV} are the surface tensions of the solid and the liquid with the vapor of the liquid and γ_{SL} is the tension of the solid-liquid interface.

The charge of the membrane can be obtained by measuring the streaming potential, and zeta potential.

2.3 Modeling of Nanofiltration Membrane

It has been 50 years since the nanofiltration concept was established in 1960s. But still a universal quantitative model for the description and prediction of nanofiltration performance has not been founded, though many theories have been established to describe the fundamental. Nanofiltration is a very complex process, because the rejection event occurs on a scale of the order of nanometer, which is very close to atomic dimensions. This would force us to consider the whole process with microscopic concept, which explains why more models of nanofiltration are transplanted from reserve osmosis. The filtration process involves several mechanisms, like steric interaction, charge interaction, adsorption and sorption-diffusion. Complex interactions between solutes, solvents and membranes make the nanofiltration modeling extremely difficult.

This section does not intend to include exhaustive physical equations, and the following will instead focus on the status of each modeling type. From a general point of view, modeling can be founded by experimental phenomena (empirical) or physical mechanism.

The empirical model, Spiegler-Kedem model, was initially founded at 1960s based on the irreversible thermodynamics and all the parameters and coefficients were determined experimentally (Kedem & Katchalsky, 1963). The composite membranes were considered as a “black box”, which meant all the transport processes were not include in the model. This model was successfully applied in reverse osmosis membranes afterwards (Spiegler & Kedem, 1966). A few following researches confirmed the model was only valid under certain conditions, but the main drawback is lack of considering the variety of rejection and the charge effect of the membrane. The concentration dependency on rejection and the electrostatic exclusion are considered in the model developed later in 1989 and 1992 (Perry & Linder, 1989; Schirg & Widmer, 1992). Even though new parameters were included, the application of extended Spiegler-Kedem model was limited due to poor predictive ability.

The other models are based on transport-mechanistic modeling. These physical models take into account the transport mechanisms occurring in the membrane, which can be divided into two branches: space-charged (SC) model (Morrison Jr & Osterle, 1965) and Teorell-Meyer-Sievers (TMS) model (Teorell, 1953). In SC models, the pores on the membrane are considered as charged capillaries. Ions are considered as point charges, which are defined by Poisson-Boltzmann equation; while ion transport is defined by extended Nernst-Planck equation. With respect of TMS models, the radial distribution is neglected. The following researches confirmed two models to show good agreement for capillaries having smaller radius and lower surface charge density, which is the case of nanofiltration (X.-L. Wang, Tsuru,

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Nakao, & Kimura, 1995). Many modified models have been proposed recently based on the similar assumption, which shows a rapid growing realization of physical models.

By limited parameters and soluble mathematic calculations, well-founded models should serve for two purposes: description and prediction. Unfortunately, despite of many accomplishes in modeling of nanofiltration, the current modeling and simulation are more descriptive than predictive. Attempt to combine all current knowledge for a predictive model led to the conclusion that much depended on fitting parameters and not on physically relevant parameters (Straatsma, Bargeman, Van der Horst, & Wesselingh, 2002). For now empirical model for certain membrane is much reliable to predict membrane performance. Hence further research is still needed.

3. REMOVAL OF EMERGING CONTAMINANTS WITH NANOFILTRATION

During the last decade, nanofiltration has become more and more popular in drinking water treatment and wastewater treatment, not only for conventional water softening, but also for the removal of micropollutants, especially organic emerging contaminants. In this section, the removal of different types of emerging contaminants as well as the removal mechanisms will be discussed.

3.1. Removal of Emerging Contaminates

3.1.1 Pesticides

The use of pesticides to control unwanted pests dates back hundreds of years. Pesticides became a severe issue since the hundreds of synthetic organic chemicals were used without regulatory. Some of them can cause immediate toxic effects or act as potential carcinogen with long-term exposure, while some of them show superior stability in natural environment, such as DDT (dichlorodiphenyltrichloroethane). The use of nanofiltration for the removal of pesticides has been investigated by many researchers. To achieve best removal outcome, optimized membrane properties, additives during filtration and different operation conditions have been tried. Table 2 shows high retention of selected pesticides with nanofiltration.

Ghaemi and coworkers performed a series of solid study about removal of nitroaromatic pesticides with modified nanofiltration membranes. They first investigated the effect of sodium dodecyl sulfate (SDS) anionic surfactant as additives in cellulose acetate (CA) nanofiltration membrane preparation. AFM measurements showed addition of SDS decreased thickness of the top layer and performance evaluation indicated higher pure water flux and rejection compared to CA membranes. The rejection of 3,5-Dinitrosalicylic acid (DNSA) and p-nitrophenol (PNP) reached 97.5% and 90% respectively under optimized condition (Ghaemi, Madaeni, Alizadeh, Daraei, Vatanpour, et al., 2012). Then they continued to study the effect of organic acids (ascorbic acid, citric acid and malic acid) as addictive in polysulfone nanofiltration membrane. Following the same strategy, retention of pesticides, 2,4-Dinitrophenol (DNP) and p-nitrophenol (PNP) reached 99% and 90% respectively with increasing hydrophilicity and water flux of the membrane (Ghaemi, Madaeni, Alizadeh, Daraei, Badieh, et al., 2012). Also the effects of addition of amphiphilic fatty acids (palmitic, oleic, and linoleic acids) were investigated on morphology, performance of cellulose acetate nanofiltration membranes and retention of nitroaromatic pesticides. Fabricated membranes presented higher efficiency in retention after the addition of palmitic acid with five pesticides as target solutes (Ghaemi, Madaeni, Alizadeh, Rajabi, et al., 2012). Košutić obtained good

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results for the removal of arsenic and pesticides from natural ground water. The NF270 nanofiltration membranes exhibited superior permeation rate values, which were more than five times higher than the corresponding values of the reverse osmosis CPA2 membrane. This can be explained by the charge exclusion mechanism during filtration process (Košutić, Furač, Sipos, & Kunst, 2005).

Interestingly some studies indicated dissolved natural organic matter (DOM) could enhance atrazine rejection in most cases and the enhancement was dependent upon the concentrations of the DOM and the atrazine and the ionic strength (Devitt, Ducellier, Cote, & Wiesner, 1998). Some following studies showed the presence of humic acid, sulfates, and chlorides can improve the elimination of certain pesticides (Košutić et al., 2005). But other contrasting results showed DOM can decrease or have negligible effect on micropollutant removal (Devitt et al., 1998). The charge exclusion is found to be the prevailing mechanism of small model compounds retention by the negatively charged nanofiltration membranes. The size exclusion mechanism also is observed to be important but not sufficient for the unionized small organic molecules rejections (Lin, Chiang, & Chang, 2007).

Besides the pesticide itself, the potential of nanofiltration membranes for treatment of groundwater polluted with some of these key transformation products was assessed. It turned out the nanofiltration membranes were capable of rejecting the regular pesticides, but did not give satisfactory rejections of the transformation products due to decreasing molecular size. Filtration system needed to be modified in order to obtain better performance (Madsen & Søgaard, 2014).

3.1.2 Disinfection By-Products (DBPs)

Many DBPs pose potential health risks due to carcinogenic effect with long-term exposure (Waller, Swan, DeLorenze, & Hopkins, 1998). In the past 40 years since the trihalomethanes (THMs) were identified as DBPs in drinking water, significant research efforts have been directed toward increasing our understanding of DBP formation and removal (Richardson & Postigo, 2012; Waller et al., 1998). Several publications have shown good rejection of DBP with nanofiltration. Vedat reported the removal efficiencies of THM by nanofiltration technique with commercial NF200 and DS5 membranes. With

Table 2. Retention of selected pesticides using nanofiltration membranes

Compound	Membrane	Feed Concentration	Retention (%)	Reference
Atrazine	NF45	300 µg/L	91.8	(Van der Bruggen, Schaep, Maes, Wilms, & Vandecasteele, 1998)
	NF90	20 mg/L	95	(Ahmad, Tan, & Shukor, 2008)
	UTC20	5 mg/l	93	(Zhang, Van der Bruggen, Chen, Braeken, & Vandecasteele, 2004)
Simazine	NF70	300 µg/L	88.5	(Van der Bruggen et al., 1998)
	UTC20	5 mg/L	83	(Zhang et al., 2004)
Diuron	NF70	300 µg/L	85.9	(Van der Bruggen et al., 1998)
Isoproturon	NF70	300 µg/L	90.3	(Van der Bruggen et al., 1998)
	ESNA	149 µg/L	98.3	(Plakas, Karabelas, Wintgens, & Melin, 2006)
Isoxathion	NTR-729HF	n/a	99.84	(Kiso, Sugiura, Kitao, & Nishimura, 2001)

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synthesized fee water, feed concentration and operating pressure show little effect on rejection, while the brominated THMs with higher molecular weight show higher removal efficiency compared with other species of THM (Uyak, Koyuncu, Oktem, Cakmakci, & Toroz, 2008).

Besides removing the DBPs directly, removing the DBP precursors is another promising strategy, like removal of bromide and other organic matters before disinfection to substantially lower the formation of DBP (Kimbrough & Suffet, 2002). Nanofiltration can lead to a high rejection of NOM and a high reduction of THM precursors in water, which can be efficient to reduce THM formation potential (De la Rubia, Rodríguez, León, & Prats, 2008). Commercial nanofiltration membranes, NF70 and NF270 were utilized to remove small THM precursors as well. High removals of THM precursors were observed at high pH values (Lin et al., 2007). Generally this strategy is more effective than directly removing DBPs as the DBP precursors are of large molecular weight.

Due to variety of DBPs, even though most NF studies reported promising DBP and DBP precursor rejections (Blau, Taylor, Morris, & Mulford, 1992; Jarusutthirak, Mattaraj, & Jiraratananon, 2007; Lee & Lee, 2007), removal pattern of individual species should be considered as well (Chellam, Sharma, Shetty, & Wei, 2008).

3.1.3 Pharmaceutically Active Compounds (PhACs)

Pharmaceutically active compounds (PhACs) present an increasingly large group of emerging contaminants. As pharmaceuticals are designed to be biologically active and chemically stable, more than 83 pharmaceuticals have been detected all over the world (Baena-Nogueras, Pintado-Herrera, González-Mazo, & Lara-Martín, 2015). Pharmaceuticals as well as their metabolites can influence none-target organisms with acute or chronic effect. Conventional sewage treatment shows unsatisfactory removal of PhACs, which is at concentration range of μg/L or lower (Heberer, 2002). Many researchers have reported almost 100% retention of PhACs with nanofiltration membranes in their studies. For example, two commercial composite membranes (SR2 and SR3) show 75–95% and 95–100% removal efficiency of five model PhACs with different physicochemical properties (i.e., cephalexin, tetracycline, acetaminophen, indomethacin and amoxicillin) (Zazouli, Susanto, Nasseri, & Ulbricht, 2009). Even in the full-scale drinking water treatment plant, nanofiltration was reported to successfully remove >85% of 12 PhACs (Radjenović, Petrović, Ventura, & Barceló, 2008).

3.1.4 Endocrine Disrupting Chemicals (EDCs)

Steroid hormones such as estrone are prominent in EDCs due to high endocrine-disrupting potency (Colborn, vom Saal, & Soto, 1993). Given the low concentration yet adverse effects in aquatic environment, EDCs have attracted significant interests recently (Andersen, Siegrist, Halling-Sørensen, & Ternes, 2003; Vos et al., 2000). However a definitive list of EDCs does not exist, as most chemicals in commerce have not been tested for endocrine toxicity. Nanofiltration membranes are demonstrated to have fair removal efficiencies for EDCs as well. Removal of estrone and 17β-estradiol with nanofiltration are summarized in Table 3. Numerous studies were also performed with other hormones as reference EDCs. Koyuncu et al. investigated the rejections of estradiol and testosterone (by 64% and 62%, respectively) by NF200 membrane (Koyuncu, Arikan, Wiesner, & Rice, 2008). Pereira et al. utilized the same NF200 membrane and obtained similar results. NF200 membrane rejected the selected hormones with efficiencies higher than 71% (except estriol with only 38% removal) directly from surface water (Pereira, Galinha,

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Crespo, Matos, & Crespo, 2012). Unlike the almost complete removal of other emerging contaminants, nanofiltration didn't work that well in EDCs removal, even the molecular weight of target EDCs was lower than molecular weight cut-off of the membrane in several studies (Sandra Sanches et al., 2012; Semião & Schäfer, 2013).

Even though, in the last decade many researches show promising result of EC revmoval. Most of studies were performed in lab scale without using "real" water. However, regardless of many breakthroughs in materials or configuration of the NF membrane itself, the potential of nanofiltration in industrial application is still underdeveloped.

3.2. Removal Mechanisms of Nanofiltration for Emerging Contaminants

As discussed in the last section, nanofiltration shows generally high retention of emerging contaminants and varying performance for different target micropollutants. Since the molecular weight cut-off values of nanofiltration membranes fall in the same range as the molecular weight of most emerging contaminants, the overall good rejection can be predicted. The reason for variations will be discussed in this section.

Size exclusion is the simplified, yet useful retention model, which basically depends on the pore size of membranes and the physical size of contaminants. In this model, average pore sizes and estimated diameter of solutes are the two key parameters. For the diameter of solute molecule, the most easily estimated method is molecular weight, and predictions of retention coefficient have been made based on molecular weight. Molecular weight cut-off, which is defined as the molecular weight of a solute with retention of 90%, is used as the primary parameter of commercial nanofiltration membranes. As molecular weight is not dimensional parameter, the hydrodynamic volume was tested and provided better prediction than the molecular weight (Meireles, Bessieres, Rogissart, Aimar, & Sanchez, 1995). In

Table 3. Retention of selected EDCs using nanofiltration membranes

Compound	Membrane	Feed Concentration	Retention (%)	Reference
Estrone	TFC-SR2	100 ng/L	13	(Agenson, Oh, Kikuta, & Urase, 2003; L. Nghiem, Manis, Soldenhoff, & Schäfer, 2004; L. D. Nghiem, Schäfer, & Elimelech, 2004; Weber, Gallenkemper, Melin, Dott, & Hollender, 2004)
	TFC-5	100 ng/L	76	
	X-20	100 ng/L	87	
	NF90	100 ng/L	89	
	NF270	100 ng/L	85	
	UTC60	50 ng/L	80	
	NTR7250	50 ng/L	57	
	PES10	100 ng/L	40	
17β-estradiol	TFC-SR2	100 ng/L	21	
	TFC-5	100 ng/L	82	
	NF90	100 ng/L	86	
	NF270	100 ng/L	85	
	UTC60	50 ng/L	72	
	NTR7250	50 ng/L	58	
	PES10	100 ng/L	50	

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order to take structure parameter into account, Stoke radius was considered as better fit, regarding the molecules as spheres (Fei & Bart, 2001). However, some other methods indicate the molecules are not spherical, and the molecular width and length are calculated as STERIMOL parameters (Kiso et al., 2001). Computer aided methods have been introduced as well, random energetic optimization by software can produce molecular size directly. Recently researchers tend to choose multiple size parameters in order to produce more complicated and accurate predictions, like distribution coefficient, molecular weight, and molar volume, etc. (S Sanches, Galinha, Crespo, Pereira, & Crespo, 2013). In addition, operation conditions, like pH, ionic strength, and concentration of contaminants, can influence actual sizes of the contaminants and the pores (Childress & Elimelech, 2000).

The other models are involving the interactions between contaminants and membranes, which includes electrostatic interaction, physical adsorption, and hydrogen bonding (Braeken et al., 2005; L. D. Nghiem et al., 2004). Estrone is a typical example that size exclusion mechanism is not the dominant factor for retention, due to hydrogen bond and strong hydrophobic interaction with membranes. The accumulation of contaminants could lower the performance of membranes, which explains relatively low retention of estrone with nanofiltration (Braeken et al., 2005; D. Nghiem, Schäfer, & Waite, 2002).

Considering the complexity of nanofiltration process, these mechanisms always work together, even in many cases one mechanism can be a dominant factor, which is difficult to predict.

4. PLANT DESIGN

Even though major studies on nanofiltration are fundamental researches, like novel membrane development and retention mechanism, plant design of nanofiltration with respect to emerging contaminant removal is very crucial in practice.

In water treatment industry, all treatment technics should work together, including nanofiltration. And the pre-treatment and post-treatment may vary based on certain plant. Nanofiltration membranes are usually applied near the end of the long line of water treatment process, while they are used as pretreatment for desalination. For the removal of trace organic contaminants, pretreatment of the feed is extremely important for nanofiltration, which is the main principle in nanofiltration design. Besides to avoid fouling, mechanical damage from solids or oxidization from disinfection can lead to severe effect on performance. Due to the pore size in nanometer range, soluble inorganic and dissolved organic components are the major foulant species (Speth, Gusses, & Summers, 2000). Even though fouling can be minimized, but not prevented, by adjustment of the parameters of filtration process (like module configurations, flow, pressure, pH and temperature) (Maartens, Swart, & Jacobs, 1999), a series of pretreatments are still necessary. In general, the pretreatment for nanofiltration can be designed based on same requirement of reverse osmosis.

In the water treatment, nanofiltration is usually not the final step; the post-treatment may be disinfection and/or pH adjustment. UV-disinfection is used as post-treatment more than chlorination disinfection method, which is installed as a back-up.

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5. CONCLUSION AND PROSPECTS

In this chapter, the removal of emerging contaminants with nanofiltration in water and wastewater treatment was discussed. Emerging contaminants, as micropollutants with low concentration, should be rejected efficiently by nanofiltration based on the fundamental understanding of filtration mechanism. Extensive studies in various scale confirmed this repeatedly with different model compounds, nanofiltration membranes. The retention mechanisms and factors affecting the membrane's retention were discussed in many researches. Computer aided analysis also improved the modeling and prediction of the nanofiltration. High retention (complete removal in some cases) of almost all emerging contaminant groups indicates a promising potential of nanofiltration in this area.

On the other hand, these findings are most obtained from laboratory-scale researches, and direct application in water treatment industry is lacking. For the practical application, the pretreatment requirement, module design and post-treatment options are important research topics associating with nanofiltration technology, and urgently need investigations.

The implementation of nanofiltration in the industry is a success story even with several challenges in practice: 1) higher energy consumption than ultrafiltration; 2) pre-treatment is needed; 3) nanofiltration membranes are a little more expensive than reverse osmosis membranes. Although it is unlikely to reach the total area of global, installed membrane for either reverse osmosis or ultrafiltration, it can be expected that large steps forward will be made in the soon future.

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Chapter 34
Physical Treatment Technologies for Landfill Leachate: Performance and Limitation

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ABSTRACT

Landfill leachate is a refractory wastewater and highly polluted with heterogeneous materials which is harmful to the environment and living organisms. Thus, leachate requires efficient treatment system to ensure the quality of final discharge is within the standard limit. Moreover the treatment process must be cost effective in order to be accepted. Many treatment processes were examined for leachate treatment including biological, chemical and physical process. This chapter discuss the treatability of leachate using physical processes such as evaporation, flotation, adsorption, membrane, ultrasonication, air stripping. It can be concluded that physical processes are not recommended to stand alone for leachate treatment. Nevertheless, adsorption and membrane technologies are very effective for post treatment of leachate. Aeration, sedimentation, evaporation, and sonication can be used effectively as pre-treatment processes.

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INTRODUCTION

Landfill leachate is considered as a highly polluted wastewater with heterogeneous contaminants that are harmful to the environment and living organisms. Typically, leachates characteristics varied according to the age of the landfill. The young leachate normally consists of biodegradable materials which are suitable to be treated by biological processes. However, intermediate and old leachate mostly contains of recalcitrant materials which are less biodegradable. Thus, physical or chemical treatment is a better solution for this type of contaminant (Bashir et al., 2014).

Satisfactory disposal of landfill leachate is dependent on its treatment prior to disposal. An acceptable treatment is required to avoidpollution of receiving waters to a level which might interfere with their best or future use (Bashir et al., 2014). Technologies for treating landfill leachate can be divided into three categories: chemical methods, physical methods, and biological methods. In this chapter, detail discussions concerning landfill leachate treatment via various physical processes are presented.

Physical methods of wastewater treatment achieve the removal of pollutants by using naturally occurring forces, such as gravity, electrical attraction, and van der Waal forces, as well as by using physical barriers (membrane technology). In general, the mechanisms involved in physical treatment do not result in the chemical structure changes of the target substances. In some cases, physical state is changed, as in vaporization. In other cases dispersed substances are caused to agglomerate, as happens during filtration. Physical methods of wastewater treatment include sedimentation, aeration, evaporation, flotation, and adsorption, as well as membranes (Woodard & Curran Inc., 2006).

The common examples of physical methods would be coarse screening to eliminate larger entrained objects and sedimentation (or clarification). In the sedimentation process, physical phenomena related to the settling of solid particles by gravity are allowed to operate. Usually, this process consists of simply holding a wastewater for a short period of time in a tank under quiescent conditions, allowing the heavier solids to settle, and removing the "clarified" effluent. Sedimentation for solids separation is a very common process operation and is routinely employed at the beginning and end of wastewater treatment operations. Another physical treatment process consists of aeration which is, physically adding air, usually to provide oxygen to the wastewater. Nevertheless, application of basic physical processes such as screening, sedimentation and aeration in treating landfill leachate is ineffective. This is due to the nature and the characteristic of the leachate. Therefore, in this chapter, the authors aim to discuss the mechanism, performance and usefulness of using other physical processes (e.g., evaporation, flotation, adsorption, separation via physical barriers, and sonication) in treating the landfill leachate. It should be noted that the additional physical phenomena used in the treatment of leachate consists of filtration (adsorption). The leachate is passed through a filter medium to separate the solids. As an example, the usage of sand filters or activated carbon filters to further remove entrained solids from a treated wastewater. Then, the flotation is used to float the surface area of the leachate and then skimming or physically remove it from the leachate was carried out as part of the overall treatment process. Moreover, evaporation, membrane technology, and ultrasound are commonly used as a post or a pretreatment of the leachate.

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PHYSICAL TREATMENT PROCESSES

Short review and definitions of the most significant physical treatment technologies utilized for the landfill leachate treatment are reported in this section. Comprehensive discussions are presented to provide better understanding about each mechanism process, performance, and limitation.

Evaporation

An evaporation process seems to offer an attractive option for leachate treatment that can cover all ages of the landfill leachate. Evaporation is a treatment process that is able to utilize natural climate condition such as relative humidity, air temperature and wind speed (Alcântara & Castilhos Junior, 2014). The use of natural condition is the main benefit of this process because the operating cost of treatment plant can be reduced. Furthermore, there is no chemical addition required in the treatment process. However, the effectiveness of this process is very dependent to climate condition. Thus, it has been studied as an alternative treatment to the conventional or available treatment for wastewater including landfill leachate especially at the regions where it can be implemented effectively.

Natural evaporation process offered "zero liquid discharge" to the environment by deposing the leachate into open ponds allowing the water to be evaporated. In the past, natural evaporation ponds were used in the evaporation treatment process of landfill leachate. However, it was less sustainable because the leachate may percolate into soil and groundwater. Therefore, artificial ponds with lining were constructed. The combination of the solar heat and wind help in naturally evaporate the leachate and leave concentrated residual in the pond. However, the process is slow and takes a long time. Thus, very large surface area is required for the pond, which is the main disadvantage of this treatment process (Macedonio et al., 2011).Nonetheless, evaporation ponds also generate odour to the nearest town and stored high organic content of water. This is the main reason for more enhancement and development of the evaporation process.

Besides natural evaporation, the landfill leachate can be treated by mechanical evaporation using several unit operations (Afsharnia et al., 2012). The most common mechanical evaporation used is the vacuum evaporation. This technique also offers a high quality of final effluent (distillate water) with the lowest concentration of pollutants for the discharge. Currently, the integrated or combination of evaporation with other treatment and technique has been reported. These processes were aimed to increase the evaporation performance and the efficiency of pollutant removal in landfill leachate. As an example, different techniques such as sono-evaporation and the combination of vacuum evaporation and reverse osmosis were reported by Afsharnia et al. (2012) and Palma et al. (2002). Recently, the use of evaporation panel was suggested in the semiarid climate region (Juazeiro do Norte, Brazil) to increase the evaporation rate, efficiency of the system and whilst reduce the installation area of the leachate treatment (Alcântara & Castilhos Junior, 2014).

Natural/Solar Evaporation

The natural evaporation process has been widely used in mining, water and energy industries (Zeng et al., 2011). The evaporation process is very dependent on the climate condition where the amount of evaporation of the water surface is determined by temperature, wind velocity and humidity (Qasim & Chiang, 1994). It is also common that the evaporation rate decreases during rainy seasons. Hence, the

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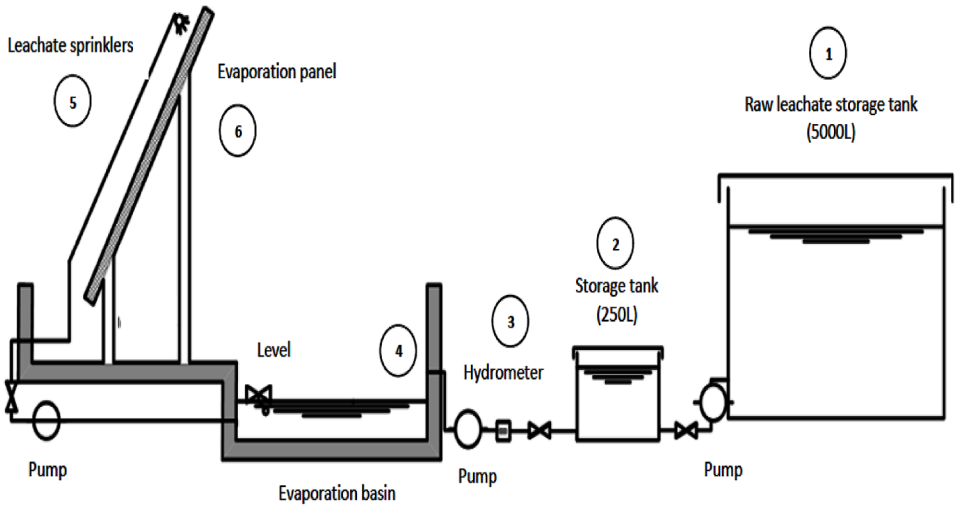
data for these parameters, including rainfall at the selected locations have to be assessed prior to the installation of this treatment. Zazueta (2011) explained the function of each parameter of the evaporation process. The relative humidity is a measure within the range of 0 to 100 percent. The low percentage of relative humidity indicates that the air is dry (low moisture) while the high percentage value shows that the air has high content of moisture. Natural evaporation is more advantages at low relative humidity where the air is dry and has great capacity for moisture. Meanwhile, the wind enhances the evaporation rate by transporting water vapour away from the evaporation surface and surrounding areas. However, the treatment process usually suffers of low evaporation rate at regions with fewer feasible climate conditions. Consequently, a large area is required to increase the evaporation rate. Therefore, many studies have been conducted to enhance the evaporation process in order to reduce the land area for evaporation pond and increase evaporation rate.

According to Ranzi et al. (2009), the natural evaporation with panel is a recent technique that is developed for leachate treatment. The application of the evaporation panel is investigated in order to increase the volume of leachate treated through the natural evaporation especially during rainy seasons. This pilot experimental study was conducted in Florianopolis, Brazil which has a subtropical humid climate. The type of materials used for the evaporation panel play an important role to ensure large volume of water is evaporated. An example of the evaporation panel that has been used was polypropylene panel with beehive structure which has high specific area. The panel was installed at 60^{o} inclination (ideal angle) with the horizontal line to prepare the surface for leachate distribution. The entire medium was wetted by rotating sprinkler whilst the air made a contact with the moistened medium and adsorbed the humidity up to almost the saturation point. Excess liquid was returned to evaporation basin for recirculation. The average evaporation that has been obtained during this study was approximately 111 L/day. Figure 1 shows the schematic diagram for evaporation with panel as suggested by Ranzi et al. (2009).

In another study, an identical pilot plant study was conducted by Alcantra & Castilhos Junior (2014). The difference between both studies was the climate condition where this area has a semiarid climate. Based on their report, average daily evaporation of leachate in this area was3.2 times higher compared to the values obtained by Ranzi et al. (2009) at subtropical humid climate. This study confirmed the

Figure 1. Schematic diagram for evaporation with panel (Ranzi et al., 2009)



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feasibility of evaporation with panel at semiarid climate. The evaporation efficiency can be calculated from Equation 1 &2 where natural evaporation, E_N (from evaporation pond), precipitation, P and volume of effluent, V_L introduced into the system were considered (Alcantra & Castilhos Junior, 2014). Total evaporation, E_T can be obtained by adding panel evaporation, E_P value and natural evaporation, E_N.

$$E_T = E_P + E_N \tag{1}$$

$$E_P = V_L + E_N + P \tag{2}$$

In addition, the contact area is another important factor that needs to be considered. In this case, the contact area referred to space between water and air where the evaporation process occurred (Alcantra and Castilhos Junior, 2014: Ranzi et al., 2009). Meanwhile Zazueta (2011) has explained the contact area through time available for evaporation to occur. As an example, the water sprayed at greater height and over greater distance has more time for the evaporation process. This is due to the physical-chemical reaction, where the greater contact surface between reagents, the greater velocity of the reaction. Thus, the increment of contact area will improve the performance of the evaporation process. This is the reason for a large size of evaporation pond and tall riser installation of sprinkler. Furthermore, the high sprinkler position has an advantage to fully utilized higher wind speed movement, which then increases the evaporation rate. Besides natural evaporation, another evaporation process method introduced for leachate treatment is mechanical evaporation.

Mechanical Evaporation

Initially, mechanical evaporation method is designed to simulate evaporation abilities to treat liquid with complex composition (Marks et al., 1994). The characteristics of leachate are important to design vacuum evaporation with optimum condition of operation. Commonly pH adjustment is necessary for prediction of vapor and liquid equilibrium for this treatment method. Acidic condition is effective to remove leachate with low volatile organic acids. Conversely, basic condition is better for leachate with high volatile organic acids. There is no optimum pH that suitable for both conditions. Therefore, the multiple stage of vacuum evaporation process may be needed to obtain satisfactory removal of pollutants in leachate. The concern parameters in vacuum evaporation are temperature range, pressure, vapor and liquid fraction and heat duty (Marks et al., 1994). According to Chiumenti et al. (2013), vacuum evaporation was operated by boiling a liquid substrate at negative pressure and temperature is lower than liquid boiling point at atmospheric condition. Basically, evaporation performance can be increased by increasing the temperature. However, the range of temperature that can be applied is limited because the boiling point of leachate is about 100°C at 760mm Hg. Hence the temperature of leachate in pre-heater stage should be less than 100°C unless it is pressurized in order to prevent boiling. Another concern is the steam pressure; as it should be within the reasonable temperature in order to convert the vaporization stage to condensation stage. If the temperature at the evaporation process is low, then the temperature at condense stage would be low too. Consequently, the amount of distillate production is small. Therefore, there is a need for the water recycle in order to obtain a high percentage of return effluent.

This method produces a high quality of distillate, but large amount of energy is required for the process which leads to high operating cost. In addition, leachate treatment using a vacuum evaporation process may be facing another problem which is scaling. Among developed evaporation technique, ap-

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plication of force evaporation (leachate evaporated through heating) has been reported by Birchler et al. (1994). They utilized the thermal energy from methane gas production in the landfill to generate the heat for leachate evaporation. Laboratory study of forced evaporation shows that the process required the pH adjustment for optimum removal (e.g. ammonia can be removed effectively in acidic condition while COD and TOC were effectively removed in basic condition). Therefore, a series of evaporation process is needed to remove these pollutants. Figure 2 shows a schematic diagram of a force evaporation process that has been installed in Uttigen, Switzerland. Another study that has been conducted by Marks et al. (1994) focused on the development of a semi continuous batch model to predict evaporation and concentration quality through flash vaporization. Marks et al. (1994) mentioned that the mechanical evaporation process may offer an effective treatment for removing various pollutants in leachate using fewer unit operations compared to conventional method that has several treatments in sequent.

The process started by heating the leachate followed by the evaporation at the reduced pressure. After that, the vapors reached to an equilibrium stage with the residual liquid at the new lower pressure and temperature in the condenser, which produced a high quality of distillate. This study concluded that multi stage flash with recirculation and condensation heat recovery increase the efficiency of returned distillate and reduced the energy usage for steam and pumping. This treatment also leaves less residual/ sludge and produces distillate water that consists of low concentration of pollutants which is safe to be released to the environment. The application of two-stage vacuum evaporation in the leachate treatment was demonstrated by Messineo et al. (2012) as shown in Figure 3.

Figure 2. Schematic diagram for leachate treatment by force evaporation (Birchler et al., 1994)

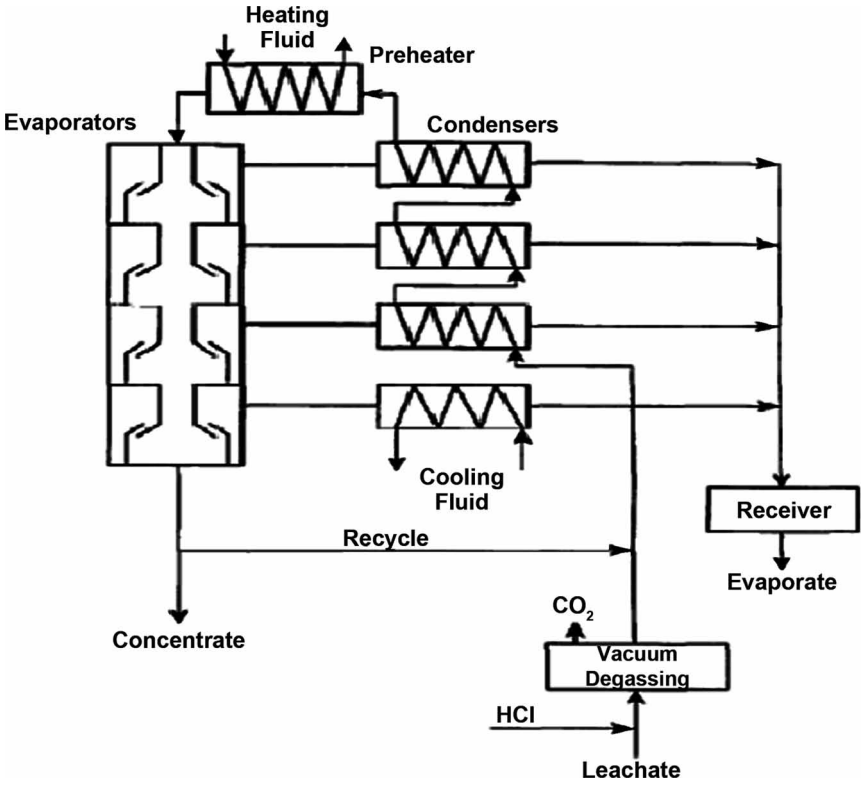

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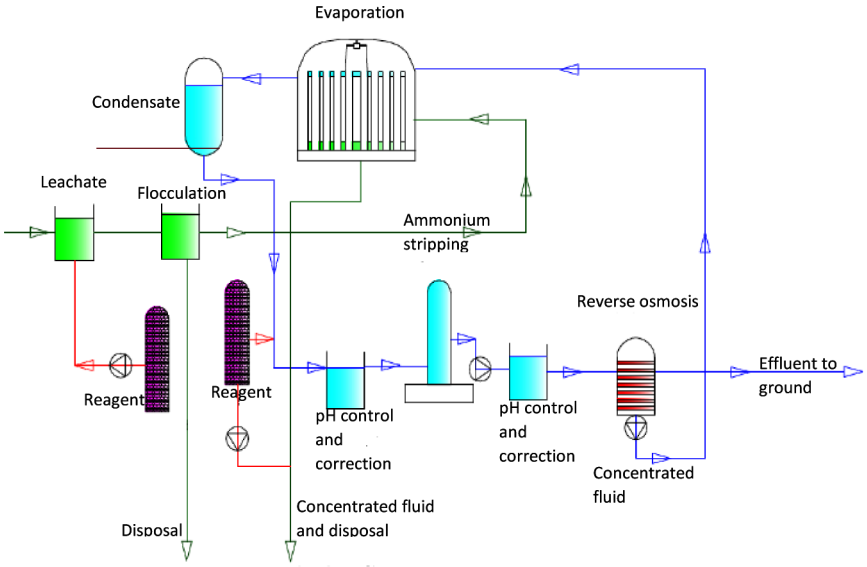
Figure 3. An application of two-stage evaporation process in leachate treatment plant (Messineo et al., 2012)



To date, several studies reported that the mechanical evaporation technique is efficient for COD reduction (Afsharnia et al., 2012; Gutiérrez et al., 2007; Palma et al., 2002). Thus, it is recommended for wastewater with high COD contaminant. For example, Gutiérrez et al. (2007) reported that the vacuum evaporation process was able to reduce more than 99.5% of COD from oil in emulsion wastewater. The efficiency of this treatment is depending on the pressure and temperature setting during the process. In vacuum evaporation, the increment of temperature and pressure automatically increases the efficiency of this treatment process, but reduces its effectiveness in removing pollutants. In this case, the volume of distillate is increased whilst the quality of distillate is decreased where higher pollutants concentrations were detected in the distillate.

Besides that, mechanical evaporation processes have been facing scaling problems. Typically, the wastewater contains a large amount of dissolved and suspended solid which leads to high concentration as the water is evaporated. The presence of suspended solid and carbonaceous components in the system contributed to the fouling problem in the evaporator part (Li and Watkinson, 2011; Marks et al., 1994). The scale is formed within the evaporator boilers/ heater when a large amount of liquids is evaporated. Various ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-} and SiO_2 also contributed to the scaling by forming salts during evaporation (Wang et al., 2014). Equations3 to 9 show the reaction between these ions that form crystalline salts which finally lead to scale formation (Wang et al., 2015; Huuha et al., 2010; Najibi et al., 1997).

$$Ca^{2+} + CO_3^{2-} = CaCO_3 \tag{3}$$

$$Mg^{2+} + CO_3^{2-} = MgCO_3(S) \tag{4}$$

$$Ca^{2+} + SO_4^{2-} = CaSO_4 \tag{5}$$

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$$Mg^{2+} + 2OH^- = Mg(OH)_2(S) \quad (6)$$

$$SiO_2 + 2H_2O = Si(OH)_4 \quad (7)$$

$$Si(OH)_4 + OH^- = HSiO_3^- + 2H_2O \quad (8)$$

$$Si(OH)_4 + OH^- = H_3SiO_4^- + H_2O \quad (9)$$

The heat losses, which lead to the low heat transfer capacity increase the operating cost and reduce the system lifetimes, is the main drawback caused by scaling. To date, various ways of scale cleaning have been used including chemical, physical, and mechanical method such as deploying anti-scaling, ion-exchange, electric, and ultrasound/ magnetic fields to prevent this problem. The most common and easy method used is addition of scale inhibitors (anti-scalants) into the wastewater to prevent scaling. However, this chemical is less effective in the presence of calcium, magnesium carbonate and silicate scale (Wang et al., 2014; Macedonio et al., 2011).

Recently, Afsharnia et al. (2012) has indicated that ultrasound (sonication) is the best solution for scaling problem. This is because the technique has many effects on compounds in solution. Sonication technique is able to degrade chemical compound through oxidation by hydroxyl radical or by pyrolytic decomposition. As an example, volatile compounds that migrate into bubble usually degrade through pyrolytic reaction occurs within the bubble. Meanwhile non-volatile compounds tend to accumulate in the liquid phase and can be degraded via hydroxyl radical reaction. In terms of scaling prevention, sonication is used to reduce the scale effect by reducing the nucleation time of several materials that form scale. The scale has usually formed in the heating area of the heat transfer equipment which leads to mass crystallization (Zhang et al., 2014). The advantages of sonication technique are less energy consumption and free from chemical application. It is also reported that the combination of sonication with evaporation (sono-evaporation) is able to increase the efficiency of evaporation up to 96%.Furthermore, Wang et al. (2015) suggested that non-thermal plasma (NTP) pre-treatment prior to evaporation process should be implemented to reduce the scale effect. Wang et al. (2015) has studied the influenced of non-thermal plasma (NTP) pre-treatment in reducing the scale effect. Basically, NTP is able to degrade many organic compounds and oxidize several inorganic ions efficiently through a variety of physical (high electric field, intense ultraviolet radiation, an overpressure shock wave) and chemical (formation of radicals and molecular species) effects in water. Similar to sonication, no chemical was added to the evaporators. This technique demonstrates the alleviation of scale effect by removing crystalline matrix (silica) and change the morphology of scale (scale become loose).

Flotation

The flotation system was originally used in mineral (ore) processing for solid/solid separation using stable froth in the mining industries since 100 years ago (Matis and Peleka, 2010; Colic and Morse, 2007; Jameson, 1999). Meanwhile, the application of flotation in water treatment started as early as 1920 in Sweden based on a vacuum system (Haarhoff, 2008). This system was similar to dissolved air flotation (DAF), which is

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the most common technique of flotation for water treatment today. However, the history of DAF system as is known to date, with the pressurized recycle to produce air bubble was started to be used in the beginning of 1960 (Edzwald, 2010).There are several differences listed by Rubio et al. (2002) between the flotation of ores and the flotation applied to water and wastewater purification including 1) size of bubbles generated to floated the particles, 2) shear rates, 3) stability of the froth at free surface and 4) bubbles surface area. Meanwhile, Matis and Peleka (2010) classified flotation technique into two categories which are dispersed air flotation/froth flotation (for minerals) and dissolved air flotation (for water).

The flotation techniques available are induced air flotation (IAF), electro-flotation (EF) and dissolved air flotation (DAF).More specific definition is given based on the types of floatation used. According to Rubio et al. (2002), IAF formed bubbles mechanically by a combination of high speed mechanical agitator and the injection system, while EF producing bubbles from electrolysis of diluted aqueous at both electrodes. However, in terms of flotation application in wastewater and domestic sewage treatment, dissolved air flotation (DAF) is the preferable flotation technique selected by civil and chemical engineers (Colic and Morse, 2007). Basically, DAF is a flotation technique that produces bubbles from reducing a pressure of water pre-saturated with air at a pressure higher than atmospheric (Leppinen and Dalziel, 2004; Rubio et al., 2002).

Firstly, DAF technique was applied as primary clarification method instead of settling process in several water treatment plants in Sweden, Finland, and Norway by the end of 1960s to 1970s (Edzwald, 2010). Since then, numerous research and studies have been conducted for DAF system development and advances. Many researchers conducted studies to investigate the potential of DAF in treating different types of wastewater. To date, the research has kept progressing to another stage and wider application of DAF system. As an example, Féris et al. (2004) studied the adsorptive particulate flotation process (APF) using 5 different adsorbents namely coal fines, coal shale, charcoal, barite and coal beneficiation tailing (CBT) for removing oils and dyes from synthetics and industrial effluents through 3 different floatation methods (e.g., IAF, MJF and DAF). Meanwhile, Zhang et al. (2014) evaluated that the efficiency of a pilot-scale bioreactor consisted of pressurized aeration and DAF (PA-DAF) for domestic wastewater treatment. There are several studies carried out for treating different types of wastewater via DAF as presented in Table 1 and 2. However, DAF is not the only flotation technique that has been improved and developed nowadays. An alternative flotation processes such as the IAF, MJF and EF have also been utilized in treating wastewater. Table 2 briefly described and list the studies that have been conducted to treat various types of wastewater using these techniques.

Even though flotation technology and application is now widely accepted and used in the purification of drinking water and wastewater treatment to remove pollutant such as colloids, ions, macromolecules, microorganism and fibres (da Rosa and Rubio, 2005; Colic and Morse, 2007; Liu et al., 2007), there are also information concerning on the application of flotation in landfill leachate treatment (Renou et al., 2008). Zouboulis et al. (2003) used flotation as the post treatment process for landfill leachate after biological treatment to remove humic acid (non- biodegradable material). In more recent years, the application of DAF as a treatment method for semi-aerobic landfill leachate was reported by Palaniandy et al. (2010). The study focused on the removing three parameters (i.e., colour, COD, and turbidity). The experimental studies were conducted in three phases starting with the saturator efficiency and the bubble volume concentration followed by the leachate treatment using DAF alone in the second phase. Third phase evaluated the effect of the coagulation process (using alum, $Al_2(SO_4)_3$) prior to DAF. Besides, the combination of ferric chloride ($FeCl_3$) coagulant with DAF was also investigated and reported by Adlan et al. (2011) to determine the efficiency of this technique in treating semi-aerobic landfill leachate.

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Table 1. DAF method application reported in wastewater treatment studies

DAF Treatment Method	Experimental Condition/ Set-up	Types of Samples	Parameters Measure/ Concern	References
Coagulation-flocculation followed by DAF	Using floatation column of the batch DAF experiments	Synthetic oil in water emulsions	COD, total surface charge (TSC), hydrophobic particles	Karhu et al.(2014)
Coagulation-flocculation followed by DAF	Full scale of DAF system	Poultry slaughterhouse wastewater	SS, Oil and Grease (O&G), COD	Nardi et al.(2008)
Coagulation-flocculation followed by DAF	A bench scale DAF unit	Synthetic industrial effluent	Turbidity	Al-Shamrani et al.(2002)
Coagulation-flocculation followed by DAF	Pilot-scale laboratory DAF unit	Refinery wastewater	BOD, COD	Hami et al.(2007)
• Coagulation micro-bubble flotation • Coagulation-DAF	Laboratory coagulation micro-bubble flotation and DAF unit	Dyeing wastewater	COD, colour and oil	Liu et al.(2010)
DAF with acidification and coagulation	Process started with acidification, then followed by coagulation and DAF	Biodiesel wastewater	Grease & Oil, COD	Rattanapan et al.(2011)

Floatation Mechanisms

The flotation techniques differ according to the method used to produce the air bubble and its application. Generally, flotation technique was defined as gravitational separation process which is operated by increasing the difference of density between continuous phase and dispersed phase with an additional gas/ air into the wastewater (Painmanakul et al., 2010). The formed bubbles were attached to floc particles and reduced the density (lesser than the water), which allowing it to float to the surface of water (French et al., 2000). The common methods used to generate bubbles are electrolytic, dispersed-air and dissolved air as mention earlier. However, the discussion is focused on the most applied flotation method (e.g.,DAF) in wastewater industries which has more possibility for the leachate treatment. In DAF system, the tank design is divided into contact area and separation area. The contact area at the front end provides an opportunity for bubble-particle collision and attachment. This area is designed to allow enough residence time for the bubbles and particles to collide and attached (Colic and Morse, 2007). The flocsthat are formed during this process are called as bubble-particle agglomerates or floc-bubble-aggregates. These bubble-particles flow together with water and unattached particles into separation zone where the bubble-particles agglomerate rise to the surface of tank. The remaining agglomerates flow with water stream and separated in the filtration stage. High efficiency of floatation process will reduce the frequency of filter media backwash and increase filter lifetime (Leppinen and Dalziel, 2004). Figure 4 shows the schematic diagram in the common DAF system. The main factor that determined the effectiveness of flotation process (collisions and attachment of particles to bubbles) is bubbles properties which consist of shape, size, charge and bubble concentrations in the contact zone.

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Table 2. Alternative flotation techniques available besides DAF for wastewater treatment

Types of Floatation	Developed/ Advanced Treatment	Descriptions	Types of Liquid/ Water Treated	Removal Parameter	References
Electro-flotation	Electro coagulation/floatation process (ECF)	This process involves applying an electric current to sacrificial electrodes inside a reactor tank where the current generates a coagulating agent and gas bubbles. In addition, electro-coagulation/ flotation is a technique involving the electrolytic addition of coagulating metal ions directly from sacrificial electrodes.	Oily wastewater, dye and textile wastewater, and municipal wastewater	Heavy metal, nitrate, nitrate, ammonia, fluoride	Emamjomeh and Sivakumar(2009)
Induced air flotation (IAF)	Induced air flotation (IAF)	Study the effectiveness of developed Jameson IAF in removal of suspended quartz particles	Synthetic wastewater	Suspended quartz particles	Taşdemir et al.(2011)
	Modified Induced Air Flotation (MIAF).	Treatment of stabilized oily emulsion with surfactants using coagulation, Induced Air Flotation (IAF) and also hybrid system of coagulation and IAF processes; called Modified Induced Air Flotation (MIAF).	synthetic oily wastewater	Oily emulsion	Santander et al.(2011)
Jet-flotation	Modified jet flotation (MJF)	Investigate rapid emulsified oil (petroleum) removal from water by flocculation followed by flotation in a modified jet (Jameson) cell (MJC).	Oil (petroleum)	Oil emulsion	Painmanakul et al.(2010)

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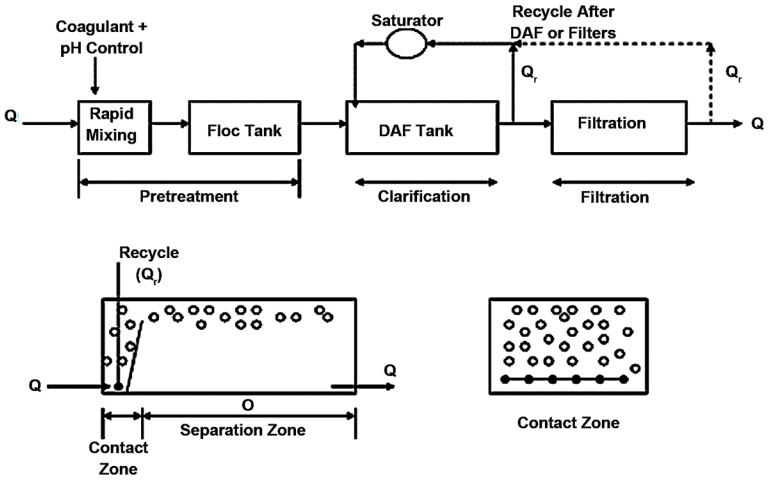
Figure 4. Schematic diagram of DAF system (Adopted from Edzwald, 2007)



Bubbles Shape and Size

In DAF, the effluent from separation zone is used as influent to saturator. This water is saturated with air at elevated pressures up to 5 atm (Colic and Morse, 2007). The bubbles are generated through reduction in pressure of the saturated water which forced to flow through small opening such as needle valves or special orifices (Leppinen and Dalziel, 2004). DAF usually generates small size bubbles which is less than 100μm. In contrast to DAF, larger bubbles are produced in IAF and dispersed air flotation with size of bubbles range between 2-5 mm and 1-10 mm respectively (Colic and Morse, 2007). The bubbles take a shape of sphere when it rises to the surface of water (Haarhof and Edzwald, 2001; Leppinen et al., 2001). Therefore, spherical shape concept was used in DAF models. As example, Leppinen model has assumed that bubble and particle that going to be removed are in spherical shape with density values of bubble typically larger than the density of particles. Thus, in order for agglomerate to rise in the same speed as a solid sphere with equivalent volume and density, the single particle need to have a number of bubbles attach to it (Haarhof and Edzwald, 2001). The shape and size of bubbles produce are basically depending on several factors such as rise velocity, heterogeneous nucleation, bubble growth, injection flow rate, and injection device (Edzwald, 2010).

The average size of bubbles occurs in the contact zone is in the range of 40 – 80 μm. However, if the saturator pressure is increased, the size of the bubbles produces will decreased.There is also a small growth in bubbles size when its float from the bottom to the surface of the water. The size of the bubbles can be calculated using Stoke's law through the measurement of rise velocity (Haarhoff and Edzwald, 2001). The small size of bubbles formed by DAF has an ability to capture a range of particles which made it useful for the removal of particulates in the wastewater. However, the used of small bubbles has a drawback, which is more time is required for the bubbles to rise to the surface. This conditions leads to a larger cell required for the treatment (Colic and Morse, 2007; Jameson, 1999). Thus, this method is inefficient to treat a large volume and high flow rates of effluents (da Rosa and Rubio, 2005). Despite of that, DAF is still more advantages compared to sedimentation process, especially for small particle (Liu et al., 2007). Leppinen et al. (2001) also stated that DAF is able to operate at higher loading rates

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than sedimentation since the rise speed of flocs can be higher than the speed of individual particles. As a result, smaller surface area or larger flow rates tank can be designed. Currently, the DAF tank with higher loading rates (>20 m/h) more than the previous tank (5 to 10 m/h) are available (Edzwald, 2007).

Bubbles Concentration

The bubbles concentration is determined based on mass, volume and number. The mass concentration (Cb) in contact zone was used to evaluate the efficiency of air transport to the contactor. The bubble volume (Φb) and the number of concentration (n_b) are important theoretical variables in modelling the contact zone performance and estimating floc-bubble aggregate rise velocity (Edzwald, 2010). The mass concentration can be estimated from Equation 10 while the bubble volume and number are calculated based on the Equation 11 and 12, respectively. The same equations are used to determine the concentration of particle concentrations before and after the coagulation-flocculation process as explained by Edzwald (2007). Both calculations are made and compared to determine whether a sufficient number of bubbles available for the attachment to occur.

$$C_b = \frac{\left\{e\left(C_r - C_{s,air}\right)R - k\right\}}{1+R} \tag{10}$$

where

C_b = Mass concentration
e = Efficiency factor
C_r = Air in the recycle flow
$C_{s,air}$ = Saturation air concentration
R = Recycle rate
k= air deficit in the incoming flocculated water (If flocculated water is in saturation, then k=0)

$$\text{ } _b = \frac{C_b}{\rho_b} \tag{11}$$

where

Φ_b = Bubble volume concentration
C_b = Mass concentration
ρ_b = Moist air density for condition of 100% humidity and with the dew point temperature equal to the water temperature is used.

$$n_b = \frac{\text{ } _b}{\pi\left(d_b\right)^3 / 6} \tag{12}$$

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where

n_b = Bubble number concentration
Φ_b = Bubble volume concentration
d_b = Mass concentration

Bubbles Interactions and Forces

According to Jameson (1999), the attachment mechanism in flotation involved of finite contact angle at the gas-liquid-solid contact line. Based on this concept, particles are made hydrophobic or non-wetting prior to the contact with bubbles. However, Edzwald (2010) stated that this concept is more suitable for IAF or dispersion air flotation where the produced bubbles are larger than 100 μm. In DAF, the repulsive and attractive forces exist between the bubbles or particles that influence the collision and attachment of the bubble-particle. Therefore, instead of wetting perimeter and/or contact angle, these repulsive and attractive forces are more important for the contact between bubbles or bubbles and particles. The bubble-bubble interaction is mostly related to coalescence. There are four types of forces and interactions that affect bubbles coalescence, which are Van der Waals, electrostatic, hydrophobic interaction and hydrodynamic repulsion.

The interactions and forces between the bubbles prevent/reduce the possibility of bubbles coalescence in the contact zone. Meanwhile, bubble-particle interaction and forces explain the collision and attachment of bubbles with particles in water. For air bubbles, the air are mainly consists of non-polar molecules (N_2 and O_2). Thus, molecular interaction has Van der Waals forces. Typically, the bubbles that are generated in DAF carry a negative surface charge. The same charge of bubbles creates electrostatic repulsive forces, which prevents the bubbles from approaching each other. It is hypothesized that negative zeta potential are caused by smaller anion that is resided at the bubble-water interface at a greater concentration than the larger hydrated cations (Edzwald, 2010). However, the negative charge at the bubbles surface can be changed to positive charge with additional of cationic surfactants or polyelectrolyte (Karhu et al., 2014).

Hydrophobic force is defined as the attractive affects bubble-bubble interaction as well as bubble-particle interaction. Despite of that, the origin of this force is unclear (Edzwald, 2010). Another force that affects bubble interaction is a hydrodynamic force/retardation. This force also called as the disjoining pressure, which explains the water between bubble that must be displace to ensure bubble coalescence or attachment of particle to bubble is successful.

Solubility of Air Bubbles

The solubility of air bubbles is also equivalently important. The recycled water entering saturator is normally in equilibrium with atmospheric air based on Henry's Law as describe in Edzwald (2007). Saturator needs to achieve steady state air composition in order to obtain high dissolution of dissolving air exit the saturator. However, the dissolving air in the saturator has kinetic mass (air) transfer limitation (Edzwald, 2010). Thus, 100% dissolution is impossible to be obtained. The efficiency of packed saturator and un-packed saturator is also different with an efficiency of 80-95% dissolving air for packed saturator and lesser for unpacked saturator (Edzwald, 2010).

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Flotation Process Performance

The DAF combines with coagulation and flocculation is known to be a successful method for treating water supplies containing algae, organic matter, colour and low turbidity water. The successful/application of DAF in treating different types of wastewater containing oil, dissolved ions, fats and COD is also reported by numerous researches (Liu et al., 2010;El-Gohary et al., 2010). Recently, Palaniandy et al. (2010) investigated the application of DAF in treating semi-aerobic landfill leachate. DAF was used with the coagulation and flocculation process to treat semi-aerobic landfill leachate in term of COD, colour and turbidity. A DAF batch experiment was conducted in three phases consist of examination of saturator efficiency (1st phase), determination DAF treatment efficiency without coagulation-flocculation process (2nd phase) and evaluation of coagulation-flocculation process followed by DAF (3rd phase). Alum was used as the coagulant for this experiment. The un-packed saturator was used for this experiment. The maximum efficiency obtained for this saturator was 73% at saturator pressure of 400 kPa and flow rate of 6 L/min. In the 2nd phase of the testing, the maximum removal efficiency for COD, colour and turbiditywere36%, 33% and 32% at 600 kPa and 6 L/min of saturator pressure and flow rate, respectively. This result implies that the main content of semi-aerobic leachate used consists of mostly insoluble organic and organic matter (small particles). Thus, the DAF alone cannot be performed effectively. This is consistent with Leppinen (2001) statement, where larger particle increased the efficiency of DAF treatment. Therefore, the coagulation-flocculation process is required to increase the effectiveness of DAF treatment. The coagulation-flocculation process was used to destabilize the colloidal material and cause the small particle to agglomerates into larger particle. Thus in the 3rd phase, (coagulation-flocculation process was conducted prior to DAF) the removal of COD, colour and turbidity increased to 79, 70 and 42%, respectively. Besides that, low removal efficiency of the DAF system without the coagulation-flocculation can also be related to the interaction and forces in the collision attachment of bubble-particle as explained by Edzwald (2010) through a single collision efficiency concept. According to this concept, bubble and particle carry a negative charge without additional of coagulant which cause the repulsive force and prevent the bubble and particle to attract to each other.

Coagulation process is an important operating control variable in floatation efficiency performance. Consequently, good coagulation chemistry condition is required in the DAF treatment to formed particle and bubble of opposite charge (produce electrostatic attraction) which is similar to the application of coagulation before sedimentation in the drinking water treatment plant. However, water with high turbidity requires higher dosage of coagulant to increase flocculation kinetics and form a larger floc to settle rapidly (Edzwald, 2007). This is the reason of optimum coagulant dosage obtained during jar test in the leachate treatment was high (9.5 g/L). In contrast, the DAF only requires for the coagulant to formed little charge or neutral condition to produce van der Waals forces between different particles (solid/air), which provides a mechanism for the attachment.

Adlan et al. (2011) discussed the effect of different coagulant used in the coagulation process prior to DAF. In their study, ferric chloride was used instead of alum as the coagulant. In addition, treatment parameters such as pH, flow rate, injection time and coagulant dosage was optimized by response surface methodology (RSM) to obtain the maximum removal of COD, turbidity, colour and NH_3-N.It was concluded that the used of ferric chloride was better than alum for the coagulation process prior to DAF in treating semi-aerobic stabilize leachate.

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Adsorption

For the past few decades, enormous amount of research have been conducted concerning application of adsorption process for leachate treatment. Earlier studies focused on activated carbon as adsorbent for the treatment process. Even today, activated carbon is the most efficient and preferable adsorbent for treating COD, heavy metals and NH_3-N. However, frequent regeneration of adsorption column and high price of activated carbon has increase the cost for the treatment process (Kurniawanet al., 2006). Therefore, low cost carbon like materials which are produce from agriculture waste such as rice husk, waste tea leaves, saw dust and bagasse ash were studied as an alternative adsorbent. Besides that, naturally available materials such as limestone and zeolite were also experimented as potential adsorbent for leachate treatment.

Fundamentally, adsorption is defined as the process of multi-components fluid (gas or liquid) mixture attached to the surface of adsorbent by physical or chemical bonding (Foo and Hameed, 2009). Previous studies on activated carbon shown that these materials have superior characteristics including vast surface area (1000 – 1300 m^2/g), large porous volume, controllable pore structure, thermo stability and low acid/base reactivity (Kurniawan and Lo, 2009; Foo and Hameed, 2009). These properties make it possible for activated carbon to remove various types of dissolved organic and inorganic pollutants in liquid and gases. Thus, it is widely used as commercial adsorbent in liquid and gas purification. According to the data reported by several researchers, activated carbon has high efficiency in removing organic constituents but less competent in removing ammonium nitrogen from leachates samples (Halim et al., 2010). Therefore, a number of potential adsorbent were investigated to find a new option to activated carbon for leachate treatment such as Zeolite, limestone, composite media, and etc. Whilst, there are also studies conducted to modify activated carbon surface to increase ammonia nitrogen removal efficiency or produce new composite media by mixing activated carbon with another adsorbent (Halim et al., 2010).

Preparation of Activated Carbon (AC)

In general, the process for manufacturing of AC involves two steps, carbonization of the raw material followed by the activation of the carbonized product. The activation process can be carried out in two ways, either by physical activation (Ph_A) or chemical activation (Ch_A). Pretreatment of the raw material normally conducted before carbonization process. Few preliminary stages involve crushing, milling and sieving for appropriate particle size are important for subsequent handling of the raw material(Alslaibi et al., 2013). During carbonization, the raw material will undergo thermal decomposition in inert atmosphere through gasification by Nitrogen gas. Carbonization process can be carried out using tubular furnaces, reactors, muffle furnace and more recently in a glass reactor placed in a modified microwave oven (Foo and Hameed, 2011). This process known as pyrolysis where the non-carbon elements such hydrogen, nitrogen and oxygen are released leaving a rigid carbon skeleton with a rudimentary pore structure. Based on previous studies, pyrolysis of lignocellulosic material such as olive stones, coconut shells or olive shells will remove most of non-carbon elements in the form of char, tar (oil) and gas where the proportion depends on the parameter during pyrolysis such as temperature of pyrolysis, nitrogen flow rate and heating rate.

Physical activation is normally made by carbonization followed by activation in partial or control gasification at high temperature (Rodriguez-Reiniso and Molina-Sabio, 1992). Activation completed through gasification using oxidizing agent or mixture of it at temperature ranging from700-1100 ^oC to develop the porosity (micropores and mesopores) of the carbonized material (Rodrigues-Reinoso and

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Molina-Sabio, 1992). CO_2 can develop narrow micropores, while steam will widen the initial micropores. Accordingly, CO_2 produced larger volume and narrower micropores (Mohamed et al.,2010) while steam created a larger volume of mesopores and micropores. Meanwhile, in Ch_A, carbonization and activation can be run simultaneously, where the raw material will be impregnated with chemical agent followed by conventional heating at moderate temperature between 400-800^{o}C (Demiral andGunduzoglu, 2010). The chemical agent acts as a deactivating agent where it inhibits formation of tar and develops AC porosity via dehydration and degradation. The pore distribution and surface area is determined by the impregnation ratio between the mass of precursor and the chemical agent chosen. The resulting AC produced is then washed with distilled water or mild acid in order to remove residual chemicals from the material. Nowadays, chemical activation is widely applied for the activation because of its lower activation temperature and higher product yield compared with the physical one (Guo and Rockstraw, 2007). Some additional studies combine the physical activation with chemical activation where it is known as physicochemical activation. In general, physicochemical activation is performed by changing the activation atmosphere of the chemical activation by a gasification atmosphere (steam, CO_2) at higher temperatures or the chemical activation is carried out directly under the presence of a gasifying agent. The combination of both types of carbon activation makes ACs with textural and chemical properties which are different from those obtained by any of the activations alone.

Interactive Behavior and Mechanism of Adsorption

Adsorption can be defined as a mass transfer process by which, a substance is transferred from the liquid or gas phase to the surface of a solid adsorbent and form attachments via physical or chemical interactions. The material removed from the liquid phase is called the adsorbate and the material providing the solid surface is called the adsorbent.

The applicability of a basic theory depends more on the mode of operation than on the particular mechanism of solute uptake. A significant feature of physical adsorption is that the rate of the phenomenon is generally too high and thus, the overall rate is controlled by mass (or heat transfer) resistance rather than the intrinsic sorption kinetics. Therefore, sorption is observed and termed as a "diffusion-controlled" process. In general, there are two types of adsorption i.e. physic-sorption and chemisorption (Seader and Henley, 1998).

1. Physisorption occurs when Van der Waals forces physically attract the adsorbate to the solid adsorbent overcoming the kinetic forces of the adsorbate in the liquid. This can result in either monolayer or multilayer adsorption.
2. Chemisorption occurs when a product of a chemical reaction between the adsorbate and the adsorbent results in a monolayer

Adsorption equilibrium may be modeled with the most commonly applied models i,e. Langmuir and Freundlich isotherm models (Shao et al., 2008; Shi et al., 2009). These two models were originally developed from adsorption. According to Droste (1997), adsorption isotherm describes the relationship between the amount or concentrations of adsorbate that accumulates on the adsorbent and the equilibrium concentration of the dissolved adsorbate. The amount of adsorbate accumulated on the adsorbent is calculated by the difference between the amount present in the initial adsorbate concentration and that remaining in solution after equilibrium with the adsorbent i.e.

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$$q_e = \frac{\left(C_o - C_e\right) V}{M} \tag{13}$$

where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_o is the initial adsorbate concentration and C_e is the equilibrium adsorbate concentration (mg/L), V is the volume of solution (L), M is the mass of adsorbent (g).

Langmuir Isotherm

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. A basic assumption is that sorption takes place at specific homogenous sites within the adsorbent.

The Langmuir isotherm can be written as follows:

$$\frac{1}{m} = \frac{QbC}{1 + BC} \tag{14}$$

The linear form of Langmuir isotherm can be written as follows:

$$\frac{1}{(x/m)} = \frac{1}{QbC} + \frac{1}{Q} \tag{15}$$

where x is the amount of material adsorbed (mg), m is the weight of adsorbent (g), C is the equilibrium concentration of adsorbate in solution after adsorption is complete (mg/L). In Langmuir isotherm models, b and Q refers to sorption energy and sorption capacity estimated from the linear relation between (1/(x/m)) and $1/C_e$,

Freundlich Isotherm

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces.

The Freundlich isotherm can be written as follows:

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{16}$$

Ceis the equilibrium adsorbate concentration (mg/L); x/m is equilibrium amount of the adsorbate, K is roughly an indicator of the adsorption capacity mg/g (L/mg)1/n); 1/n is the constant indicative of the intensity of the adsorption. A value for $1/n < 1$ indicates a normal Langmuir isotherm while $1/n > 1$ is indicative of cooperative adsorption. The plot of log q_e versus logC_e gives a straight line with slope of 1/n. A value of K can be calculated from the intercept value.

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The Freundlich isotherm is based on the assumptions that the adsorbent had a heterogeneous surface composed of different classes of adsorption sites with adsorption on each class following the Langmuir isotherm (Benefield, 1982). The Freundlich isotherm describes reversible adsorption and it is not restricted to the formation of the monolayer (Chen et al., 2003).

Kinetics Models

The experimental efficiency is controlled by the kinetics of adsorption. Several kinetic models are available for predicting the mechanisms involved in the adsorption process. The most commonly used kinetic models are pseudo-first-order and pseudo-second-order and intra-particle diffusion model (Shao et al., 2008).

The pseudo-first-order model:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{17}$$

The pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{18}$$

where q_e and q_t are the amount of pollutants adsorbed at equilibrium (mg/g) and at time t, respectively. k_1 (min^{-1}) and k_2 (g/mg min) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order models, respectively.

Traditionally, the kinetics has been described by the first order equation typical of that derived by Lagergren in 1898. In recent years, pseudo-second order rate law has been considered as one of the most appropriate models (Ho and McKay, 1999). Normally, Pseudo first-order kinetic explains that adsorption is due to physisorption-type mechanism (Rao et al., 2002). The pseudo second-order rate indicates how the adsorption capacity of theadsorbate depends on time.

Intra-Particle Diffusion

Intra-particle diffusion is generally characterized by a relationship between the solid phase concentration (q_t) and the square root of time (Kobya, 2004). It can be written as:

$$q_t = k_{id} t^{0.5} \tag{19}$$

where, q_t is the percentage of adsorbate adsorbed (mg/g/$min^{0.5}$), t is the contact time and k_3 is the rate constant for intra-particle diffusion (1/min). Kobya (2004) reported that the higher values of k_{id} indicate an enhancement in the rate of adsorption while large values show better adsorption mechanism which means that the bonding between the adsorbate and the adsorbent is very strong.

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Process Performance

It is found that 91% of COD was removed from landfill leachate via granular activated carbon (GAC) (Morawe et al., 1995). Meanwhile, application of activated carbon in powder form was conducted by Diamadopoulos (1994). About 95% of COD removal was achieved during his study. Table 3 summarized related study to adsorption of landfill leachate using different types of adsorbents. Additionally, Kargi and Pamukoglu (2004) reported that PAC exhibits better performance in COD removal compared to powder zeolite in combined adsorption and biological treatment leachates. In contrary, powder zeolite shows significantly better removal efficiency of NH_3-N compared to PAC in the study (Kargi & Pamukoglu, 2004).

Another comparative study was experimented between GAC and limestone for NH_3-N removal using semi-aerobic landfill leachate from PulauBurung (Aziz et al., 2004). This study revealed that GAC is a superior adsorbent than limestone for NH_3-N removal. In conclusion, the effectiveness of adsorbent for NH_3-N removal can be arrange as zeolite > activated carbon > limestone.

Wassay et al. (1999) examined removal of heavy metals in leachate using GAC, granular activated alumina (GAA) and ferric chloride solution. Only GAC shows high removal efficiency of Cd(II), Cu(II), Mn(II), Pb(II) and Zn(II) with the removal percentage ranging from 78 to 96%. Based on the equilibrium study, adsorption capacity of GAC for heavy metals was 21 mg/g and 19 mg/g for Freundlich and Langmuir isotherm model, respectively.

Lately, the study conducted is more focus on the investigation of other adsorbent such as limestone, zeolite and activated alumina, or low cost adsorbent obtained from waste materials such as rice husk ash, bagasse ash and synthetic zeolite. Several factors including high cost of activated carbon, low removal efficiency of NH_3-N by activated carbon, high consumption of activated carbon, frequent regeneration and existing/ availability of materials for low cost adsorbent has driven many researches to find an alternative adsorbent (Li et al., 2010; Halim et al., 2010). Application of low cost adsorbent from coal fly ash for removal of heavy metal ions was reported by Mohan and Gandhimathi (2009). This study shows that 2 g/L of fly ash has a removal efficiency of 39%, 28%, 74%, 42% and 71% for Cu, Mn, Pb, Zn, and Cd, respectively. It is less effective compared to activated carbon in removal of heavy metals as reported by Wassay et al. (1999). However, the results showed that this material has a potential as alternative adsorbent for heavy metal removal in landfill leachate. Currently, low cost adsorbent is extensively study by many researches as an alternative to activated carbon.

PHYSICAL BARRIERS (MEMBRANE TECHNOLOGY)

The conditions of the leachate nowadays which contains harmful chemicals and higher toxicity reach a level where higher purification is needed to protect the environment. Such higher level of purification can be achieved by membrane technologies. A membrane is defined as a material that forms a thin wall capable of selectively resisting the transfer of different constituents of a fluid and therefore, affecting the separation of the constituents (Visvanathan et al., 2000). Normally, the best physical structure of the membrane material is based on a thin layer of material with a narrow range of pore size and a high surface porosity. Various membrane processes that are applied in landfill leachates treatment are; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The membrane filtration has proved to be feasible and economic solution, and have been applied all over the world (Ushikoshi et al., 2002; Košutić et al., 2014).

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Table 3. Landfill leachate treatment using various types of adsorbents

Adsorbent	Pollutants	Pollutant	Removal	References
		Concentration, mg/L	%	
GAC	COD	na	91	Morawe et al.(1995)
PAC	Hydrophobic organic chemicals (HOC)	na	89.2	Liyan et al.(2009)
	COD	451	24.6	
	COD	7000	87	Kargi and Pamukoglu, (2004)
	NH_3-N	700	16	
	COD	951 - 3750	63 - 92	Cotman and Gotvajn 2010)
	NH_3-N	39.1 - 800	1.0 - 6.0	
	Fe	3.360 - 3.440	79 - 97	
Zeolite (clinoptilolite)	COD	951 - 3750	25 - 32	Cotman and Gotvajn(2010)
	NH_3-N	39.1 - 800	45 - 93	
	Fe	3.360 - 3.440	36 - 48	
	Cr	0.489 - 0.513	32 - 49	
	Zn	0.188 - 0.231	44 - 56	
	Mn	0.328 - 0.344	36 - 50	
	Ni	0.111 - 0.132	14 - 17	
Powder zeolite	COD	7000	76	Kargi and Pamukoglu(2004)
	NH_3-N	700	28	
Limestone	NH_3-N	1909	19	Aziz et al.(2004)
Biometic fat cell (BFC)	HOC	na	81.1	Liyan et al.(2009)
	COD	451	8.9	
coal fly ash	Cu	0.258	39	Mohan and Gandhimathi(2009)
	Mn	0.151	28	
	Pb	0.204	74	
	Zn	0.143	42	
	Cd	0.25	71	
	COD	4480	28	
Palm shell-AC (PSAC)	COD	10800	86.5	Lim et al., (2009)
Composite media	COD	2257	92.6	Halim et al.(2010)
	NH_3-N	1640	86.4	

Microfiltration (MF)

Typically, MF (pore sizes; 50-150nm) is applied to filter microbial cells, large colloids and small particles. MF is not appropriate to be used for leachate treatment alone. However, it is strongly required as a pre-treatment method with another membrane process (UF, NF or RO) or in conjunction with chemical treatments in order to eliminate colloids and suspended matter. Ameen et al. (2011) applied the microfiltration

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as polishing stage after biological treatment of leachate. The MF is capable of extensive removal of solids and suspended matters. In spite of its excellent removal, the MF might not be able to sustain over long period of operation because of physical fouling which causes permanent damage and deterioration to the membrane. Therefore, air-diffuser was introduced to minimize the build-up of particles on the membrane surface. However, the usage of MF was questionable when partnership with other finer filtrations. Previous work by Piatkiewicz et al. (2001) who applied a sequence of membrane filtrations (MF, UF, and RO) concluded that the installation of MF before the UF is unnecessary since the performance of post-treated by the sequence of MF and UF was insignificant as compared with UF alone. Furthermore, their MF required back-flushing every 15 mins to keep the consistency of the filtration rate. The retention time was between 25-35%. Another drawback, MF was unable to effectively treat dissolved organic and inorganic impurities. Thus, hybrid MF-PAC (microfiltration-powdered activated carbon) was introduced to remove microbial contaminants, turbidity and dissolved organic substances. This technology requires less energy consumption as compared with RO and NF, but offers similar organic removal efficiencies (Ince et al., 2010). Visvanathan et al. (1994) reported that about 89.1% COD removal can be achieved by this technology.

Ultrafiltration (UF)

UF is highly efficient to eliminate the macromolecules and tiny particles. It is highly dependent on the construction materials. The UF is commonly installed before the RO or NF/RO system (Bohdziewicz et al., 2001). Since RO has smaller pore size, its fouling-resistance against large molecular weight components of leachate is quite low, in which the UF can be used to minimize the impact. Several studies have applied UF in hybrid processes such as activated sludge-UF-chemical oxidation and activated sludge-UF-RO (Renou et al., 2008).The UF is also exposed to fouling. Previous study indicated that the fouling layer after leachate treatment was 99% inorganic (Syzdek and Ahlert, 1984). The layer did not hinder the passage of organic carbon across the membranes but still resulted in a pressure drop and lower flux. In order to minimize the fouling, the shearing rate could be continuously applied on the membrane surface. According to Bohdziewicz et al. (2001), the installation of UF after biological treatment of landfill leachate was able to remove COD, suspension, and dry matter up to 50, 100 and 7%, respectively. The complete removal of dry matter was very effective to protect and prolong the operations of the subsequent purification by NF/RO system.

Nanofiltration (NF)

Owing to its properties between UF and RO, NF has a place in the removal of recalcitrant organic compounds and heavy metals from leachate (Marttinen et al., 2002). In general, NF has a high rejection for sulphate ions and dissolved organic matter but very low for chloride and sodium. The rejection depends strongly on the solute type, charge valency, diffusion coefficient, and hydration energy. The feed pH of the leachate is critical to control since it influences the charge of the membrane which is closely related to its rejection capacity (Chaudhari & Murthy, 2010). Several studies have applied NF to treat landfill leachate. A recent study applied NF to treat leachate showed more than 85% rejection of total suspended solids, heavy metals, conductivity, and COD. However, the rejection for nitrate and ammonia nitrogen was much lower at 45.4% and 20.5%, respectively (Mohammad et al., 2004). The overall process can be improved if combined with conventional biological-physicochemical treatment. The molecular weight cut-off (MWCO) of NF is also important to be considered as found by Ince et al. (2010).

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Previous study combined NF with electro coagulation to treat landfill leachate (Mariam and Nghiem, 2010). The treatment resulted in 67% and 80% of TOC and turbidity removals, respectively, which were an improvement from conventional chemical coagulation. It indicated that electro coagulation is also able to mitigate the fouling on NF. Unlike RO, NF technology has a looser membrane structure enabling higher fluxes and lower operating pressure for the treatment of leachate (Kurniawan et al., 2006). The main problem of NF technology is the membrane fouling.

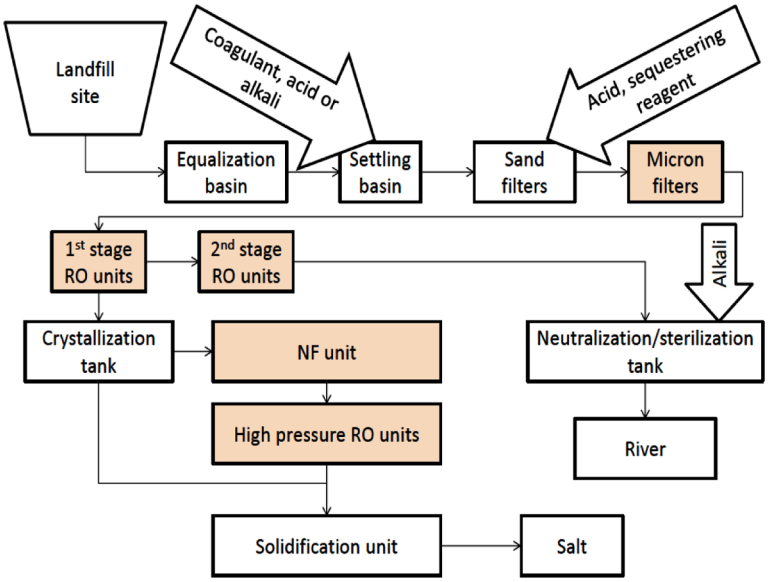
Reverse Osmosis (RO)

Reverse osmosis is able to reject heavy metal concentrations at high efficiency. The usage has started since 1984 where tubular and spiral wounded modules were used to treat landfill leachate. In 1988, Pall-Exekia developed a disc-tube-module to allow the system to be cleaned from scaling, fouling and bio-fouling in an effective manner (Peters, 1996). Basically, RO is used to post-treat effluent of NF and operated at high pressure (Ushikoshi et al., 2002). Example of application of RO units in the treatment of landfill leachate is shown in Figure 5.

RO was applied to treat biological-treated leachate to increase its corresponding effluent quality to meet local standard. The system managed to reduce 97% of COD and 60% of BOD levels. However, the RO was ineffective in removing Total Nitrogen (N_{tot}) to the below discharge limit. In addition, NF was used to produce similar outcomes but better removal of P_{tot} and N_{tot} than RO (Kuusik et al., 2014). The RO was also effective in removing dioxins (99.9%) from leachate (Ushikoshi et al., 2002).

Košutić and his group (2014) utilized RO/NF to further treat effluent of coagulation and filtration treatment of leachate. The yellow effluent turned out colorless after the RO treatment along with significant reduction of the COD, NH_4^+-N, turbidity, pH, TOC and traces of heavy metals which were in compliance with the local standards. The COD was reduced for more than 94.6%. The heavy metals removals were assisted by anion rejection had by the charged NF membranes.

Figure 5. Leachate treatment system at Yachiyo (Ushikoshi et al., 2002)



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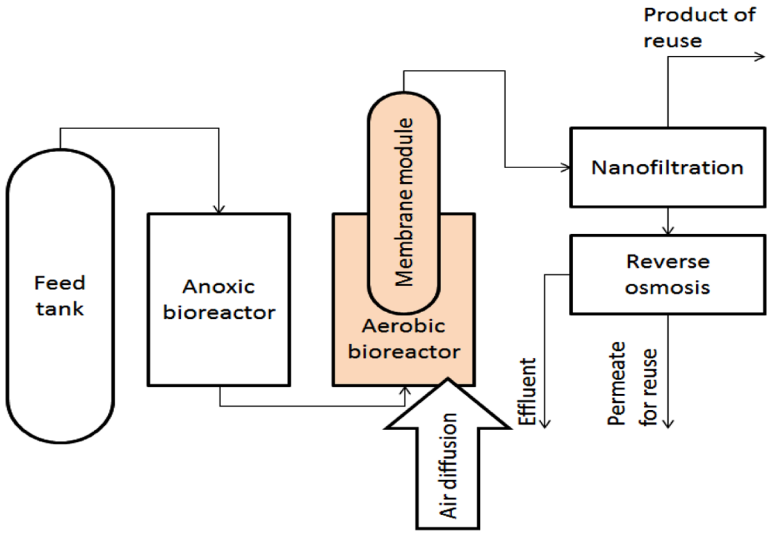
According to Chianese et al. (1999), the operating pressure of RO has effects on the removal efficiency of COD. Higher COD level can decrease the permeate flux through the RO membrane. However, the rejection of COD could be increased by increasing the operating pressure. The work reported an increase of COD rejection from 96 to 98% when the operating pressure was increased from 20 to 53 atm. However, the removals of heavy metals (Cu, Zn, and Cd) were not heavily affected by the increased pressure. RO technology was reported as the most effective in COD removal among different physico-chemical processes evaluated.

Membrane Bioreactors (MBR)

Membrane bioreactor is the combination of membrane separation technology and bioreactors. It is capable to process high concentration of biomass with a low sludge production and outstanding effluent quality. The bioreactor itself functions to effectively decompose the non-biodegradable large molecular organic matter of leachate (Wang et al., 2014). It is an efficient anaerobic biological digestion system by retaining most microbial cells in the reactor to digest high biomass concentration (Ahmed and Lan, 2012). It is capable of treating raw leachate with COD of 13,000 mg/L and achieved removal efficiency of approximately 60% at steady performance (Xie et al., 2014). Figure 6 shows the schematic diagram of MBR combined with NF/RO process. From the diagram, the MBR is placed as the first filtration treatment prior to NR/RO system. Effluent from MBR treatment alone is not enough for safe discharge. Bohdziewicz et al (2008) reported COD removal over 95% using anaerobic submerged membrane bioreactor. However, the removal efficiency degraded as the leachate concentration was increased due to inhibition of microbiological activity.

Like other filtration membranes, the MBR is also susceptible to fouling. In previous study, the MBR was integrated with granular activated carbon (GAC) to assist the treatment of landfill leachate. The presence of GAC at correct dosage could minimize the impact of fouling on the MBR, besides improving the efficiencies of removals of COD and heavy metals (Cd, Cu and Cr). The impact was minimized due

Figure 6. Schematic diagram of anaerobic MBR combined with NF/RO process (Wang et al., 2014)



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to the improvement of settleability and compatibility of flocs, as well as the increase in particle size. The removal rate of COD and NH_3-N were approximately 90% and 81%, respectively, and relatively stable during the 40 days of process (Wang et al., 2014).

A number of leachate pilot trials have been conducted. Two full scale MBR leachate treatment plants are due to become operational in the UK in 2006. More than 50 full-scale plants have been constructed in Germany, France, Spain and other countries. The main drawbacks of membrane technology and RO implementation in landfill leachate treatment are membrane fouling (requiring extensive pretreatment or chemicals for periodic cleaning of the membranes resulting in a short lifetime of the membranes and decreased process productivity) and the generation of large volume of concentrate which is unusable and has to be discharged or further treated. Also, the membranes required high energy consumption as it needs high operating pressure which shortens the life of the membrane (Renou et al., 2008).

ULTRASONICATION

Basic Principles

Ultrasound is the term given to sound waves above 20 kHz which is the frequency above the range audible to human being. Depending on the application and frequency, ultrasonication is broadly divided into three areas: i) low frequency or conventional power ultrasound (20-100 kHz), (ii) medium frequency or sonochemical effects ultrasound (300-1000 kHz) and iii) high frequency or diagnostic ultrasound (2-10 MHz) (Mason and Lorimer, 1988; Peng et al., 2014). The effect of ultrasound in liquid medium was first recognized by Alfred L. Loonis in 1927.However, the major development in sonochemistry took place in 1980s after the arrival of inexpensive high-intensity ultrasound generators. Recently, the majority utilization of ultrasound in chemical reaction includes synthesis (organic, organometallic and inorganic), polymer chemistry (degradation, initiation, and copolymerization), and nanomaterial preparation and some aspects of catalysis (Mason and Lorimer, 1988).

There are three possible reaction sites in ultrasonically irradiated homogeneous liquids: i) the gaseous interiors of collapsing cavities; ii) the interfacial liquid region between cavitation bubbles and the bulk solution, where high temperature and high temperature gradients exist; and, iii) the bulk solution at ambient temperature, where small amounts of hydroxyl radicals (•OH) diffuse from the interface. The high temperatures (5000 K) and pressures (1000 atm) induced by cavitation in collapsing gas bubbles in aqueous solution lead to the thermal dissociation of water molecules into hydrogen radicals (•H) and hydroxyl radicals (•OH) (Pang et al., 2014; Wang et al., 2008). The removal of pollutants was completed through the production of radicals in the bubble of cavitation that can react with refractory compounds. Sonication in aqueous condition triggers rapid formation, growth, and violent collapse of cavitation bubbles (Figure7).

The implosion of cavitation bubbles produces high energy shockwaves within interfacial films surrounding nearby solid particles. The shockwave has the potential to create microscopic turbulence which highly capable of disintegrating the nearby solid particles besides releasing extreme temperature (Mason and Lorimer, 1998). These chain reactions are known as sonochemical effect where pyrolytic decomposition occurs inside the bubbles. Further details of the phenomena and related theories can be found in Mason and Lorimer (1998)and Sridhar et al. (2010).

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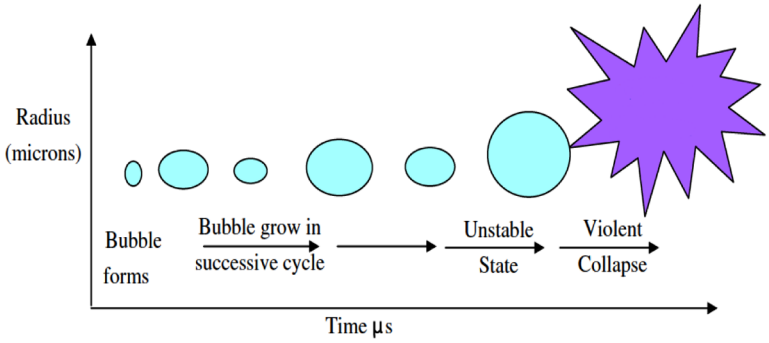
Figure 7. Development and collapse of the cavitation bubble (Sridhar et al., 2010)

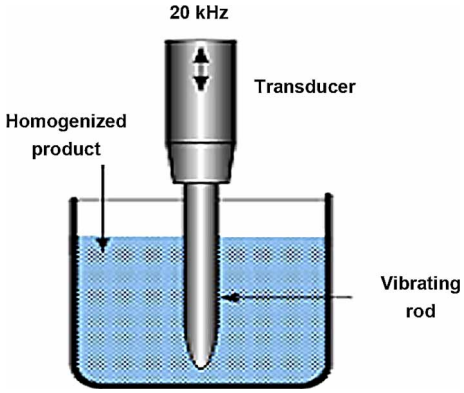


Treatment Efficiency

In environmental engineering, it is used to disintegrate organic contaminants present in water or wastewater which includes leachate treatment. In lab scale experimentation, the source of sonication was introduced directly to the treatment by a probe placed inside the treatment tank or simply immersing the tank itself inside an ultrasonic homogenizer as shown in Figure 8.

In general, the use of ultrasound to degrade chlorinated aromatic and aliphatic compounds, phenol, chlorophenols, nitrophenols, and organic dyes has been reported and well-summarized by Chowdhury and Viraraghavan (2009). The application of sonication has also been extended in the treatment of landfill leachate but presently, available reports are very limited indicating vast opportunities for further investigation (Oz and Yarimtepe, 2014). Wang and his group reported the removal of organic matters and ammonia nitrogen from landfill leachate (Wang et al., 2008). After 180 min of sonication, the removal of ammonia nitrogen reached up to 96%. The ammonia nitrogen was suspected to partly degrade through thermal reactions triggered inside the bubble of sonication. The COD reduction increased depending on the power input which was up to 16% of removal at 150W. The sonication is actually meant to assist thus, it was paired with other processes. Gonze et al. (2003) utilized ultrasound to treat biologically pre-treated landfill leachate as additional treatment since it consumes a lot of energy. The sonication increased the toxicity of the effluent at the beginning of treatment due to the formation of

Figure 8. Ultrasonic homogenizer (substech, 2015)



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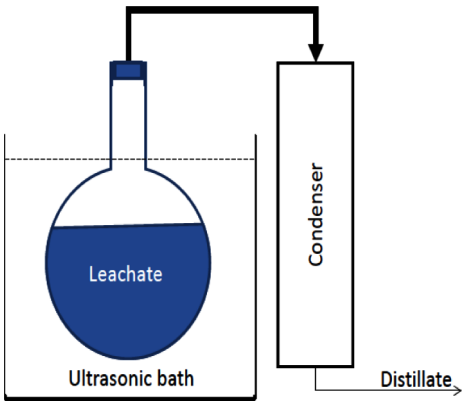
toxic intermediate products. The removal of TOC (70%) and COD (70%) were improved significantly, and it enhanced biodegradability.

The usage of sonication as pre-treatment was also applied to enhance biodegradation of refractory compounds in leachate, which in turn enhanced the treatment efficiency during anaerobic digestion process (Bohdziewicz et al., 2005). The sonication prior to fermentation increased the COD removal efficiency by 7%. The increment was believed to be originated from the changes of chemical structure of slow biodegradation compounds triggered by the sonication. Another pre-treated sonication was studied by Neczaj et al (2007) in partnership with sequencing batch reactor (SBR). Under different modes, the sonicated condition consistently provided enhanced removal rates of COD (80-92%) and nitrogen compounds (67-75%). However, the increment was less than 10% which might not economically feasible since larger energy was consumed. Afsharnia et al. (2012) examined the effect of sonication on the leachate evaporation by distillation. Their experiment rig is as shown in Figure 9. With 25 kHz and 500W and within 10-40 min, the sonication was able to enhance the COD reduction from 84 to 88%. The sonication however, has no effects on electrical conductivity (EC) and heavy metal reductions.

Ammonia Air-Stripping

Ammonia stripping is driven by concentrated aeration of treated leachate at high pH (10.5 –11.5).The practice is very capable removing high ammonium levels. The process is running in the stripping tower, filled with aerated media, which is overflowed by leachate. Treated leachate is collected at the bottom of the tower and gases raise up to the top. The air,polluted with ammonium, has to be treated with sulphuric or chloric acids. Recirculation of treated leachate is often needed to attain discharge limits. Ammonia stripping could be cost-efficient only at very high ammonium levels in the wastewater. Costs are spent on lime addition for increasing pH before the treatment and acid addition afterwards (www.leachate.co.uk, 2014).

Figure 9. Leachate sonication and evaporation (Afsharnia et al., 2012)



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HOW TO USE OF PHYSICAL TREATMENT PROCESSES EFFECTIVELY

In general, physical processes contribute effectively in trading landfill leachate. Nevertheless, physical processes are not sufficient to meet the final discharged standard. Thus, normally a combination of several biological, chemical and physical processes is used to treat leachate. Physical pretreatment methods are particularly useful in treating leachate from older/closed landfills that have lower biodegradable organic carbon, or as a polishing step for biologically treated leachate. For example, the most efficient processes (E.g., adsorption and RO) are not recommended for highly concentrated raw leachate due to the operational cost and commonly used for post treatment of landfill leachate in particular prior to discharge to surface water.

In adsorption process via activated carbon, back-flushing is vital as the surface of the carbon becomes coated with the impurities and it avoids clogging. The disposal of the carbon and the flushing effluent should be tackled as they required significant cost. Thus, the process is mainly suitable for: (i) The removal of hazardous organics from industrial leachate and (ii) Removal of color and residual refractory TOC and COD from stabilized leachates. Under optimum conditions, carbon adsorption can achieve99% removal of most organic contaminants but, the capital outlay for their installation is very high and running costs can be high too (EPA, 2000).

RO can be used to cut the amount of a leachate by producing a smaller amount of more concentrated solution "brine" which can comprise 25 to 40% of total amount. It should be noted that the membrane used is very brittle, has a limited life of about 2 years and is susceptible to blockage and pollution; and would only be appropriate at the later stages of a treatment facility in combination with evaporation. Applications of RO may be suitable for leachates with a high inorganic loading and low volumetric flowrates. The capital and running costs of fixing such system would be high. Provision is required for the treating or disposing of the highly concentrated liquors which would be created (EPA, 2000).

In the evaporation process, the leachate is evaporated by a low heat source and separated into distillate and concentrate. The distillate may require additional treatment before discharge as it would include any volatile substances left in the leachate after pre-treatment; and the concentrate could be distilled more into distillate and sludge, the sludge requiring either thermal treatment or disposal to landfill. The practice has not been broadly adopted as it is expensive and like RO, a pre-concentration technique producing a condensate or sludge residue which must be disposed of. Accordingly, there is little design information accessible on this treatment technique (EPA, 2000).

The application of floatation process in wastewater treatment is increasing. Nevertheless, wastewater has a wide range of pollutants since it come from different sources which make it difficult to be treated. At present, the most common floatation technique applied for wastewater treatment is coagulation-flocculation process followed by DAF. However, this method is currently proved ineffective for semi-aerobic landfill leachate treatment. DAF treatment is known to be weak against high turbidity water. Thus, many aspects need to be considered to increase the efficiency of flotation process for the treatment of landfill leachate. Coagulation-flocculation process known to be one of the critical factors that determines the efficiency of the flotation process. Thus, the right coagulant dosage is required to find good coagulation chemistry which ensures the collision and attachment between bubble and particle (Adlan et al., 2011).

Other physical processes such as aeration, sedimentation, air stripping, ultrasonication are commonly used as pretreatment process for landfill leachate. Basically, to reduce organic loading or ammonia, this can lead to enhance the performance of advanced treatment processes.

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CONCLUSION

The age of landfill play a key role when deciding the suitable treatment process for leachate. Typically, biological process is more appropriate for young leachate while physico-chemical treatment is more effective for intermediate and old leachate. Physical processes employed by several researchers to treat leachate. They found that adsorption and membrane technologies are effective in removing pollutants from leachate. However, due to the operation cost, initial organic loading and other aspects, it is recommended to use these processes for post-treatment or leachate polishing. Although employment of flotation process was ineffective, better performance was observed when leachate treated via flotation-coagulation process. Evaporation process seems to offer an attractive option for leachate treatment that can cover all age of landfill leachate. However, further treatment for distillate and sludge are strongly required. Other processes such as sedimentation, aeration, ultrasonication, and air stripping can contribute as pre-treatment processes.

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Chapter 35
Heavy Metal(loid) Remediation Using Bio-Waste:
A Potential Low-Cost Green Technology for Cleaning Environment

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ABSTRACT

Heavy metal(loid)s are hazardous, biologically non-essential, non-biodegradable and persistent in nature, which can accumulate in plants and animals as well as in environment especially agri- and aqua- culture ecosystems. It is severely responsible for causing several health hazards problems in human, such as, cardiovascular, pulmonary, hepatic, nephrological, dermatological, neurological disorders as well as carcinogenic effects. Removal of these heavy metals from living systems is extensively expensive and also unsuccessful in sent percent removal. Therefore, in order to protect the environment, the removal of heavy metal(loid)s from polluted effluents is essential before discharging into environment. Besides various treatment technologies, sorption of metal(loid)s using bio-wastes are highly potent alternatives in recent years. The present chapter deals with the removal efficiencies of various bio-wastes, orange peels, waste tea leaves, rice husk, wheat stalk, sugar cane bagasse, coconut husk, sun flower stalk, corn cob, nut shell, water hyacinth, crab shell particle, activated carbons etc. The present discussion has also revealed that bio-waste could be a low-cost eco-friendly and green emerging alternative technology in treating the metal(loid)s contaminated environment without posing any further adverse environmental impacts.

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INTRODUCTION

Industrialization, urbanization and population explosion are the prime reason for tremendous environmental pollution in last few decades (Bhakta, Son, & Munekage, 2009; Bhakta & Munekage, 2010). Massive amount of pollutants generating from anthropogenic activities are indiscriminately discharging into the environment which contaminating the life system through the food chain (Jillian, Robert, & Rajakaruna, 2015). Effluents from industries like chlor-alkali, electrical, electronic, electroplating, glass manufacture, photography, oil refinery, pesticide, paint-pigment, plastic, paper and pulp, pharmaceutical, gun, steel etc. contain heavy metals such as, Hg, Cd, Pb, Cr, Cu, As, Ni etc (Tack, Vanhaesebroeck, Verloo, Rompaey, & Ranst, 2005). in extensively high concentration and are disposed into sea, river, canal or pond directly and contaminate them. These metals percolate into ground water and contaminate. Irrigated water is also not safe from heavy metals. Aquatic plants and animals and ultimately human beings are being affected greatly. Domestic wastes (such as, batteries, paints, electrical and electronics goods etc.) have also similar contribution.

Heavy metal(loid)s are hazardous, biologically non-essential, non-biodegradable and persistent in nature and have severe several toxic impacts on lives (Bhakta, Ohnishi, Munekage, Iwasaki, & Wei, 2012). They enter into the body of plants and animals through absorption of water in plants and drinking of water and ingestion of food in animal and get accumulated within tissue. These metals bind to functional groups such as amino ($-NH_2$), imino (=NH), sulfhydryl (-SH), carboxyl (-COOH), phenolic (C_6H_5-), phosphoryl ($-P_2O_5$), imidazole ($C_3H_4N_2$) and phosphate ($-PO_4$) of bio-molecules and form stable coordination complexes within the tissues (Perez Marín, Aguilar Meseguer, Ortũno, & Śaez, 2008; Gönen & Serin, 2012). They tend to form more stable complexes with sulphur and nitrogen ligands than oxygen ligand. Thus, heavy metals are accumulated in liver, kidney, brain, bones, teeth, lungs and blood and damage and impair various systems in human. This accumulation when crosses the critical level causes death of the living machine.

Therefore, decontamination of environment from the severe pollution of heavy metal(loid)s is an urgent issue to scientists. To overcome this problem, many technologies have been developed by researches, sorption, precipitation, coagulation, membrane filtration, etc. so far. Sorption is one of the important technologies in treating the polluted water using various inorganic (chemical) and organic based sorbent media in this respect. However, most of them are expensive and having adverse impact to environment. There is always significant demand in developing the low-cost green eco-friendly technology in this respect. In recent years, biomass based sorbents have drawn much attention to the scientist for applying as a potential sorbent in treating various pollutants of polluted water especially heavy metal(loid)s. Most common domestic biomass wastes (such as - banana peel, orange peel, cotton fiber, cellulose paper, *Eichhornia* plant, coconut coir, waste tea leaf etc.) and different industrial and agricultural bio-wastes (such as, sugarcane baggasse, rice husk, wheat and rice straw, pineapple crown top, sun flower stalk, olive stone, sea weeds, crab shell etc.) have the capability in binding of heavy metal by the process of adsorption and /or absorption, and thus, they can remove heavy metals from polluted water significantly.

The objective of this chapter is to evaluate the bio-sorbent potentiality of biomass waste as a potent low-cost agent of eco-technology in the heavy metal(loid)s remediation of environment. The chapter also concisely discussed applicability of various bio-wastes for remediation of heavy metal(loid)s from contaminated aquatic ecosystem or aqueous solution without harming environment.

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CHEMICAL PROPERTIES OF BIO-WASTE

Bio-wastes possess many functional groups such as -COOH, -OH which play important role to bind metal ions coordinately and form a stable complexes resulting sorption. According to Perez Marín, Aguilar Meseguer, Ortũno, Śaez. (2008) and Gönen and Serin (2012), orange peel is made up of cellulose, hemicellulose, pectin, limonene ($C_{10}H_{16}$) and many other low molecular weight compounds which contain hydroxyl (-OH) and carboxyl group (-COOH) as important functional group for heavy metal binding. Banana peel contains pectin such as galacturonic acid which provides –COOH as functional group (Arunakumar, Walpola, & Yoon, 2013). Study also revealed that lignin contains –COOH and –OH as functional groups (Todorcius et al., 2015) those help to remove metals from aqueous media. FTIR analysis showed that activated carbon possessed nitrile (C≡N), alcohol (-OH) and carboxyl group (-COOH) (Rajesh, Pujari, & Uppaluri, 2014), tea wastes possess phenolic hydroxyl group (-OH), alcoholic hydroxyl group (-OH), carboxyl group (-COOH) and amino group ($-NH_2$) (Dwivedi & Rajput, 2014). It is apparent that the binding of metals with these functional groups and formation of complex is the basic principle of bio materials in removing toxic pollutants especially metals from ambient environment.

COMMON BIO-SORBENT PREPARATION PROCESS

Although, there are variations in developing the bio-sorbent from biomass, basic processes followed in different cases are almost same. Bio-wastes are processed to develop adsorbent in the following subsequent ways:

- **Collection:** Bio-wastes such as, orange or banana peel, cotton fiber, cellulose paper, *Eichhornia* plant, coconut coir, waste tea leaf, sugarcane baggasse, rice husk, wheat and rice straw, pineapple crown top, sun flower stalk, olive stone, sea weeds, crab shell etc. are collected from local market or houses.
- **Washing:** The collected wastes are washed thoroughly under tap water to remove any particulate matter and are sprayed with distilled water thereafter.
- **Chopping:** The large biomass can be chapped into small pieces.
- **Drying:** Chopped wastes can be dried by air or hot air oven at specific temperature (generally 70 - 80^0C) for certain period.
- **Pyrolysis:** This step is followed only to prepare activated carbon (AC). A certain amount of dried sample is taken and heated at high temperature (generally 500^0C) using micro-oven or other device for a period to carbonize fully and then it is cooled.
- **Crushing:** Dried materials or pyrolysed biomass are crushed to powder by mortar and pestle or mix grinder machine.
- **Sieving:** Powdery substances can be sieved by sieve of various mesh size. After sieving, the dried powder or carbonized powder can be used as sorbent.
- **Depigmentation:** This process is followed in some cases for producing the bio-sorbent. Biosobent substrates are soaked with alkaline-ethanol solution made of 95% C_2H_5OH and 1% NaOH at 1:1 ratio by volume at 25^0C for 24 hours and pigments like chlorophyll, β-carotene and other low molecular weight compounds are removed. Or, substances are boiled in distilled water at 85^0C for 30 minutes to remove colors. Now, the de-pigmented substances are hot air oven dried at specific temperature for specific periods.

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CHEMICAL ACTIVATION OF BIO-SORBENT

The metal removal activity of bio-sorbent or other sorbent can be improved by means of activation using various chemical agents or heating process. Some activation processes generally followed in this regard are discussed hereunder:

- **Amination(-NH_2):** According to Shrestha, Kour, Homagai, Pokhrel, & Ghimire (2013), samples are charred with concentrated H_2SO_4 and then is washed with distilled water till neutrality. It is oven dried at 80^0C for 24 hours. The charred samples are chlorinated with $SOCl_2$ in the presence of pyridine at 0^0C and then heated at 70^0C for 30 minutes. Now, it is washed with distilled water. The chlorinated sample is mixed with ethylene-di-amine (NH_2-CH_2–CH_2-NH_2) and Na_2CO_3 in the presence of di-methyl-sulphonide ($DMSO_3$) and heated at 70^0C for 6 hours. Then, the aminated adsorbent is washed with 0.1M HCl and followed by distilled water till neutrality. Finally, the sample is oven dried at 70^0C for over night.
- **Xanthate:** It is described by Liang et al. (2012) as follows. About 50 ml of 4M NaOH are added in dried sample (about 15 g) taken in an Erlenmeyer flask, and is stirred magnetically for 3 hours at 25^0C. Then, 10 ml of carbondisulfide (CS_2) is mixed and allowed to settle it for one hour. The precipitated mixture is washed with acetone and then is dried in desiccator. Finally, the product is xanthate that can be used as adsorbent.
- **H_2SO_4 Activation (Liang et al., 2012):** Sizable and dried sample is mixed with concentrated 1N H_2SO_4 in a ratio of 1:2 (w/v) at a temperature of 150^0C for 24 hours. Then the mixture is washed with distilled water, kept in 1% $NaHCO_3$ solution and then is filtered. Finally, the solid matter is oven dried at 105^0C till to obtain a stable weight which acts as strong adsorbent.
- **NaOH Activation (Liang et al., 2012**): About 200 g of dried matter is mixed with 1L of 0.1M NaOH solution and is left for 24 hrs. Then it is neutralized with distilled water wash. Now, it is oven dried at 105^0C and is ready to use as potential sorbent.
- **CH_3OH Activation (Liang et al., 2012):** A mass of raw material after chopping is mixed with methanol (purity: 99.9%) as per as 9 g/633ml and a small quantity of 0.1N HCl is added. The mixture is heated at 600^0C for 48 hrs. Then it is washed thoroughly with distilled water and filtered. Finally, the sample is oven dried at 50 – 60^0C till to gain a constant weight.
- **Methylation (Liang et al., 2012):** Dried sample is mixed with a formaldehyde-acetic acid solution as per as 9 g/180ml and is shaken for 6 hrs. The blended solution is prepared by mixing of HCHO with CH_3COOH in a ratio of 1:1 (v/v). It is then washed with distilled water, filtered and oven dried at 50 – 60^0C up to a constant weight.
- **Acetylation (Liang et al., 2012):** Refluxing of chopped raw matter in acetic acid as per as 12g in 64 ml at 80^0C for 10 hrs adds acetyl group (CH_3-CO-) to the adsorbent. The acetylated substance is washed with distilled water filtered and oven dried at 50 -60^0C up to a constant weight.

SORPTION MECHANISM OF BIO-SORBENT

The mechanism of bio-sorbent is mainly based on the high affinity of functional groups to metal ions to attached to solid sorbent to make a stable complex till the saturation of all functional groups. Bio-

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sorption follows many mechanisms which may vary bio-mass to bio-mass and also may adopt many mechanisms simultaneously in a sorption process. Some mechanisms described by a number of scientists are summarized here in the following:

Trans-Membrane Transport

This mechanism is mediated by trans-membrane protein across the membrane from extracellular medium into cytosol (Ma, Jacobsen, & Giedroc, 2010). Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{+}, Mn^{2+}, Fe^{3+} and Cd^{2+} can be transported by this mechanism (Ma, Jacobsen, & Giedroc, 2010). Metal binding to cell wall is essential prior to transportation (Ahalya et al., 2003). This mechanism is applicable only for living cells like bacteria (*Escherichia coli)*, fungi (*Saccharomyces cerevisiae)* etc.

Physical Adsorption

The van der Waal`s force causes the adsorption of divalent ions like Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+} etc. to the cell wall of dead plant biomass. The components (cellulose, hemicellulose, pectin, limonene, etc.) of cell wall act as potent adsorbent in this process sorption.

Ion Exchange

Cell wall polysaccharides (such as alginates in marine algae) of living microorganisms uptake divalent metals (Cu^{2+}, Cd^{2+}, Zn^{2+} etc.) with exchanging of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}. This mechanism has been described in *Aspergillus niger* (Ahalya, Ramachandra, & Kanamadi, 2003).

Complexation

Complex formation between di-metalic ions with amino ($-NH_2$) or carboxyl groups (-COOH) of polysaccharide components of cell wall forming coordination bond is another mechanism for removal of Ca^{2+}, Mg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Hg^{2+} from extracellular solution and these metals get accumulated within cell. Most of the microorganisms (*Pseudomonas syringae, Zoogloea ramigera* and alga *Chiarella vulgaris etc.)* are found to uptake metals by this mechanism.

Precipitation

It is associated with mechanism of formation of metallic compound which precipitates in the solution. This is one of the active defense mechanism of microorganism in the presence of toxic heavy metals like Cd^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+} etc. Here the metal interacts with cell surface and a metallic compound is formed.

BIOSORPTION INFLUENCING FACTORS

Metal sorption capacity of bio-sorbent is significantly influenced by a number of factors, such as, initial concentration of metal ions, pH, temperature, quantity of adsorbent used and number of functional group. The highest metals sorption capacity of bio-sorbent is found at specific conditions or states of

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aforesaid factors, i.e., optimum condition of influencing factors. It is varied from sorbent to sorbent on the basis of their chemical properties and functional groups responsible for sorption mechanism. The per cent of removal was greater with decrease in initial concentration of metal ions (10 – 200 mg/L) and with increase in amount of adsorbent used at pH 5 and 25^0C (Gönen and Serin, 2012). Most of the experiments showed that maximum removal was recorded at the pH range 4 – 7 (Yasuda, Ozaki, Nohata, Ohshiro, & Sonda, 2010; Gönen and Serin, 2012; Mohammed, 2012; Ahn & Kim, 2016). The amount of adsorption increased with increasing pH vales up to 7 (Ahn & Kim, 2016). Under optimum condition, the amount of adsorption was followed the order $Pb^{2+} > Cu^{2+} > Cd > Zn^{2+} > Ni^{2+}$ (Shrestha et al., 2013; Dwivedi & Rajput, 2014) and Co > Cd > Zn (Mohammed, 2012). Temperature was a great influencing factor. Lower temperature was conducive for better adsorption whereas higher temperature inhibited the adsorption (Rakshit, 2004). Metal – sorbent interaction studied in all experiment between 25^0 – 30^0C reported that the adsorption capacity was not influenced by the temperature because adsorptions were isothermal (Bhakta, Rana, Lahiri, & Munekage, 2014; Dwivedi & Rajput, 2014; Ahn & Kim, 2016). Presence of undesirable metal ions – K^+, Ca^{++}, Na^+, Mg^{++} etc. and surfactans in the aqueous solution reduced adsorption capacity but sulfonated (-HSO_3) and carboxylated (-COOH) adsorbent showed better adsorption in the presence of surfactants (Ahn & Kim, 2016). Adsorption capacity also depended on porosity and fineness of adsorbent (Rakshit, 2004) and was proportional to porosity, surface area (Figure 1) and to some extent to incubation period (Figure 2) (Bhakta et al., 2014). It is also found that sorption mechanism is also significantly depended on the amount of sorbent and concentration of metals in the solution (Bhakta & Munekage, 2013).

Figure 1. Porosity, surface area and Hg binding in porous matrix of activated carbon. 1- outer surface carbon-metal complex formation, 2- inner surface complex formation, 3 – lateral diffusion, 4 – ion particle growth and diffusion back to aqueous solution after saturation
After Bhakta et al., 2014.

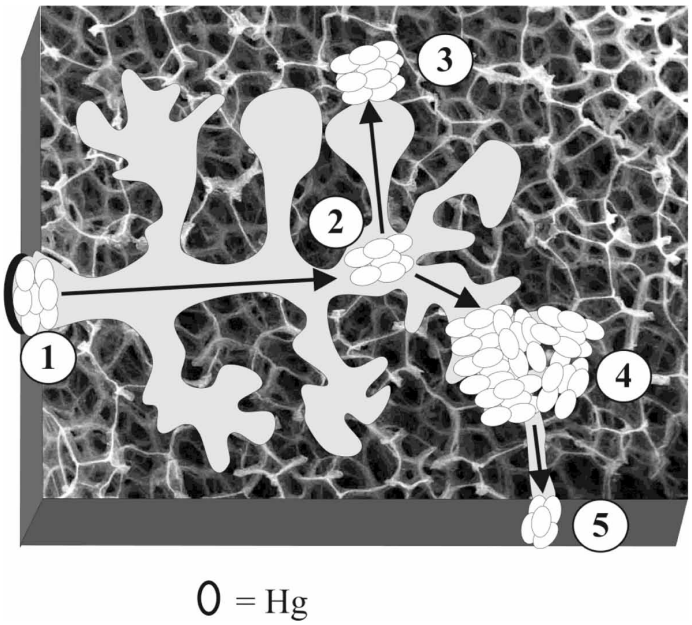

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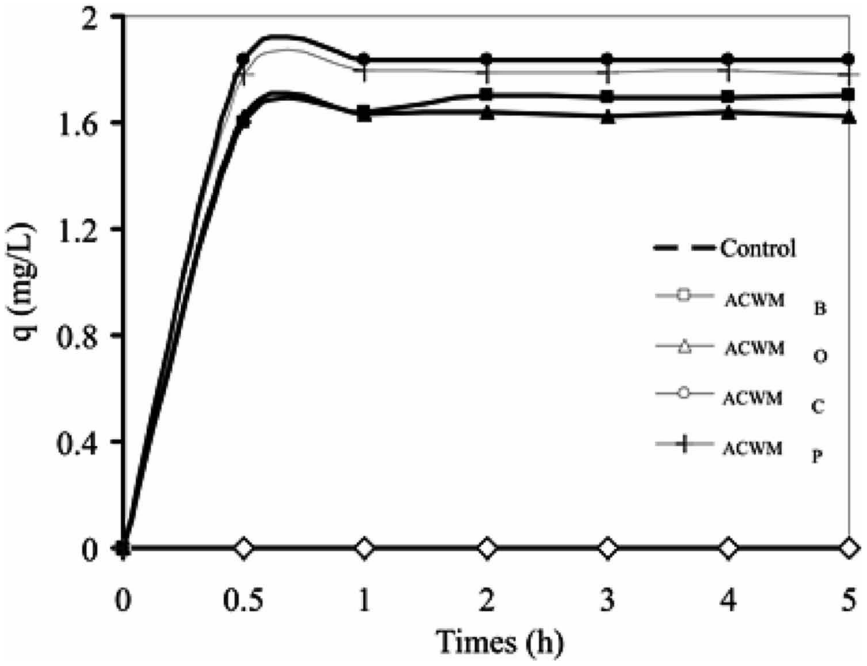
Figure 2. Hg sorption capacity of activated carbon developed from banana peel ($ACWM_B$), orange peel ($ACWM_O$), cotton fiber ($ACWM_C$) and paper waste ($ACWS_P$) in aqueous phase
After Bhakta et al., 2014.



SORPTION KINETICS

The metal sorption capacity of adsorbent can be estimated using mass balance relationship at room temperature in following (Bhakta & Munekage, 2013).

$$q_e = \{(C_0 - C_t) \times V\}/M \quad (1)$$

where, q_e – sorption capacity (mg/g), C_0 and C_t – concentration of heavy metal (mg/L) in aqueous medium at time 0 and t respectively, V – volume of the solution and M – quantity of adsorbent Sorption isotherm capacity can be calculated by Freundlich and Langmuir isotherm equations. The Freundlich isotherm equation is as foloows:

$$x/m = kc^{1/n} \text{ or, } \text{Log } (x/m) = \text{Log } k + 1/n \text{ Log } c \quad (2)$$

where, x – quantity of metal adsorbed (g), m – quantity of adsorbent (g), x/m – amount of metal adsorbed per unit mass of the adsorbent, c – equilibrium concentration of metal, k and n – empirical constants depending on the nature of adsorbent and adsorbate and the temperature.

The relationship between the number of active sites of the surface undergoing adsorption and pressure is explained by Langmuir equation –

$$\theta = kp/(1+kp) \quad (3)$$

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where, θ – number of sites of the surface which are covered with gaseous molecules, p – pressure, k – equilibrium constant for distribution of adsorbate between surface and gaseous phase.

Langmuir isotherm adsorption equation is valid at low pressure because, (1+kp) is negligible and θ = kp ; but at high pressure (1+kp) equals to kp. Then, θ = kp/kp = 1 that is not found in reality.

Adsorbent sorption capacity for metals can also be calculated by the alternative Langmuir equation –

$$q = q_{max}\, bc_{eq} / (1 + bc_{eq}) \quad (4)$$

where, q - metal accumulated per adsorbent (mg/g), q_{max} – maximum uptake of specific metal corresponding to site saturation, ceq – metal residual concentration at equilibrium and b – ratio of rate of adsorption and rate of desorption

Monolayer adsorbate of Langmuir isotherm was replaced by BET equation which was on the basis of poly layer adsorbate developed by couple action of van der Walls force (physical adsorption) and valence forces (chemisorption) with adsorbent. The surface area of adsorbent can be quantified by the following BET equation -

$$p / v(p^0-p) = 1 / v_m.c + (c-1)/v_m.c \text{ x } p/p^0 \quad (5)$$

where, v – volume of gas adsorbed under pressure p, p^0 – saturated vapor pressure at same temperature, V_m – volume of gas adsorbed when the surface is covered with a unimolecular layer and c – a constant for a given adsorbate. When, $c = e^{(E1 - EL)/RT}$ in which, E_1 – heat of absorption in first layer and E_L – heat of liquefaction of the gas

The metal removal percentage from aqueous media can be quantified following the equation:

$$Re = \{(C_0 - C_t) /C_0\} \text{ x } 100 \quad (6)$$

where Re – removal (%), C_0 and C_t – concentration of heavy metal (mg/L) in aqueous medium at time 0 and t respectively.

SOME CASE STUDIES

Although, varieties of waste biomass have been employed as bio-sorbent to remediate the contaminated water using the metal bio-soorption mechanism, some of them are summarizing in following:

Orange Peel

The adsorption property of a xanthate produced from mixing dechlorophyllated and dried orange peel with carbon disulfide (CS_2) was investigated by Liang et al. (2010) and was shown that the maximum adsorption capacity was 77.60 mg/g for Cu^{2+}, 76.57 mg/g for Cd^{2+}, 218.34 mg/g for Pb^{2+}, 49.85 mg/g for Zn^{2+} and 15.45 mg/g for Ni^{2+}. Orange peel after proper washing with double distilled water was oven dried at 70^0C for 24 hours and was then crushed to powder. About 50 g of the crushed matter was socked with a mixed solution of 250 ml of C_2H_5OH and 250 ml of 1% NaOH at room temperature for 24 hours to remove chlorophyll pigments and other low molecular weight compounds.

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Khalfaoui & Meniai (2012) used crushed and dried orange peel and chemically activated orange peel as sorbent in an experiment of Cu^{2+} removal from aqueous solution and reported that the removal efficiency was 75% in case of orange peel and more than 99% in activated peel. The orange peel was activated with concentrated H_2SO_4, NaOH, CH_3OH and acetic anhydride ($C_4H_6O_3$).

An adsorption study carrying out mixing 0.2 g of orange peel with 100 ml of $Ni(NO_3)_2$ of 10 – 200 ppm using an orbital shaker operating at 200 rpm revealed that greater percentage of Ni^{2+} removal was achieved with decrease in initial concentration Ni^{2+} and maximum removal was observed at pH 5 at room temperature (Gönen & Serin, 2012). Solutions were adjusted to the optimum pH prior to the addition of adsorbent.

Rajput et al. (2015) also conducted similar experiment using 0.5 g of finely crushed (particulate diameter: < 3.35 mm) and dried orange peel and maximum 78% Pb^{2+} ions was removed at optimum condition at room temperature from a solution of $Pb(NO_3)$ of 1000 ppm.

Banana Peel

Arunakumar et al. (2013) used banana peel as adsorbent to remove heavy metals from their aqueous solution and showed that the adsorption capacity of banana peel was 2.55 mg/g for Co^{2+}, 5.71 mg/g for Cd^{2+}, 5.80 mg/g for Zn^{2+}, 6.88 mg/g for Ni^{2+}, 7.97 mg/g for Pb^{2+} and 28.0 mg/g for Cu^{2+}. They also reported that more than 100 millions tone of banana are produced annually world wide and about 40 million tones of peel remains unused.

Waste Tea Leaves

Mohammed (2012) used black tea waste as an adsorbent to remove Co^{++}, Cd^{++} and Zn^{++} from wastewater. In an experiment, he allowed to interact 0.5 g of black tea waste with the aqueous solution of these heavy metals for 30 minutes at pH 6 and observed that the adsorption capacity of the black tea waste was 15.39 mg/g for Co, 13.77 mg/g for Cd and 12.24 mg/g for Zn. Tea waste collected from tea stall and restaurant was used to adsorb Cd^{++} and Cu^{++} from the aqueous solution of $Cd(NO_3)_2$ of 1 g/L and $Cu(NO_3)_2$ of 1 g/L respectively and a removal efficiency of 87% for Cd and 89% for Cu was observed (Dwivedi and Rajput, 2014). The crude tea waste was decolorized boiling in distilled water at 85^0C and was then dried in hot air oven at 105^0C for 12 hours. These dried leaves were pounded to powder of about 120 µm in size and that was used as sorbent as per 0.5 g for 100 ml solution.

Shrestas et al. (2013) removed Cd^{++} and Pb^{++} from wastewater using aminated tea leave as sorbent. The tea leaves were first oven dried at 80^0C for 24 hours and then they were pounded and sieved to pass through 212 µm mesh. Then the sizable leaves charred with concentrated H_2SO_4 followed by distilled water wash and oven drying at 80^0C for 24 hours. The charred sample was chlorinated with $SOCl_2$ in the presence of pyridine followed by amination with ethylene diamine $(CH_2NH_2)_2$ in the presence of Na_2CO_3 and dimethylsulphonide ($DMSO_3$) at 70^0C (Figure 3). The dried aminated leaves were active absorber for Hg^{++} and the adsorption capacity were 83.04 mg/g for Pb^{++} and 57 mg/g for Cd^{++}.

Green tea leaf is also a good adsorbent for heavy metals. Catechin extracted green tea leaves was used in removal of Cr^{6+}, Fe^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} from their aqueous solution and the removal was increased with increasing the catechin extraction time i.e., a negative correlation between Catechin content in leaf and % of removal (Yasuda et al., 2010). The extraction at pH 4 accompanied with stirring for 30 minutes at room temperature was best for optimum adsorption for Cr^{6+}, Fe^{3+} and Pb^{2+}

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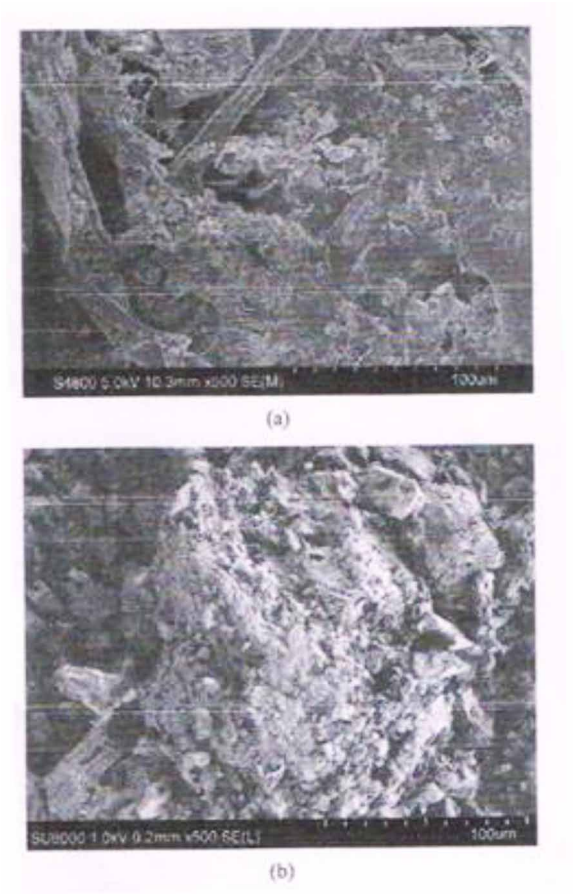
Figure 3. Scanning electron microscope images of waste tea leaves before (A) and after amination with ethyle diamine (B)



whereas, at pH 6 for Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}(Yasuda et al., 2010). Chemically modified used tea leaves i.e., thiolated (-SH), sulfonated ($-HSO_3$) and carboxylated (-COOH) tea leaves can be used as Cu^{2+} sorbent. Cu^{2+} were removed up to 53%, 22% and 19% by thiolated, carboxylated and sulfonated used tea leaves respectively at pH 7 (Ahn and Kim, 2016). They observed that, the adsorption efficiency of thiolated leaves was decreased in the presence of salt and surfactants whereas, the sulfonated and carboxylated leaves showed better adsorption in the presence of surfactants.

Rice Husk

Rice hush collected from rice mill is also a good adsorbent. Ye, Zhang, Zhang, Wu, and Du (2012) estimated its physical properties - surface area - 438.05 m^2/g, bulk density – 0.3086 g cm^3, porosity – 0.38 by fraction and chemical composition (by weight) – cellulose – 34.4%, hemicellulose-29.3%, lignin – 19.2% and ash – 17.1%. Ngah and Hanafiah (2008) used rice husk as an adsorbent for removal of Pb, Cd, Zn, Ni and As from both ground and surface water and found that treated hush showed better performance than untreated ones because, it created problems like – low adsorption capacity, high BOD, COD and

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Total Organic Carbon (TOC). Dada, Ojediran, and Olalekan (2013) treated the rice husk collected from mill to soak H_3PO_4 from its solution and used the treated husk as adsorbent in his experiment for heavy metal removal and found that the adsorption capacity of the adsorbent for Pb^{2+} was 138.89 mg /g at pH 6.3 – 6.5. Lashkenari, Davodo, and Eisazadeh (2011) reported that the adsorption capacity of polyanilinated rice husk for As (III) was 34.48 mg /g at pH 10 and at a dosage of 10 g/L.

Rice Straw

Raw rice straw is very poor or no metal sorbent because it lacks of any functional group for metal binding. Rice straw treated with NaOH was a good adsorbent for removal of Cr^{6+} and Ni^{2+} from their aqueous solution and its adsorption followed Lagergren second order kinetics (Brahmainah et al., 2015):

$$t/q_t = 1/k_2q_e^2 + (1/q_e)t$$

where, k_2 – rate constant (g/mg-min.), q_e and q_t – amount of adsorbate adsorbed (mg/g) at time t and time at equilibrium time e. Washed, Dried and powdered straw samples was used for the study. About 16 g of powdered sample was mixed with 240 ml of NaOH solution and was kept for 24 hrs at room temperature. It was then oven dried at 100^0C for 24 hrs which was treated as potential sorbent.

Sugar Cane Bagasse

Sugar cane bagasse procured from food canning processing industry could remove 96.4% of Cd^{2+} from an aqueous solution of 20 mg/L. The bagasse was first washed with distilled water, then oven dried at 60^0C for 24 hrs. The dried substance was milled to powder and sieved into a particle size of 0.5 – 4 mm which was used as adsorbent (Kumar & Sahu, 2013). Sugar cane bagasse polymerized with acrylic acid and acrylamide using N,N-methylene bis-acrylamide as a cross linker used as an highly effective adsorbent as much as 268 mg/g for Cu^{2+}, 300 mg/g for Cd^{2+} and 700 mg/g for Pb^{2+} (Kong, Ren, Wang, & Chen, 2014). About 98% removal of arsenic (As) was also reported using sugar cane bagasse with adsorption capacity 11.9 mg/g at pH 9.0 (Tagermina, Ebadi, Nasernejad, & Ghafori, 2014).

Wheat Straw

Partially de-lignified Ca^{++}-Mg^{++} ion exchanged product was developed from ligno-cellulostic wheat straw to remove Pb^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+} and to de-toxicate Cr^{6+}. A strong affinity to Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} and a weak affinity to Co^{2+}, Ni^{2+} and Mn^{2+}, were observed (Krishnami, 2016). Lignin is a polymer and possesses many functional groups like – (-COOH) and (-OH). Lignin extracted from wheat straw by boiling in alkaline solution acted as strong adsorbent for Cu ions (Todorcius, Bulgariu, & Popa, 2015). The adsorbent was prepared by addition of 1.25 g of lignin powder to 25ml of Cu $(NO_3)_2$ solution of 10^{-2} mol/L and was shaken for 24 hrs to obtain equilibrium condition and then the lignin was separated by filtration.

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Sunflower Stalk

Jalali & Aboulghazi (2013) reported that fine particles derived from sun flower stalk was a potent sorbent that showed maximum removal efficiency 97% for Pb^{2+} and 87% for Cd^{2+} from a solution of 1g/L at pH 5.0 and adsorption capacity 182 mg/g and 70 mg/g for Pb^{2+} and Cd^{2+} respectively. The adsorbent was prepared by washing with de-ionized water until the effluent was colourless. The stalk then was oven dried at 60^0C for 24 hrs, ground to power and passed through 2.0 mm sieve.

Coconut Husk and Shell

Coconut husk rich in tanin is a good adsorbent. It removed 90% of both Cu^{2+} and Pb^{2+} at pH 5.0 (Abdulrasad & Baseru, 2010). Coconut shell treated with acid and coated with chitosan resulted 93% removal performance for Zn ions at pH 6.0 and temperature 25^0C during 3 hrs of interaction of adsorbents of 30 g/L with metal solution (Lim & Aris, 2014).

Palm Fruit Fiber

Palm fruit fiber was an excellent bio-sorbent which was proven in an experiment done by Ideriah, David, and Ogbonna (2012) that resulted 100% removal of Pb and Cu ions at pH 10 and room temperature (Figure 4).

Nut Shell

Chemically treated cashew nut shell showed a great removing potential of heavy metal ions from their contaminated aqueous solution with maximum adsorption capacities - 406.6 mg/g for Cu^{2+}, 436.7 mg/g for Cd^{2+}, 455.7 mg/g for Zn^{2+} and 456.3 mg/g for Ni^{2+} following Langmuir isotherm (Kumar et al., 2012). They reported that Cu ions were removed by 100% at pH 5.0 and at 30^0C. Chest nut shell treated with 4% NaOH solution was more efficient sorbent for removal of Cd^{++}, Pb^{++}, Pb^{++} and Zn^{++} s compared to chest nut shell treated with acid formaldehyde because alkaline treatment caused swelling of adsorbent with increased surface area of adsorbent coupled with more negative charge on particle surface (Vàzquez et al., 2012).

Corn Cob

Excellent metal removal efficiency by corn cob was observed as much as 95.05% for Cr^{6+} at pH 5.4 and 4.18 hrs of interaction, 99.9% for Ni at pH 6.5 and 2.38 hrs and 91.35% for Zn at pH 6.5 and 0.15hrs from electric industrial effluents by fixed bed column technique (Ali, Khalid, & Majid, 2014). Corn cob collected from market was crushed by grinder and mixed with de-ionized water in a shaker for 24 hrs and then washed with fresh de-ionized water. These were put in a large glass baking dish and dried at room temperature. Now, the sorbent was treated with 10% HCl solution for 6 hrs at 30^0C followed by wash with double distilled water and oven dried at 125^0C for 24 hrs. Then the samples were sieved to 4 mm and stored in plastic bottle for usages as potential sorbent.

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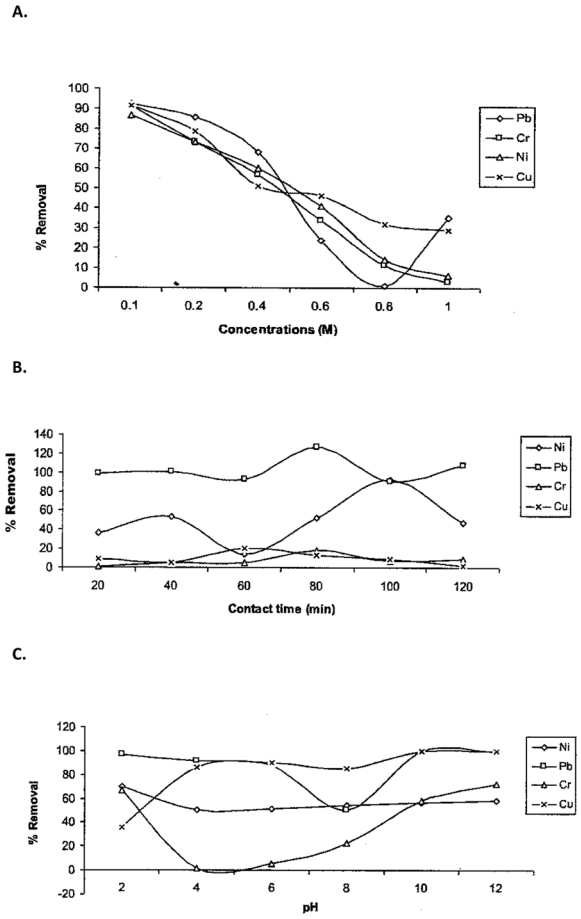
Figure 4. Removal efficiency of metal ions by palm fibre with respect to different concentrations of metal ions (A), interacting time (B) and pH values of aqueous solution of metal ions. 2.0 g of dried fibre was used in 50 ml of metallic solution.
After Ideriah et al. 2012.



Weeds

The most irritating aquatic weed water hyacinth (*Eichhornia crassipes*) has tremendous adsorption capacity for metal ions. An experiment carried out by Dixit, Dixit, and Goswami (2015) using pulverized matter from dried water hyacinth as sorbent revealed that the removal efficiency were 98 - 99% for Pb, Cd, Cr and Zn (Table-1).

The marine algae (*Sargassum myriocystum*) has been reported to be one of the potential adsorbent for Pb ions when 2g of dried algal biomass was mixed with a solution of Pb of 1000 mg/L with pH 5 and allowed to interact for 60 minutes at room temperature and a maximal removal of Pb^{2+}s was observed by 89.75% (Sweetly et al., 2014). Fresh algae were washed with distilled water to remove salt and sand particles and oven dried at 60^0C overnight. It was then acid washed to remove sorbent inhibitors – Ca^{2+}, K^+, Mg^{2+} and Na^+s. Solid samples then was the dried at room temperature for 3 - 4 days until stable weight. The adsorptive performance of sea weed (*Caulerpa serrulata*) for copper, lead and cadmium ions

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Table 1. Removal efficiencies of water hyacinth of several heavy metals from aqueous solution of different concentration at room temperature

Heavy Metal	Initial Concentration (mg/L)	Quantity of Adsorbent Used (g/L)	Removal Efficiency (%)
Pb	10	2.5	93
Cd	10	3.0	82
Cr	10	1.5	82
Zn	10	4.0	75
Pb	50	3 – 4	98 – 99
Cd	50	3 – 4	98 – 99
Cr	50	3 - 4	98 – 99
Zn	50	3 - 4	98 - 99

After Dixit et al., 2015.

from an aqueous solution was investigated by Mwangi and Ngila (2012) before and after ethelenediamination of the adsorbent and was resulted that the adsorption capacities of aminated sea weed were 5.27 mg/g for Cu, 2.12 mg/g for Cd and 2.16 mg/g for Pb ions whereas, the capacities for untreated sorbent were 3.29 mg/g, 4.57 mg/g and 1.06 mg/g for Cu, Cd and Pb ions respectively at pH 4 – 6. About 10g of green weeds was suspended in 200 ml of N,N-dimethyl formamide (DMF) followed by drop-wise addition of 35 ml of thionyl chloride ($SOCl_2$) at 80^0C under mechanical stirring. The chlorinated weeds were then washed NH_4OH solution to neutralize and the sample was vacuum dried at room temperature. Thereafter, the sample was reacted with 25 ml of ethylene 1-2-diamine under reflux with mechanical stirring for 3 hours. The solution was filtered through a sintered glass filter and vacuum dried at room temperature for 24 hrs.

Crab Shell Particle

Crab particles have strong affinity to heavy metals and chemical treatment causes more and stronger affinity. Budin, Subhramanium, Tair, and Ali (2014) produced particle from shell of crab (*Scylla serata*) and cockle (*Anadara granosa*) and used as sorbent as per as 0.5 g/L to remove lead and chromium ions from an aqueous solution of Pb and Cr of 1 g/L respectively and observed that the maximum removal efficiency of shell particles was 97.45% for Cr^{6+}s and to some extent low for Pb^{2+}s at pH 4.0 and room temperature. They also reported that sorption capacity of crab shell particle was better than cockle shell. The crab was first boiled and its shell was separated. It was then washed with distilled water and sun dried. The dried shell was pulverized and sieved of 0.5mm in size that was used as sorbent.

The adsorption capacity of pretreated crab shell particle (*Portunus sanguinolentus*) – 71.46 mg/g at pH 4.5 and 25^0C for zinc ions was also reported from an experiment of Zn^{2+}s removal from an aqueous of 100 mg/L performed by Senthil and Parthiban (2011). Waste shells of the crab were collected from Marina sea beach, washed with distilled water and then sun dried. It was now crushed to desired size by ball mill. The particle was washed with 0.1M HCl solution for 4 hrs to remove $CaCO_3$. It was then washed with de-ionized water and sun dried. Thereafter, these particles were soaked in 1%NaOH solution overnight at room temperature to remove bulk protein. The residues (chitin) were then rinsed with

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de-ionized water and oven dried at 100^0C for 6-7 hrs. The chitin was soaked in 50% NaOH solution for 2 hrs to remove some or all acetyl residues (CH_3CO-) and all chitin molecules were converted to chitosan molecules which were finally sun dried and acted as potential sorbent.

Activated Carbon (AC)

Activated carbon is also a highly potent sorbent for heavy metal due to its numerous pore, large active surface area and good mechanical properties (Cai and Jia, 2010). Heavy metal ions – $Cr^{6+,}$ Cd^{2+} and Cu^{2+} were removed from aqueous solution by the sorbent – activated carbon developed from peel of Colombian orange through pyrolysis treatment at 823 K and the adsorption capacity of activated carbon was exhibited greatest for Cu^{2+} ions because of its size and pH (Moreno-Pirajan & Giraldo, 2012).

Bhakta et al. (2014) experimentally showed that activated carbon generated from microwave mediated pyrolysis of banana peel, orange peel, cotton fiber and cellulose paper waste, was a potent mercury (Hg^{2+}) sorbent. He reported that the Hg sorption efficiency or capacity was directly proportional to the surface area, porosity and carbon content (C) in that activated carbon. He estimated the following parameters (Table-2) and calculated the Hg removal efficiency of activated carbon used as sorbent as per 0.05 g/L for removal of Hg from an aqueous solution of $HgCl_2$ as concentration as 100 µg/L and concluded that the removal performance was better in cotton fiber and paper waste than other banana and orange peel (Table-2). He also cited that other components (such as, K_2O, CaO, SiO_2 and Cl) in activated carbon (Table-3) inhibited sorption process and thus reduced sorption capacity of activated carbon to Hg ions.

Rice husk carbonized at 400^0C showed the adsorption capacity as high as 2.69 mg/ g for Ni^{2+}, 5.28mg/g for Zn^{2+} and 6.01mg/g for Pb^{2+} (Taha et al., 2011). An equilibrium and kinetic study of Ni^{2+} using activated carbon developed from bamboo (*Bambuseae*) as potential adsorbent carried out by (Rajesh et al., 2014) resulted that the BET surface area, metal uptake and metal removal efficiency of the adsorbent were 116 m^2/g, 121.72 mg/g and 92.47% respectively from a an aqueous solution of Ni of 50 – 300 mg/L at pH 2-10, adsorption dosages 0.02 – 0.1g/50ml and interaction time 15 – 300 minutes. The bamboo stem was cut into small pieces and then pulverized and sieved to 78µm. About 10 – 20 g of the powder was mixed with 14 ml of H_3PO_4 and heated at 150^0C in muffle furnace operated with N_2 gas flow at atmospheric pressure for 2 hrs. The mixture was sintered at a temperature range of 600 – 700^0C for 4 hrs. It was then cooled to normal temperature in flowing N_2 gas. Finally, the sample was washed with distilled water till pH 7 and dried at 105^0C for the use as adsorbent.

Table 2. Surface area, porosity, carbon content and removal efficiency of activated carbon generated from orange and banana peel, cotton fiber and cellulose paper waste

Activated carbon generated from	BET surface area (m^2/g)	Micropore surface area (m^2/g)	Micropore volume (cc/g)	Hg Removal efficiency (%)
Banana peel	115	51	0.0628	85
Orange peel	109	43	0.0519	84
Cotton fiber	138	65	0.0910	95
Cellulose paper waste	119	54	0.0791	94

After Bhakta et al., 2014.
BET: Brunauer Emmett and Teller

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Table 3. Constituents of activated carbon developed from different waste employed for Hg sorption study

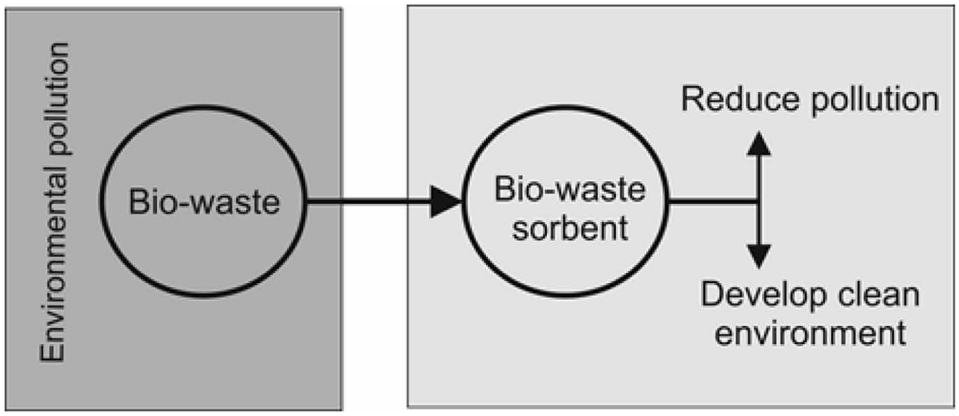
Constituents (wt %)	Activated Carbon Derived from			
	Banana Peel	Orange Peel	Cotton Fiber	Paper Waste
C	64.29	89.0	95.04	94.4
P_2O_5	5.29	5.24	5.57	5.59
K_2O	27.15	2.59	-	-
SiO_2	4.59	-	-	-
Cl	1.29	-	-	-
CaO	0.08	3.16	-	-

After Bhakta et al., 2014.

COST EFFECTIVENESS AND ENVIRONMENTAL BENEFIT OF BIO-WASTE TECHNOLOGY

The generation of bio-wastes is unlimited throughout the world. They are available and easily collected from houses, markets and industries without any cost. The preparation of bio-sorbent is very simple and follow some physical processes such as washing, drying, powdering and sieving but some sorbent undergo chemical treatment for addition of more functional groups such as ethylenediamination, methylation, acetylation etc. for binding metal. Carbonization process takes place in micro oven. There is no mechanical complexity no such costly infrastructure is required. Application of adsorbent is direct mixing with contaminated water. Small quantity of sorbent is well efficient in removing metals approximately 90%. All mechanical set up are cost reducing. Technology does not demand expert engineers and personnel; rather, skilled labours are enough to carry out the process involved in technology. The spent sorbent of bio-waste has no further adverse environmental impacts since; it can be recycled and can be converted into building materials (such as ingredient of brick). Besides, this technology converts the bio-waste into wealth (Figure 5). Therefore, it is absolutely a low-cost economically feasible technology for the present scenario of environmental pollution.

Figure 5. Bio-sorbent of bio-waste is a wealth of environment



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CONCLUSION AND FUTURE PROSPECTS

Summarily, it can be concluded that bio-waste are capable to remediate the heavy metal(loid)s from their concerned solution at significantly higher rate (75% - 100%) at specific pH and at around room temperature. Additionally, chemical modifications can increase its removal efficiency. The removal efficiencies of various bio-wastes, orange peels, waste tea leaves, rice husk, wheat stalk, sugar cane bagasse, coconut husk, sun flower stalk, corn cob, nut shell, water hyacinth, crab shell particle, activated carbons etc. are extensively high and can be recommended as a low-cost media for treating the metal(loid)s contaminated environment. It would be a low-cost, environment friendly, feasible metal(loid)s treatment green technologies in developing and under developed countries.

Recently, researches also reported that algae are promising for heavy metal remediation due to its low cost, non polluting and high sorptive capacity (Dwivedi, 2012). The capacity depends on the interaction between heavy metals and alginate compounds located within cell wall of algae. So, further research will be focused on binding mechanism and some chemical modification for better sorption. These algae can also provide clue for development of more effective sorbent. Culture of microalgae in heavy metal contaminated medium can be a great effective green technology in heavy metal remediation. Because, extracellular polysachharides, lipid and fatty acid components in cell membrane may bind heavy metal and thus microalgae can be a potential sink for heavy metal. Filamentous fungi have a great sorptive potential for Pb, Zn, Cd, Cr, As and Ni because they can produce large amount biomass within short time (Siddiquee et al., 2015). So it can be a potential sorbent.

Development of potential sorbent from bio-waste and its application in removal of heavy metal(loid)s from wastewater or their contaminated aqueous solution are a low cost, eco-friendly and green technology which is available and feasible in underdeveloped countries. Further research is needed to increase its perfection and performance. Further study is also needed to search alternative high performance low cost biomass waste and green technology. In conclusion, it can be summarized that bio-waste has significant prospect as a low-cost and green metal(loid)s removal technology for leaning the contaminated environment.

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KEY TERMS AND DEFINITIONS

Bioaccumulation: Formation of stable complexes between bio-molecules and non bio-degradable inorganic substances within tissue.

Bio-Waste: Unnecessary biomass produced from living body of animals and plants.

Chemical Modification: Covalent addition or alteration of functional group or groups of bio-molecules by chemical treatments for better efficiency.

Green Technology: Biomass based technology which has no harmful effect on environment.

Heavy Metal: Metal and metalloid with high density ($> 5 g\ cm^{-3}$) in earth`s crust.

Metal Binding Groups: Functional groups of bio-molecules which can bind metal ions covalently, non-covalently or ionically and form a complex.

Remediation: Removal of hazardous substances from an environment.

Sorption Kinetics: Rate of adsorption or absorption process or reaction of heavy metal to bio-molecule.

Sorption: Adherence or entrance of metallic ion within cell or tissue.

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Chapter 36
Biological Treatment Technology for Landfill Leachate

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ABSTRACT

Biological process for environmental preservation and treatment is not a new technology. It was used a decade ago until now. The most important tools in biological processes are the microorganism and upstream instruments (bioreactor, pond and others) to run the process. Furthermore, the efficiency of the process depends on many factors such as temperature, pH, type of microorganism, conditions, and other nutrients. To understand the factors that will affect the process, mechanisms of microorganisms to treat or protect the environment must be considered. For leachate treatment, biological process is one of the most widely used techniques for low cost and environmentally friendly.

INTRODUCTION

An understanding about the mechanism and principle of microorganism is advantageous to ensure the success of leachate treatment by biological process. Therefore, this chapter starts with an explanation on the principle of microorganism, followed by the mechanism of leachate treatment through biological process. Biological treatment could be divided into two processes; upstream and downstream. Upstream

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is related to process in the lagoon, bioreactor, pretreatment or additional treatment. Meanwhile, downstream is a process to purify effluent and discharge to river or return to landfill. Both of these systems are the main topic of discussion in this chapter. The dangers of untreated leachate to biological life such as human and environment are discussed at the end of this chapter.

PRINCIPLE OF BIOLOGICAL TREATMENT

Biological treatment is a type of treatment that uses biological material as an activator like microorganism and organic material. Leachate treatment using biological process is due to the respect to the environment and cost of process. Several requirements are needed by biological or microorganism in order to grow, such as nutrients, microbiological components, environmental condition, inhibition factors and pretreatment process. We will further discuss the topic about the concept and requirements of biological treatment for landfill leachate, especially by microorganisms. Microorganism is a small and tiny biological creature. It can be grouped as bacteria, fungi, algae and yeast. Classification is based on their characteristics through biochemistry test and DNA sequencing.

Nutrients

Nutrients are one of the most important things to a microorganism. It provides energy sources to the bacteria and supports cellular biosynthesis. In a natural environment, certain bacteria can grow in a certain environment due to the compounds that contain some amount of nutrient. Requirement of nutrients varies due to types of microorganism and environment. These nutrients can be found in the form of organic and inorganic compound, water, macromolecules and micro molecules. These nutrients serve several functions of the cell. Table 1 shows the function of every major nutrient to the bacteria cell.

Table 1. Major nutrients of bacteria and its functions (Todar, 2012)

Nutrient	Source	Function
Carbon, C	Organic compounds, CO_2	Main constituent of cellular material
Oxygen, O	Water, Organic compounds, CO_2, O_2	Constituent of cell material and cell water, O_2 is electron acceptor in aerobic respiration
Nitrogen, N	NH_3, NO_3, Organic compounds, N_2	Constituent of amino acids, nucleic acids nucleotides, and coenzymes
Hydrogen, H	Water, Organic compounds, H_2	Main constituent of organic compounds and cell water
Phosphorus, P	PO_4	Constituent of nucleic acids, nucleotides, phospholipids, LPS, teichoic acids
Sulphur, S	SO_4, H_2S, organic sulphur compounds	Constituent of cysteine, methionine, glutathione, several coenzymes
Potassium, P	Potassium salts	Main cellular inorganic cation and cofactor for certain enzymes
Magnesium, Mg	Magnesium salts	Inorganic cellular cation, cofactor for certain enzymatic reactions
Calcium, Ca	Calcium salts	Inorganic cellular cation, cofactor for certain enzymes and a component of endospores
Iron, Fe	Iron salts	Component of cytochromes and certain nonheme iron-protein and a cofactor for some enzymatic reactions

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Other nutrients that are needed by the microorganism, but in a small amount, are called as trace elements. These elements are needed due to their function as a cofactor for the essential enzymatic reaction in the cell of microorganism or as a vitamin for the microorganism. The trace nutrient usually comes out in the form of ion elements like Mn, Co, Zn, Cu, and Mo. Table 2 shows the function of those nutrients to the microorganism cell.

Nutrition consumption and metabolic adaption can be used as an indicator to characterize microorganism. Nutrients are consumed by microorganisms to build up the organic molecules and thus, enhance the building of their cells. Cell of microorganism can be divided into two; toprokaryotes and eukaryotes. In terms of nutrient requirement, the major difference between the types of cell is that prokaryotes are much more highly required compared to eukaryotes. In the biological treatment process, the nutrients contained in the wastes become one of the major factors for the growth of microorganisms. This is because they used the organic material as a food source and all of the organic matters are measured using Biochemical Oxygen Demand (BOD) technique and Chemical Oxygen Demand (COD). In this biological treatment, the microorganism removes the organic matter that is contained in the waste water and reduces the pollutant.

Bacteriology

Bacteria are one of the most abundant microorganisms that are commonly applied in the biological treatment. Normally, bacteria can be identified by their species or families based on three elements, such as morphology, biochemistry reaction and DNA sequence. The common morphologies of bacterial are coccus(spheres) and bacillus (round-ended cylinders). However, some bacteria have unusual morphologies, such as helically twisted cylinders (spirochetes), cylinders curved in one plane (selenomonads) and other morphologies(Madigan and Martinko, 2005; Salton and Kim, 1996).

Figure 1. presents the types of cocci morphologies. This first group of bacteria is called coccus due to their spherical morphology. The diplococcus is the coccus bacteria that are in pair arrangement. Meanwhile, bacteria in a chain arrangement is called streptococcus and lastly,a cluster of coccus is known as staphylococcus. This type of bacteria causes a much different type of common diseases. The examples of the bacteria are *Staphylococcus aureus*, *Neisseria meningitides* and *Streptococcus pyrogenes.*

Table 2. Micronutrients for microorganism's cell

Nutrient	Source	Function
Manganese, Mn	Manganese salts	Major classes of ion transporters in prokaryotes (Andrea *et al.*, 2007).
Cobalt, Co	Cobalt salts	As a cofactor and activator for enzymes (Hausinger, 2007), fixes nitrogen during amino acid production, single cobalt atom is the central metal component in the vitamin B_{12}(Raux*et al.*, 2000).
Zinc, Zn	Zinc salts	An essential trace element for the growth of most organisms, required for multiple cellular function(Gielda & Dirita, 2012).
Copper, Cu	Copper salts	Copper atom contained in the protein, required for defense against oxidative damage, act as electron carriers(Magnani & Solioz, 2007).
Molybdenum, Mo	Molybdenum salts	Enzyme component (xanthine oxidase, sulphite oxidase, aldehyde oxidase) (Spears, 1999).

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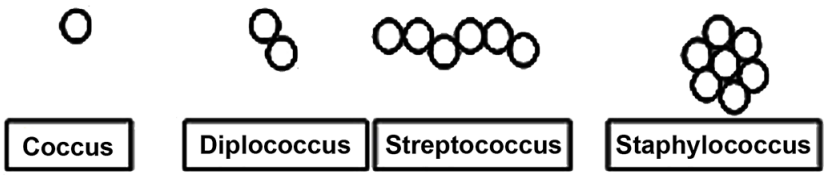
Figure 1. Morphologies of coccus type bacteria (Okafor, 2011)



Meanwhile, Figure 2 shows the morphologies of bacilli group. This type of bacteria group is in cylindrical form. The arrangements of these bacteria are in single-cell bacteria called bacillus or in the chain shape like streptobacillus. They also have several types of arrangement for bacillus group, like diplobacillus, trichome, palisade, and coccobacillus. This type of bacteria can give positive and negative impact to our health. Some examples of bacillus species are *Escherichia coli*, *Corynebacteriumdiphteriae*, and *Bacillus anthracis*.

Figures 3, 4 and 5 show other morphologies such as vibrio, spirillum and spirochete. Vibro's morphology has a comma-like shape or curve rod shape (Figure 3). Basically, this type of bacteria lives in the aquatic environment. Most of these bacteria can cause diseases. The example of vibrio bacteria is cholera that can cause diarrhea and dehydration symptoms to patient(Saritha, 2015).

Figure 4. presents the morphology of spirillum. This morphology has a more rigid spiral shape. It has no outer sheath and endoflagella, but bacteria with many turns can look like spirochetes. Some examples of spirillum bacteria are *Campylobacter jejuni* and *Helicobacter pylori*(Perez and Martin, 1996).

Figure 5. shows the morphology of spirochete, which is a long, thin and flexible corkscrew shape. It typically moves in a distinctive rotating manner that allows it to become mobile in mucus-lined tissue or a place that is viscous. This bacteria contain outer sheath and endoflagella, but lack bacterial flagella. The examples of this type of bacteria are *Treponemapallidum* and *Borreliaburgdorferi*.

For more details of bacterial characteristics, biochemistry test should be conducted, where the reaction of bacteria with some chemicals will be recorded and analyzed. Besides that, DNA analysis can also be applied for faster and accurate result (Busse et al., 1996).

Figure 2. Morphology of bacillus type bacteria (Saritha, 2015)

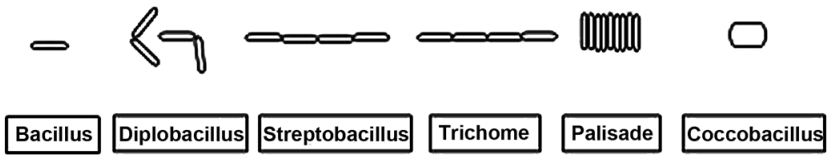


Figure 3. Morphology of vibrio type bacteria

Figure 4. Morphology of spirillum type bacteria

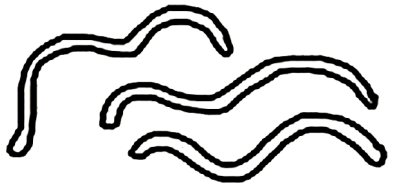


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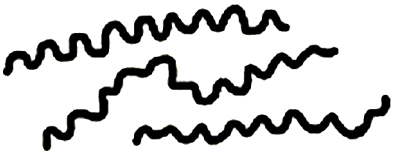
Figure 5. Morphology of spirochete type bacteria



Nowadays, the leachate treatment already includes the use of bacteria to enhance the treatment process and also to reduce its capital and processing cost. There are many types of bacteria involved in the treatment of leachate. Table 3 shows the studies done by previous researchers on the treatment of leachate around the world.

Based on the Table 3, it is already well known for the biological treatment of waste water around the world. There are a lot of advantages by using the biological way to treat waste water due to its minimal capital and maintenance cost, efficiency in degrading pollutants like organic matter and its improved flexibility of waste water treatment using bacteria.

Environmental Condition

In the real situation, application of bacteria in the biological treatment will consume proteins, carbohydrates, lipids and trace elements in the substrate or wastewater. However, the performance of bacteria depends on their metabolite and environmental conditions. In terms of environmental condition, it totally depends on the type and characteristics of the bacteria. Every bacterium has its own environment required in order to survive and grow in the optimum range. Typically, some bacteria can survive in a hot environment (thermophilic bacteria), while some have the tendency to give optimum reaction in cold or common temperature (phsyophilic and mesophilic bacterial) (Boundless, 2015). In many cases, bacteria have the tendency to give optimum reaction in high moisture condition and some of them can tolerate saline environment and etcetera. Therefore, the environmental condition must be considered in order to provide the most suitable environment for bacteria to grow. This section will discuss environmental conditions in detail for common bacteria that have been used in the biological treatment.

Table 3. Leachate treatment through biological process

No	Case	Bacteria	Result
1	Study about various method used to treat of untreated leachate (Kamaruddin *et al.* 2014).	*Pseudomonas* isolates, *Bacillus* isolates, *Burkholderia* isolates	Over the years studies show that the changes of compound in leachate due to mankind activities make the treatment varies according to the compounds in the leachate.
2	Study about treatment of fresh leachate from MSW incineration plant with high strength using EGBC reactor (Dang *et al.*, 2013).	Methanosarcina (Archaea), Firmicutes (Eubacteria).	After fermentation, 86.7% of COD removal.
3	Study about the effect of using immobilisation technique to the bacteria for nitrification process(Isaka *et al.*, 2007).	*Nitrosomonassp.*	It shows that the rate of nitrification of ammonia is higher at temperature 10˚C for more than a year.

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Gaseous Requirement

Gaseous environment is the most important requirement to influence the environmental condition of the bacteria. Condition of gases in the environment can be divided into three types; aerobic, anaerobic and facultative condition. An aerobic condition is a situation where the bacteria need oxygen for their growth and acts as its essential nutrient. Meanwhile, an anaerobic condition is the condition where some bacteria cannot tolerate oxygen at all (strict anaerobe). For facultative bacteria, the bacteria have the possibility to grow in both conditions.

Commonly, in poor oxygen environment like at the bottom of the sea or inside a swamp, anaerobic bacteria can easily be found. However, aerobic bacteria can also be found in this environment, where they still can probably survive in low oxygen or if it is facultative bacteria. Most of the common anaerobic bacteria can be found in poor oxygen environment like *Methylococcuscapsulatus*(Chistoserdova et al., 2005).These bacteria will reduce methane gases (normally producedby anaerobic bacteria from methanogenic group) by converting them into methanol and other products. Other aerobic bacteria are *Vibrio diabolicus* SF16, which are used to remove $NH_4^{\pm}N$ content (Duan et al., 2015). Alleman(1999) used b*acillus spp* in the thermophilic condition for biological treatment of wastewater.

Most strict anaerobic bacteria could not tolerate oxygen from outside but it can tolerate gases such as nitrogen or carbon dioxide. On the other hand, some of the bacteria cannot tolerate at a small amount of oxygen at all, even in salt form (Walter, 1969). Some examples of anaerobic bacteria are *Saccharomyces cerevisiae*, *Zymomonasmobilis*, *Escherichia coli* and *Clostridium acetobutylicum*(Singh et al., 2012). These bacteria are used in the production of bioenergy fuel like bio-ethanol and bio-buthanol.

Facultative bacteria, which could grow in aerobic and anaerobic conditions, have high possibility to isolate from the source of environment. However, their metabolite and production are probably a bit different, even if it comes from the same species of bacteria if it compares the culture from aerobic and anaerobic conditions (Walter, 1969).

Temperature

Most bacteria grow well at their optimum temperature. The common bacteria easily isolate from an environment within their range of optimum temperature between 37˚C to 45˚C. This type of bacteria is called mesophilic, which is mostly used in the biological treatment for heavy metal, carbon and nutrient removal. Bacteria in this group are also used in mining industries as a bioleaching that replaces the ordinary leaching technique that is expensive and environmentally unfriendly(Makita *et al.*, 2004). However some of the bacteria from this group also have the tendency and possibility to cause human diseases as they can grow well in human body temperature, especially from the pathogenic group (Sahlström, 2003).Thermophilic bacteria are bacteria that can tolerate a high temperature environment. The ranges of temperature for thermophilic bacteria are between 40˚C up to 80˚C. Basically, these kinds of bacteria can be found in places like volcano area, hot springs and a very hot place. The examples of thermophilic bacteria are *Thermoanaerobacteriumsaccharolticum*,*Thermoanaerobacteriumthermosaccharolyticum*, *Anoxybacillusspp* and *Geobacillusspp*(O-Thong *et al.*, 2011). These bacteria can be used in the industries for the production of bio hydrogen from cassava starch processing wastewater (CSPW).

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Psychrophilic bacteria are bacteria that can survive at a temperature below 25˚C and usually, these kinds of bacteria can be found in cold weather places like the north and south poles. Usually, psychrophilic bacteria have names like 'arctic'. However, some psychrophilic bacteria that do not have the sign of their psychological condition on their name, like *Pseudomonas sp* CBZ-4, are used in the cold weather to degrade carbamazepine, that is contained in the pharmaceutical wastewater(Li *et al.*, 2013).

pH

pH is one of the indicators used to measure the acidity and alkalinity of the aqueous solution. pH of the solution is measured by referring to the concentration of hydrogen ion in the solution. Greater amount of hydrogen ion in the solution will lead to lower pH and vice versa. Many groups of bacteria can grow best in the pH range of 6 to 8. An example of bacteria that can grow in the solution within this pH and used for biological treatment is *Ganodermalucidum*. This bacteria is used in the industries to treat textile dye wastewater (Selvakumar *et al.*, 2012). Other bacteria like *Methylomirabilisoxyfera* is used in the wastewater treatment, where ammonium and residual dissolved methane can be removed at the expense of nitrite and nitrate (Luesken *et al.*, 2011).Several groups of bacteria can tolerate highly acidic and alkaline environment. Normally, these types of bacteria are known as halophilic bacteria. The advantage of these bacteria is that it can be used to treat wastewater in extreme conditions. For example, *Marinobacterhydrocarbonoclasticus* and *Halomonasspp*thatcan survive in high salt concentration and high pH of around 8 to 9, are commonly used in denitrification of wastewater (Li *et al.*, 2013).

Inhibition

Before biological system could be operated, identification types of culture need to cleared. Moreover, mixture or single cultures want to be introduced. If the mixture culture is selected, then the environment condition needs to be improved. For example, if aerobic bacteria have been chosen, the pH and aeration need to be studied. Lack of this factor could bring inhibition to bacteria. Normally, these inhibitory substances can be one of the factors for treatment failure. This inhibition can be traced by measuring the byproduct produced; for instance, in the anaerobic digestion, the byproducts are methane gas and organic acid. The lowest production from common rate means that inhibition is probably happening (Chen *et al.*, 2008).

For the treatment of waste water, mainly leachate, anaerobic treatment is preferable. This is because protein and carbohydrate are more efficiently degraded in anaerobic treatment. On the other hand, leachate also contains pollutants like ammonia; phosphate, nitrogen, and sulfur.In the aqueous solution, there are two forms of ammonia material like ammonium ion and free ammonia. The free ammonia can cause inhibition to the anaerobic treatment because it can passively diffuse into the cell and cause problems like proton imbalance and potassium deficiency. For the waste water treatment, ammonia inhibition can be controlled by lowering the ammonia content in the leachate at an acceptable level but not totally removed because ammonia is one of the sources of nitrogen to the anaerobic bacteria (Cheung *et al.*, 1997).

Sulphate can also become an inhibitor element. Sulphate is one of the common chemicals that can be found in the wastewater. In anaerobic treatment, sulphate will be reduced by using Sulphate Reducing Bacteria (SRB). These bacteria will degrade sulphate to become a simple compound. One of the major problems in applying SRB is the competition of common nutrients between SRB and other bacteria that will lead to the accumulation of sulphate. Other inhibition is the toxicity of sulphide, which affecting

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other bacteria. During the process, SRB will degrade sulphate to a simple compound namely sulphide, which will inhibit the growth of SRB if it is above the acceptable amount. In addition, the increase of pH can also elevate the toxicity level of sulphide to the bacteria (Muyzer& Stams, 2008). In order to control the inhibition of sulphate for anaerobic treatment, several processes can be done, including diluting the landfill leachate. Recently, the removal of sulphide can be done by using physio-chemical and chemical techniques, which will be discussed later.

The third inhibitor is heavy metal. Heavy metal is a non-biodegradable material that can potentially become toxic to the bacteria and cause failure in anaerobic treatment of landfill leachate. The toxic effect of heavy metal can be seen in the disruption of enzyme function and structure by binding the metal to the group of protein molecule or replacing the material in the enzyme prosthetic groups. However, there are some heavy metals that are essential for the enzyme parts that contribute to the enzyme functions like iron, zinc, nickel, cobalt and etc. The inhibition of heavy metal to the bacteria is based on concentration, chemical form, process-related factors like pH and redox potential in the landfill leachate. Some of the heavy metals are used in many physio-chemical treatments of leachate, such as precipitation of sulphide, sorption of solid fraction, and formation of complexes in the solution (Chen *et al.*, 2008). To remove heavy metals from leachate, detoxification must be done by using several techniques such as adding sulphide, activated carbon, kaolin, bentonite, and diatomite in the treatment.

Even organic compound is food for bacteria but it can also become an inhibitor. Organic compounds inhibit the growth of bacteria if they are poorly soluble in the water. It may also adsorb to the surface of the bacteria and accumulate to high level in digesters. The nonpolar pollutant that accumulates in the bacteria membrane can cause the membrane to swell and leak. Some of the organic compounds that inhibit the growth of bacteria are benzene and its derivatives, phenol and its derivatives, alcohol, ether, ketones, and etc. Factors that affect the toxicity of organic compounds are toxicant concentration, biomass concentration, toxicant exposure time, cell age, feeding pattern, acclimation and temperature.

Pretreatment

Nowadays, rubbish is thrown into the landfill because it is the most cost effective way to dispose municipal solid waste (MSW). Every country has their own technology to manage landfill in order to make it less polluted and safe for the people. However, when using landfill as a method to dispose MSW production, leachate should be considered. Leachate is the water that comes from the landfill when the majority of soluble materials in the waste will come along with the water that comes out from the landfill. This contaminated water contains a lot of polluted material such as heavy metals, chemicals, organic materials and others that cannot be degraded by the bacteria. As a result, this leachate eventually pollutes rivers, lakes, and ground water severely. In addition, the production of leachate depends on the rate of rain fall onto the landfill that contributes to the rate of leachate production. A higher amount of leachate is produced during the wet season compared to dry season (Tränkler *et al.*, 2005).

Thus, to solve the leachate problem, treatments of leachate are required. To keep the treatment environmental friendly and cost effective, biological treatment is the best option. However, due to high content of a variety organic and chemical compounds in the leachate, several pretreatments are required in order to treat the leachate before going to the biological stage. Physical-chemical treatment has been suggested for use such as screening, flocculation, sedimentation, flotation, filtration, natural evaporation coagulation, precipitation, chemical oxidation, chemical reduction, disinfection, and carbon adsorption (Baig *et al.* 1940).

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However, due to high maintenance and non-environmental friendliness of the physical-chemical process, the reaction or removal that emerges from this treatment will be minimized sufficiently to prepare the leachate for biological stage. After that, microorganism becomes suitable to grow and consume nutrient, organic matter and significantly treat landfill leachate. Understanding the profile of the leachate is important to ensure that whether the leachate requires a pretreament or not. Biological treatments have some limitation. Generally, the amount of COD is greater than BOD, but if the ratio of BOD/COD is too small, it indicates that the leachate needs a pretreatment from physical-chemical process. High concentration of oil, grease, heavy metal and inorganic material isone of the factors that indicate the requirement of a pretreatment (Imen et al 2001).

Mechanism of Biological Process

Nowadays, wastewater treatment applies modern technologies and knowledge in order to upgrade the quality of treated water and also to reduce its operational cost. Each wastewater treatment is classified by their nature of the process involved, namely physical, chemical or biological treatment. For the mechanism of biological treatment process, bacteria are mainly used in the decomposition of biochemical matter in the wastewater to produce stable end product. The mechanism chosen for each treatment is based on the severity of pollutants contained in the waste water.

Nitrification and Denitrification

Ammonia is a compound of nitrogen and hydrogen that bonds together in the form of NH_3. Normally, ammonia is in the form of gas and it has a pungent smell. In the landfill leachate, ammonia is produced when the organic compound that contains nitrogen element breaks down to a simpler form. In general, nitrogen is the fourth most abundant element in the world. The landfill leachate contains a large amount of organic waste, which is mainly food waste. Due to that, the ammonia content in the landfill leachate becomes high, which could obviously cause harm and pollute the environment when it is discharged without undergoing proper treatment. Nitrification is the process where the ammonia will be converted into nitrite and eventually it will be converted into nitrate by biological treatment. The nitrification process occurs due to biological oxidation process that occurs between ammonia and oxygen. In the degradation of ammonia into nitrite, the ammonia will undergo nitrifying process by bacteria under aerobic condition to become nitrite (NO_2). Then, the nitrite will undergo another biological oxidation process where it will be nitrified by nitrifying the bacteria under aerobic condition to become nitrate (NO_3).After the nitrification process is done, the denitrification process will take place. In the denitrification process, the nitrate will be converted into other products through assimilatory and dissimilatory cellular functions. In assimilatory cellular function, the nitrate will be converted into nitrite and it will be further converted into nitrite, and eventually will become ammonia. These conversions will be done by specific bacteria under anaerobic condition (Yang & Zhang, 1995).

In contrast, dissimilatory denitrification occurs when the nitrate becomes the electron acceptor in energy metabolism and it will be converted into various gases such as carbon dioxide and nitrogen gas. There are several elements that are needed by the process to make the dissimilatory denitrification process become efficient, which are oxygen gas and carbon sources. The condition of the leachate is normally under anoxic condition when it can be considered that the oxygen level of landfill leachate is lower than in aerobic condition. Therefore, the leachate must be aerated properly to supply sufficient

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oxygen to the leachate. The other element is carbon sources. The carbon sources become important due to their function to become an electron donor for the denitrification process to take place. The sources of carbon may already be contained in the leachate or will be added manually. The proportion of carbon to nitrogen and to phosphorus must be 100:5:1 in order for the process to occur (Yang & Zhang, 1995).

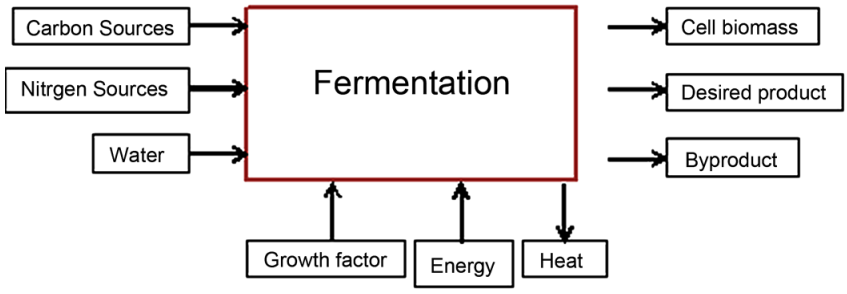
Digestion and Fermentation

Biological Oxygen Demand (BOD) is the amount of dissolved oxygen needed by the aerobic bacteria in the leachate or wastewater to breakdown the organic material that is present in the solution at a certain temperature over a specific period of time. Meanwhile, Chemical Oxygen Demand (COD) is one of the techniques to measure the amount of materials that can be oxidized in the presence of a chemical oxidizing agent. In landfill leachate treatment, the COD and BOD values become one of the indicators to the pollution level of the leachate. Basically, in the leachate, the value of COD must be larger than the value of BOD because the COD value is composed of materials that can be oxidized by chemicals and taken by biological material, while the BOD is a material that can be consumed by biological organism as carbon sources. Therefore, by referring to the value of COD and BOD removal, we can indicate the efficiency of the leachate treatment based on these two indicators (Ghosh *et al.*, 2014).

In anaerobic digestion, degradation and fermentation will occur in the same digester. The bacterial will degrade carbon and nitrogen sources to produce specific products under fermentation (anaerobic condition). Process in the anaerobic digestion can be divided into four stages. Hydrolysis process will start from beginning. In this stage, enzyme will degrade complex organic matter to simple organic matter such as protein to amino acid, carbohydrate to simple sugar and lipids to fatty acids. Enzyme from this stage is produced by bacteria, which are available in the digester. Then acidogenic or fermentation bacteria will take part and convert simple organic matter to other products such as acetic acid, simple fatty acids and gases such as hydrogen and carbon dioxide. Then, this is followed by acetogenic bacteria to degrade complex fatty acids to acetic acid. Finally, bacteria from the methanogenic group will take part and convert acetic acid and hydrogen to methane and carbon dioxide. Figure 6 shows the schematic diagram for fermentation process.

From the figure above, we can see the requirement of the bacteria for the treatment of landfill leachate. The carbon sources come from the organic material in the leachate. The measurement of organic material that can be consumed by the bacteria can be done by referring to the BOD value as it indicates the organic carbon that can be utilized by the bacteria.

Figure 6. Schematic diagram for bacteria fermentation process (Zacharof & Lovitt, 2013)



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Most of the landfill leachates contain a lot of other materials like sulphur, ammonia and organic matter. These materials can be degraded in the leachate by altering the bacteria fermentation by introducing specific types of bacteria that can consume the material as food sources. For example, *Nitrobacter* bacteria can convert ammonia content into nitrate (Sun *et al.*, 2015).

Metal and Nutrient Removal

Usually, leachate is contaminated with high concentrations of a variety of heavy metals, solvents and chemicals, which come from dumped waste in the landfill or reaction between all of those components. Table 4 lists the MSW composition in Pulau Burung Landfill Site (PBLS), Penang.

Table 4. shows the variety of waste dumped at the landfill. The highest percentage of waste composition in PBLS comes from food waste followed by plastic, others and paper. This is because Penang state has one of the highest populations per square meter after the capital city of Malaysia (Kuala Lumpur). It is also due to a lot of industrial parks located in Penang that contribute the variety of solid waste. As a result, numerous chemicals, heavy metals and compounds will be contained in the leachate. The leachate components of PBLS are shown in Table 5.

Based on the composition of leachate, there are several treatments that are required to reduce these compounds to an acceptable amount before being discharged into the environment. For example, if the leachate from landfill has frequently identified high contents of ammonia, then it is reduced by using the nitrifying and denitrifying techniques that have been discussed in subtopic 3.1. For the heavy metal removal, numerous pretreatments are used and the removal efficiency of metal is quite high. In previous researches, fly ash made from coal was used as an adsorbent to trap heavy metal ions such as zinc, lead, cadmium, manganese, copper and etc. (Cho *et al.*, 2005; Mohan & Gandhimathi, 2009;Cetin & Pehlivan, 2007). There is also heavy metal removal from leachate using biological treatment as presented in Table 6.

Table 4. Composition of MSW from PBLS (Yusoff, 2012)

Waste Components	Weight (%)
Organic Food	57.4
Paper	8.56
Plastic	13.93
Rubber	2.8
Textile	2.79
Glass	2.28
Ferrous	1.3
Other	10.94

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Table 5. Composition of leachate in PBLS (Aghamohammadi et al., 2007)

Parameters	Range	Average	Effluent Standard Bb
pH	8.3–8.8	8.5	5.5–9.0
TCOD (mg/L)	2533–2880	2860	100
SCOD (mg/L)	2310–2850	2360	–
BOD5 (mg/L)	252–760	377	50
BOD5/TCOD	0.09–0.26	0.17	0.5
Alkalinity (mg/L as CaCO3)	5658–5662	5660	–
Colour (PtCo)	4000–4560	4200	–
TKN (mg/L)	1440–2191	1745	–
Ammoniacal nitrogen (mg/L)	1188–1812	1400	–
NO2-N (mg/L)	20–110	40	–
NO3-N (mg/L)	1–50	14.2	–
Turbidity (FAU)	418–420	419	–
<MathML>	90–110	100	–
<MathML>	38–40	39	–
Total suspended solids (mg/L)	78–80	79	100
Fe (mg/L)	6.1–19	6.6	5
Zn (mg/L)	2.06	2.06	1
Pb (mg/L)	3.4	3.4	0.5

Table 6. Biological treatment for removal of heavy metals

No	Case	Bacteria
1	Study on the effectiveness of nutrient and heavy metal removal in anaerobic waste by using aerobic treatment (Farooq, S., & Gabriel, P. F., 1983).	Aerobic biological bacteria
2	Study on the biosorption of various heavy metals by using algae in the wastewater (He & Chen, 2014).	Various brown, green and red algae

STABILIZATION PONDS AND BIOREACTOR

Stabilization ponds and bioreactors are most important for biological treatment. The performance of biological system depends on this matter. Table 7 shows the types of ponds and bioreactors that are commonly using for leachate treatment.

Stabilization pond is a pond that consists of one or more shallow ponds in a series for treatment and the natural process of algae and bacteria occurs in a mutually dependent relationship (Indah Water Konsortium, 2014). Meanwhile, a bioreactor is a vessel specifically designed to grow and maintain the microorganism in which the condition inside the vessel can be controlled.

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Table 7. Leachate treatment and objective (Environmental Protection Agency, 2000)

Treatment Objective	Main Treatment Options	Type of Landfill
Removal of degradable organics (BOD)	Aerobic system • Aerated lagoon/extended aeration • Activated sludge reactor • Sequencing batch reactor (SBR) Anaerobic system • Upflow anaerobic sludge bed (UASB)	 II II
Removal of ammonia	Aerobic system • Aerated lagoon/extended aeration • Activated sludge • Sequencing batch reactor (SBR) • Rotating biological contactor	 II
Denitrification	Anoxic system SBR	II II
Removal of methane	Aerobic system (limited)	I, II, III
Final polishing	Reed beds Sand filtration	II II

Note: I=Non-hazardous industrial waste, II=MSW and co-disposal, III=Hazardous waste

Aerobic Ponds and Bioreactor

Aerobic treatment is the treatment of leachate in the presence of oxygen. In this process, the microorganisms will generate energy through enzyme-mediated electron transport using molecular oxygen as electron acceptor (Environmental Protection Agency, 2000). There are many types of aeration treatments, such as activated sludge reactor, rotating biological contactor (RBC) and aerated lagoons.

Activated Sludge

The principal that appears in activated sludge process is that it uses a community of microorganisms in a reactor that is constantly supplied with organic matter and oxygen (Wiszniowski *et al.*, 2006). The microorganisms will consume the organic matter in a leachate and undergo metabolism to produce new cell and products, which consist of water, carbon dioxide and minerals (Wiszniowski *et al.*, 2006). Instead of using pure culture, the activated sludge consists of bacteria, yeast, fungi, protozoa and higher organisms which interact with each other (Wiszniowski *et al.*, 2006). According to the Environmental Protection Agency (2000), in activated sludge process, diffusion or surface aeration is used to maintain aerobic condition in a reactor. After some time, a mixture of new and old cell is passed through into a settling tank, but a portion of the settled cell is recycled to maintain the desired cell concentration in a reactor and the rest are sent to sludge handling facility. The schematic diagram of activated sludge process is shown in Figure 7.

In a landfill site designed by the Environmental Protection Agency, which was published in 2000, emphasizing the aerobic process such as activated sludge, there will be a residue of 0.1 to 0.6 g of sludge generated per g COD removed at about 1.0% solids concentration. Activated sludge process strongly depends on several parameters, which are concentration of feed, sludge retention time (SRT), hydraulic retention time (HRT), biomass concentration in aeration tank (MLSS, Mixed Liquor Suspended Solids), organic

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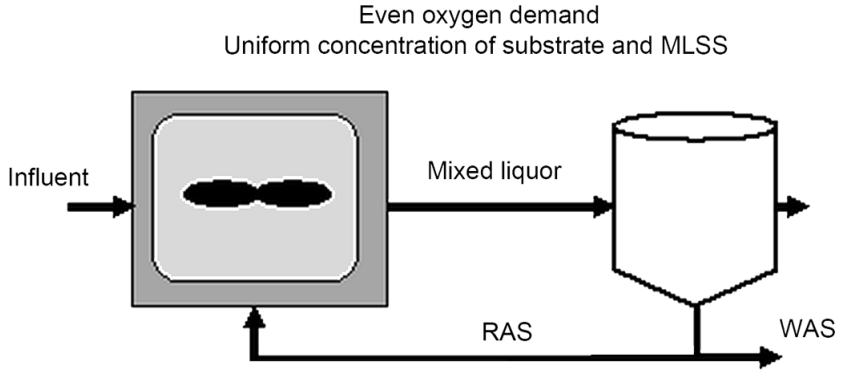
Figure 7. Schematic diagram of mixed activated sludge process (Environmental Protection Agency, 2000)



loading, food to microorganism ratio (F/M ratio), sludge wastage rate, and sludge settling characteristics in sedimentation tank (Setiadi & Fairus, 2003).However, this method has some disadvantages, such as:

A. If the production of sludge is high, large areas are required (Setiadi and Fairus, 2003)
B. Inadequate sludge settling ability and needs longer aeration times (Zouboulis *et al.*, 2001)
C. High energy demand and excess sludge production
D. Microbial inhibition due to high amount of ammonium-nitrogen strength (Renou *et al.*, 2008)

The performance of conventional activated sludge process is significantly affected by several parameters such as concentration of feed, sludge retention time, hydraulic retention time, biomass concentration in aeration tank, organic loading, food to microorganism ratio, sludge wastage rate and sludge settling characteristics (Setiadi & Fairus, 2003). In the past century, basic activated sludge process has been modified depending on various purposes such as complete-mix activated sludge that allows more uniform aeration in the tank, step-aeration activated sludge, which distributes the influent to several points in aeration tank, contact-stabilization activated sludge, which allows high concentration of biomass to be in contact with the influent for a period of time, tapered aeration process that loads organic influent at the head of aeration tank and pure oxygen activated sludge, which is based on the rate of oxygen transfer. Furthermore, to enhance the performance of activated sludge process, many researchers suggested integrating membrane technique in the leachate treatment (Setiadi & Fairus 2003; Renou *et al.*, 2008; Yamamoto *et al.*, 1989).

Aeration Lagoon

The idea that lies behind aeration lagoon is very simple. The retention time of the leachate is long enough so that many microorganisms can grow per time as the leachate is transported out of the lagoon. Long retention time is necessary in order to oxidize ammonia nitrification. The cost for the operation and maintenance of aerated lagoon is relatively low (Stegmann *et al.*, 2005).The advantages of aerated lagoon are that it can cope with various leachate strength, flows and the most flexible type of leachate treatment. However, it also serves many disadvantages such as large area requirement, odor and aerosol formation, low energy efficiency and high heat loss due to surface and mechanical aerator (Environmental Protection Agency, 2000).

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Rotating Biological Contactor (RBC)

RBC consists of a series of circular plastic discs (polyethylene, polyvinyl chloride or polystyrene) mounted on a common horizontal shaft. It is approximately 40% submerged in a leachate and slowly rotates either by a mechanical or a compressed air drive. It usually rotates at 1-10 revolutions per minute (RPM) (Wiszniowski*et al.*, 2006). Figure 8 shows the schematic diagram of RBC.

Microorganisms from the leachate will adhere to the plastic disc and within 1-4 weeks, it will form a biofilm ranging from 1 to 2 mm thickness. This biofilm will be exposed to air when the plastic disc rotates out of the leachate. After some extent of thickness, the biofilm will be sloughed off the plastic disc (Wiszniowski *et al.*, 2006). Generally, RBC is used for weak leachate.

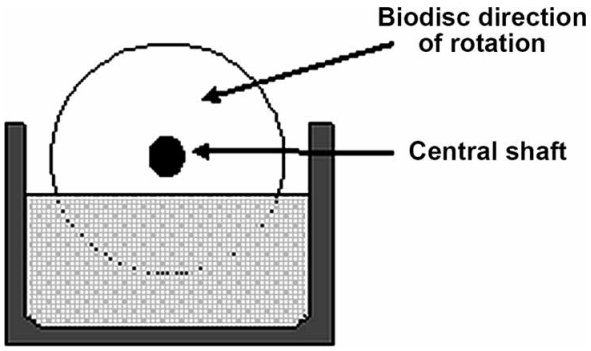
Anaerobic Ponds and System

Anaerobic process is slightly different from the aerobic process where no oxygen is required. Electron acceptors in this process are inorganic compounds such as nitrate, sulphate and carbon dioxide (Environmental Protection Agency, 2000). The EPA (2000) stated that anaerobic process provides several benefits such as lower sludge production, lower energy demand (no oxygen required) and recovery of methane may provide energy. Anaerobic process is an effective process, but the remaining of BOD and COD are still high and at the end, it still needs to be treated to meet the effluent standard with means of aerobic process (Stegmann *et al.*, 2005). Normally, anaerobic treatment is required if the production of leachate is too high or the landfill is huge and has been operated for a long period of time. Many kinds of anaerobic bioreactors have been introduced for leachate treatment such as AF (Anaerobic Filters), ASBR (Anaerobic Sequencing Batch Reactor) or UASB (Up-flow Anaerobic Sludge Blanket) (Wiszniowski*et al.*, 2006).

Anaerobic Filters

Anaerobic filters (AF) is filled out with a support material arranged in sheet, ring or sphere configuration, which will provide the best attachment place for microbial in the form of biofilm and can be operated in upflow or downflow feed mood(Bodik *et al*., 2000).

Figure 8. The schematic diagram of rotating biological contactor (RBC) (Environmental Protection Agency, 2000)



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AF is a high rate system that gathers all disadvantages of anaerobic system and thus minimize the disadvantages (Renou *et al.*, 2008). Henry *et al.* (1987) reported that the removal of COD from landfills with different ages was at 90% with a loading rate of 1.26-1.45 kg COD m^{-3} d^{-1}.

There are several advantages of AF, which are, this system is suitable to treat low strength leachate, the produce sludge is in minimal quantity, and the maintenance and handling are easy. The disadvantages of the AF system is dead zone formation as a result of sludge compaction and it tends to clog because of poorly designed distribution system (Bodik *et al*., 2000).

Anaerobic Sequencing Batch Reactor

Anaerobic sequencing batch reactor (ASBR) consists of four steps, which are feeding, reaction, settling and liquid withdrawal (Zaiat *et al.*, 2001). This system is not suitable for low-strength leachate since the low gas production will result in insufficient turbulence, which will lead to stagnant zone in a reactor and/or external mass-transfer resistance (Brito et al., 1997).

ASBR can eliminate the use of clarifier because it can achieve solid capture and removal of organic in one vessel (Timur & Özturk 1999). According to Timur and Özturk(1999), the COD removal effeciencyrate was between 64-85% and net daily biomass conversion yield was about 0.1g volatile suspended solids (vss) per g of COD removed.The removal of nutrient (COD, NH_4-N, PO_4-P) from landfill leachate by using SBR was investigated by Uygur & Kargi (2004), who reported 75% COD, 44% NH_4-N and 44% PO_4-P removals after 21 hours of operation. This high removal was achieved when the investigator combined the anaerobic reaction with aerobic and anoxic reaction in SBR.

Up-Flow Anaerobic Sludge Blanket

Up-flow anaerobic sludge blanket (UASB) is a modern anaerobic process which have high treatment efficiency but short hydraulic retention time (HRT) (Lin *et al*., 2000). UASB performs more preferably at higher organic loading rate compared to other anaerobic treatments (Govahi *et al*., 2012). The author also emphasized that UASB is suitable to treat leachate with a COD value higher than 800 mg/L and BOD/COD value ratio higher than 0.3.

UASB offers very good treatment, which can remove 77-91% COD but leachate that was treated by UASB is not suitable for direct discharge of leachate into sewerage system, thus further treatment is required (Kennedy & Lentz, 2000). Kettunen *et al.*(1996) reported that UASB treatment can be done on leachate that hasa temperature of as low as 11ºC. Thus, this will minimize the need of heating up leachate prior to treatment especially in cooled weather country, which will provide more cost effective treatment (Renou *et al.*, 2008). The main disadvantage of this treatment is its sensitivity to toxic substances (Sung *et al*., 1997).

FACULTATIVE SYSTEM

Another system is facultative, which normally runs in the lagoon and has already been introduced for a long time as the treatment of leachate. Facultative lagoon is not mechanically agitated or aerated. From wastewater technology fact sheet that was published by United Sates Environmental Protection Agency in 2002, it is clearly stated that a facultative lagoon is separated by two layers, which is aerobic and an-

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aerobic. Aerobic layer is located near the surface of pond, while anaerobic layer is a layer at the bottom of the pond where the sludge deposits. The advantage of this system is that the maintenance cost is very low due to the system that is designed to make use of gravity flow. It is also easy to operate. According to the fact sheet, the performance of this system is partially reliable even though the BOD removal is up to 95%,and the total suspended solid exceeds 150mg/L (United Sates Environmental Protection Agency, 2002).

Advanced Bioreactor

Recently, membrane reactor technology found its way in treating the landfill leachate. According to Ahmed & Lan (2012), membrane bioreactor (MBR) is an advanced biological treatment process that can replace traditional secondary clarifier of an activated sludge process using a membrane separation unit. The authors also suggested that MBR is more advantageous in treating old leachate, which shows better effluent quality, process stability, smaller footprint, and increased biomass or mixed liquor suspended solids (MLSS) retention. Meanwhile, Laitinen *et al.* (2005) mentioned that membrane bioreactor can achieve high quality of treated water in a reduced sludge production. In general, MBR can be separated into two parts; biological unit,, which is responsible for biodegradation and membrane module, which is responsible for the separation. This membrane model normally uses ultrafiltration (UF) or microfiltration (MF) in the configuration of hollow fiber, plate and frame, flat sheet or tubular (Ahmed & Lan, 2012). They also added that the common design of bioreactor includes continuous stirred tank reactor (CSTR), plug-flow reactor (PFR), sequencing batch reactors (SBR) and upflow anaerobic sludge blanket (UASB) reactor. There are two types of MBRs, which are categorized by the position of the membrane; submerged or external reactor and submerged system becomes more attractive due to the more compact system (Bohdziewicz*et al.*, 2007).An article published by Ahmed &Lan in 2012 can be classified as a complete review on MBR technology in treating landfill leachate. In their article, it is reported that the COD removal was as high as 90% using MBR. In addition, Bohdziewicz*et al.* (2007) also reported that the COD removal was 90% for landfill leachate treatment using MBR.

Table 8. Effluent quality from SBR and MBR from the previous work done Laitinenet al. (2005)

Parameter	SBR Effluent	MBR Effluent
pH	8.2 ± 0.3	8.4 ± 0.2
Conductivity, mS/m	320 ± 90	350 ± 40
Suspended solids, mg/l	290 ± 210	1.2 ± 0.9
BOD_7, mg/l	190 ± 140	8.3 ± 9.6
COD_{Cr}, mg/l	500 ± 110	340 ± 30
Total P, mg/l	16.9 ± 4.2	0.77 ± 0.37
Soluble P, mg/l	10.89 ± 0.35	0.75±0.37
NH_3+NH_4 –N, mg/l	1.84±0.39	2.4±2.2
NO_3+NO_2 –N, mg/l	150±60	140±40
Alkalinity, mmol/l	8.5±3.5	12.0±4.3
Turbidity, FNU	250±210	0.9±0.31

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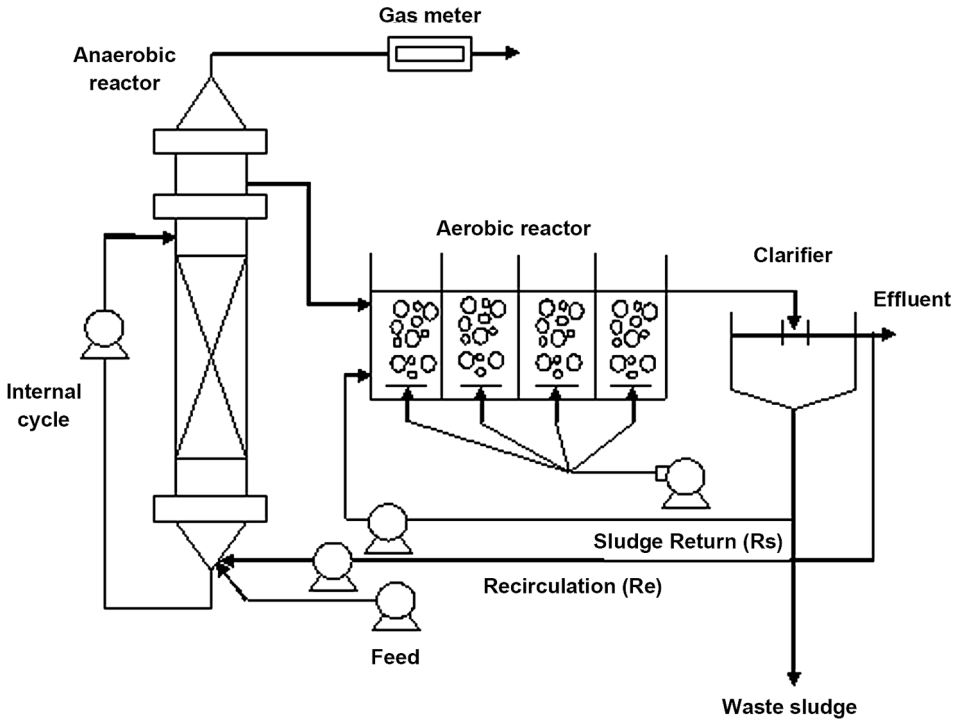
SBR is a form of activated sludge process in which aeration, settlement, and decanting can occur in a single reactor. The process employs a five-stage cycle: fill, react, settle, empty and rest (Environmental Protection Agency, 2000). According to Laitinen *et al.* (2005), SBR system seems suitable for the treatment of landfill leachate in which the volumes and concentrations of the water produced can vary with time. However, some problems arise when using SBR system, such as high deviation values and bulking problems in the system, and also leakage of the sludge. There is a lot of improvement that can be done in SBR system in order to make it more efficient and reliable. Table 8 clearly indicates that the SBR system fluctuates so much. Laitinen *et al.* (2005) also concluded from their studies that both systems, i.e., SBR and MBR, removed total ammonia nitrogen effectively.

Integrated Biological Process

Sometimes, the combination of two types of biological system will lead to high performance for leachate treatment rather than using only one system. Im*et al.* (2001) reported the use of aerobic and anaerobic treatment process in treating leachate. They carried out denitrification and methanogenesis in anaerobic reactor, while organic removal and nitrification of NH_4^+-N were carried out in an aerobic reactor.

Im *et al.* (2001) emphasized the use of this combined reactor that can treat old and new leachate, and the removal rate of COD and BOD was also high. This system can be used for a longer time once installed in a leachate treatment facility. Figure 9 shows the schematic diagram of anaerobic-aerobic system.

Figure 9. Schematic diagram of anaerobic-aerobic system (Im et al., 2001)



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Natural and Ecosystem Treatment

Respect to green environment, manipulation resource of natural and ecosystem without disturbing their chemistry and physically are widely useful. Wetland is one of the natural ecosystem resources that had been applied for treating polluted water through human simulation. In the United Kingdom, this system is called "reed beds" or "reed bed treatment systems" (RBTS), but internationally they are called constructed wetland (CW) (Sector Guidance Note IPPC S5.03, 2007). This system will reduce COD and BOD, oxidize ammoniacal-N, remove suspended solids, and also reduce concentrations of nitrate and phosphorus.

This system depends on the reed to transfer oxygen to their rhizomatous root system, which will stimulate the growth of bacteria in the surrounding soil and in turn will break down the organic substances in the root zone (Environmental Protection Agency, 2000). This treatment system is considered as 'green' and low in capital cost operation because real plant is used. Besides, the system is more natural and can provide habitat for animals. It can be constructed horizontally or vertically. Figure 10 shows the schematic diagram of horizontal RBTS.

Downstream

After complete the upstream process for pretreatment, treatment or additional treatment, leachate cannot directly discharge to river or return back to landfill but it need going to downstream system. The main concern of downstream system is to sort out any components not allowed to river. From the figure 11, the downstream unit operation would be physical processes where sludge will be thickened and filter pressed, and lastly will be dumped into landfill. The treated liquid will be filtered through sand filtration and activated carbon bed to ensure that the effluent released in the river stream follows the discharge standard from legal authority.

Figure 10. The schematic diagram of horizontal reed bed treatment systems (RBTS) (Sector Guidance Note IPPC S5.03, 2007)

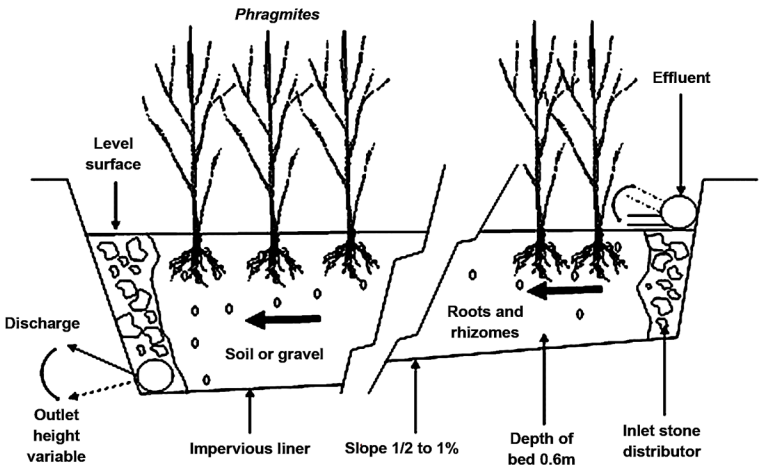

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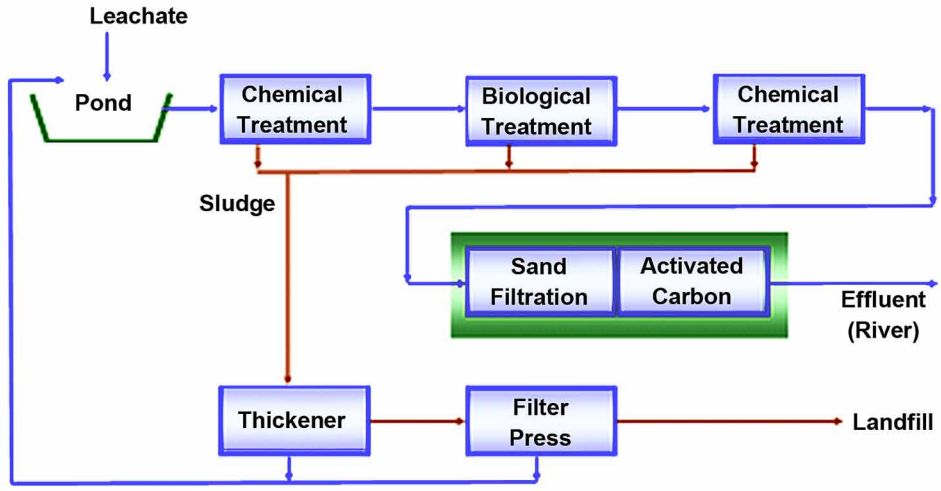
Figure 11. Flow scheme of leachate treatment plant (Damieckiet al., 2007)



There are some rules that need to be followed for the place to discharge the leachate in Malaysia. The point of discharge must be within the boundary of landfill, immediately after the final unit of leachate treatment system. Second, the location must be easily accessible and does not pose any safety hazards to the personnel for inspection side and leachate sampling. The discharged leachate must be through pipe, conduit or channel. Fourth, the discharge point can be physically identified by installing a metal identification sign "Final Discharge Point". Lastly, the point of discharge and its surrounding must be properly maintained in order to be free from any obstruction and hazards during site inspection or leachate sampling (Environmental Quality act and Regulations, 2014).

Although biological treatment methods are known to be simple, cost effective and reliable, there are several limitations to that such as high concentration of ammoniacal nitrogen which is known to inhibit the biological degradation by microorganism, biological treatment gives good performance for treating young landfill leachate but cannot treat old leachate which mainly consists of recalcitrant matters and many substances that inhibit biological activity and low concentration of substrate such as phosphorus which is required by microorganism activities thus required addition of substrates (Tugtas *et al.*, 2013). Therefore, in general, biological treatment is used in combination with physical and chemical processes in order to achieve an effective leachate treatment.

Other alternative method integrated in the downstream system for leachate treatment is photocatalytic oxidation by titanium dioxide (TiO_2) which is widely used as photocatalyst because of its non-toxicity, photochemical stability, and low cost (Chemlal *et al.*, 2014). Using TiO_2 advanced oxidation method has resulted a stabilized leachate treatment, complete refractory fractions mineralization, 90% and 87% reduction of initial BOD_5 and COD for leachate treatment in Oued Smar landfill, Algeria (Chemlal *et al.*, 2014). In addition, techniques such as membrane treatment, bio-electrochemical treatment, ozone treatment, electro coagulation and electro-fenton oxidation were also implemented to increase the effectiveness of leachate treatment (Abu Amr *et al.*,2014; Cheml al *et al.*, 2014; Iaconi et al, 2011; Lin and Chang, 2000; Kashani *et al.*, 2012; Robinson 2005; Tugtas *et al.*, 2013). Using membrane bioreactor for treating leachate was proven to be the most efficient technique, but membrane fouling will be the biggest issue among operators (Robinson 2005; Ahmed and Lan 2012). Using bio-electrochemical

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treatment via microbial fuels cells (MFC) produced high removal of volatile fatty acids (VFA) that can be exploited as polishing step for pre-treated landfill leachate (Tugtas *et al.*, 2013). In addition, it was reported that using Fenton oxidation for mature landfill leachate has achieved 60-86% of COD removal (Socias *et al.*, 2015). Also, ozonation process is also effective for landfill leachate treatment due to high oxidative power that will enhance fragmentation of organic compounds to carbon dioxide (Abu *et al.*, 2014). However, these treatments are not economically acceptable for large scale applications. Hence, strategies based on integrated chemical-physical-biological processes must be further studied to obtain the most feasible system.

Handling and Disposal Activated Sludge

Activated sludge exhibits wide mixture of properties depending on origin and previous treatment step. Thus, before handling or disposing the activated sludge, characterization parameters such as dry matters and volatile solids must be known in order to select the best method to be adopted for further applications. The selection of sludge handling and disposal should also include the energy requirements, cost efficiency of sludge thickening and dewatering, staffing requirements, sludge digestion or stabilization requirements (includes toxic effects of heavy metals or other substances), treatment of side-stream flow (i.e. digester and thickener) and sludge storage. The goal of treatment is to reduce sludge volume and make it suitable for ultimate disposal and also utilizing gas generated if biological treatment involved in the process. Table 9 shows the list of parameters used, their relation to the treatment and disposal steps (Brester*et al.*, 1997).

From Figure 11, the established method for sludge handling and disposal in Malaysia via sludge thickening and filter press method. Thus, only these methods will be described briefly in this part. Sludge thickening is employed to reduce the volume of sludge. There are two basic types of thickeners work by gravity or floatation and use either continuous or batch process. Gravitational thickeners use settling tanks with or without mechanical thickening devices. The design is basically on hydraulic surface loading and solids loading. Sometimes, the use of chemical additives such as lime or polyelectrolyte promotes higher loading rate. Floatation thickening causes sludge solids to rise to the surface where they can be collected via dissolved air floatation process. This process is suitable for activated sludge treatment where solids content of 4% or higher will be obtained. Sludge dewatering reduces the moisture content (60-80%) of the sludge so that it can be more easily disposed of by landfill, incineration, heat drying or composting. Sludge dewatering can be done using several techniques such as belt press filtration, sludge drying beds, vacuum filtration, centrifugation and filter press. Filter press is a plate and frame batch device that has been used for difficult process to dewater the sludge. It has the ability to produce a very dry cake and clear filtrate that makes it favorable for sludge handling. The advantages and disadvantages of filter press are listed in Table 10 (Joint Departments of Army and Air Force USA, 1998).

There are also several methods to dispose activated sludge such as land filling, agricultural use, composting and incineration. For land filling, sludge can be disposed using two method either mono deposits where only sludge is disposed of or mixed deposits where the sludge from municipal waste water treatment plant is disposed of together with the municipal solid waste. Selection of the feasible site has to be fulfilled especially safety distance from residential areas, public roads, river dikes and others. The important point is that the site should not cover even temporarily by inland waters or near to the area of water bases (aquifers). Re-cultivation of the sludge deposit has also been taken into consideration when selecting land filling method (Bresters *et al.*, 1997).

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Table 9. Disposal and use operations parameters (Bresters et al., 1997)

Method of Treatment and Disposal													
		Stabilisation											
Parameter	Sedimentation	aerobic	anaerobic	chemical	thermal	Thickening	Dewatering	drying	Transportation	Landfilling	Composting	Agriculture	Incineration
Temperature		X	X				X	X					X
Density						X		X	X				
Rheological properties							X	X	X	X		X	X
Settleability	X					X	X						
Solids concentration	X	X	X	X	X	X	X	X	X	X	X	X	X
Volatile solids		X	X	X	X				X	X	X	X	X
Digestability			X										
pH		X	X	X			X				X	X	
Volatile acids			X										
Fats and oils		X	X									X	
Heavy metals			X							X	X	X	
Nutrients		X	X								X	X	
Particle Size	X					X	X						
CST						X	X						
Spec. Resistance						X	X						
Compressibility							X						
Centrifugability							X						
Calorific value													X
Leachability										X			
Microbiol properties		X	X								X	X	

*Table 10. Advantages and disadvantages of filter presses **

No.	Advantages	Disadvantages
1	High solids content in cake	Large quantities of inorganic conditioning chemicals are commonly used for filter press
2	Able to dewater hard-to-dewater sludge, although very high chemical conditioning dosage or thermal condition may be required.	High capital cost especially for diaphragm filter presses.
3	Very high solids capture	Noise level caused by feed pumps can be very high
4	Only mechanical device capable to producea cake dry enough to meet landfill requirements in some locations.	Requires grinder or pre-screening equipment on the feed.

*Joint Departments of Army and Air Force USA, (1998)

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Risk of Untreated Leachate to Biological Life

Landfill leachate constitutes a very wide range of serious pollution hazards namely metals and toxic organics that can create environmental problems. It also can be a threat to both groundwater and surface water (Mendoza & Izquierdo, 2008). Various compounds can be found in landfill leachate such as dissolved organic matter, volatile fatty acids, heavy metals and organic xenobiotic micro compounds such as chlorinated solvents, petroleum products and pesticides, making them immediate treatment imperative (Mendoza & Izquierdo, 2008, Zainol*et al.*, 2013; Tugtas *et al.*, 2013; Xie *et al.*, 2014; Lema *et al.*, 1988). Many factors may contribute to the characteristic of landfills leachate, i.e., age, precipitation, climatic conditions, type and composition of waste (depending on the surrounding population) (Zainol *et al.*, 2013; Tugtas *et al.*, 2013; Xie *et al.*, 2014). For example, large amount of biodegradable organic matter contained in young landfills will promote rapid anaerobic fermentation resulting in the production of volatile fatty acids (VFA). In matured landfill, methanogenic microorganisms will convert VFA to biogas such as CH_4 and CO_2 (Renou *et al.*, 2008; Tugtas *et al.*, 2013).

Chemical pollutants contained in the leachate could be absorbed by aquatic species and may pass through the food chain and bio accumulate over long-term exposure if the leachate is not treated effectively (Sanchez-Chardi & Nadal, 2007; Sanchez-Chardi *et al.*, 2007; Long *et al.*, 2010). For example, mercury as contaminants may be stored in specific organ in which will accumulate over time known as bioaccumulation. This substance has the potential to pass on to the next level of consumers known as biomagnifications (Mulamoottil *et al.*, 1999). An understanding of leachate composition and an integrated strategy for risk assessment are crucial and necessary on long term impacts especially on possible adverse effects on human and ecosystem health (Isidori *et al.*, 2003; Baderna *et al.*, 2011). Previous studies

Table 11. Acceptable conditions for discharge leachate (Ministry of Natural Resources and Environment, 2010)

Parameter	Unit	Standard	Parameter	Unit	Standard
Temperature	°C	40	Manganese	mg/l	0.20
pH value		6.0-9.0	Nickel	mg/l	0.20
BOD_5 at 20°C	mg/L	20	Tin	mg/l	0.20
COD	mg/L	400	Zinc	mg/l	2.0
Suspended solids	mg/L	50	Boron	mg/l	1.0
Ammoniacal Nitrogen	mg/L	5.0	Iron(Fe)	mg/l	5.0
Mercury	mg/L	0.005	Silver	mg/l	0.10
Cadmium	mg/L	0.01	Selenium	mg/l	0.02
Chromium, Hexavalent	mg/L	0.05	Barium	mg/l	0.10
Chromium, Trivalent	mg/L	0.20	Fluoride	mg/l	2.0
Arsenic	mg/L	0.05	Formaldehyde	mg/l	0.10
Cyanide	mg/L	0.05	Phenol	mg/l	0.001
Lead	mg/L	0.10	Sulphide	mg/l	0.50
Copper	mg/L	0.20	Oil and Grease	mg/l	5.0
			Colour	*ADMI	100

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reported that ammonia plays an important role in leachate composition and toxicity both for human and ecological because it is a reducing agent with long term persistence (Isidori *et al.*, 2003; Baderna *et al.*, 2011). In vitro study showed that leachate inhibits cell proliferation at low doses probably inducing a reversible cell-cycle arrest at high doses that can lead to death (Baderna *et al.*, 2011). Leachates also have been previously shown to induce abnormal sperm morphology (Bakare *et al.*, 2005) and chromosomal abnormalities in bone marrow of mice, indicating that landfill leachate is genotoxic in mammalian cells (Sang & Li, 2005; Koshy *et al.*, 2007). Furthermore, the involvement of oxidative stress in municipal landfill leachate has induced toxicity in boar sperm (Adedara *et al.*, 2013). Therefore, precaution steps must be taken when dealing with landfills leachate to prevent unnecessary contacts that can cause severe injury to living organism. The risk can be either in the form of acute or chronic toxicity or subtle effect that will accumulate in the body of the exposed organism (Mulamoottil *et al.*, 1999). Therefore, this contaminated liquid must be treated before safely disposed to prevent contamination of water resources. Table 11 shows the specification of leachate discharge standards in Malaysia.

CONCLUSION

Even application of biological process for leachate treatment is not new technology but improvement especially in technical part about of this process is required. Integrated biological process or combination with new technology is needed to be explored due of possibility to increase quality and quantity of leachate treatment. Besides that, understanding about principal, mechanism and reaction of microorganism to leachate are advantages to design great system.

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Chapter 37
Scientific Insights Into Modified and Non-Modified Biomaterials for Sorption of Heavy Metals From Water

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ABSTRACT

Adsorption techniques are widely used for the removal of various classes of pollutants from water due to their mild and facile operating conditions. The operations involved in the adsorption techniques are environmentally friendly, economical, highly selective on pollutants, highly efficient and easily operative. However, the adsorption of heavy metals from water using biomaterials (biosorption) is a relatively new and interesting technique which holds a great potential. Its effectiveness in lowering the heavy metals concentration to sub-ppb levels is appealing and has attracted increasing attention. The technique is believed to replace the existing technologies in the near future. This chapter discusses the prospects of biomaterials in the removal of heavy metals from waste water, the modification techniques that can enhance biosorption efficiency, and the factors influencing the biosorption processes.

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1. INTRODUCTION

The increase in population, advances in technology and excessive use of resources have disturbed the ultimate existence of human beings. Water is the platform from which lives evolved and on which life exists. Notwithstanding, the amount of fresh water necessary to sustain the geometric rise in population is limited. More than one billion people live in a shortage of drinking water, and the figure is expected to reach four billion by 2025 (UNEP 2008). The available fresh water that is unevenly distributed within nations is faced with the problems of climate change, pollution, and inefficient management strategies. No denial, the world is seriously facing water crisis.

The presence of heavy metals (cadmium, mercury, lead, arsenic, chromium, nickel, zinc, and selenium) in the aquatic environment due to industrial, agricultural and domestic activities has confounded the existing problems of water scarcity with pollution. Heavy metals are widely known for their toxicity, bioaccumulation, and their propensity to pose serious threats to the ecosystem (Saleh and Gupta 2012). The conventional methods of removing heavy metals from effluents include flotation, coagulation, chemical precipitation, reverse osmosis, ion exchange, electro-dialysis, ultrafiltration, nano--filtration, *etc*. (Gupta *e*t *a*l., 2012). However, the conventional methods have several disadvantages such as lack of specificity to the metal ions, relatively expensive, and generate excessive sludge as a by-product (Lakherwal 2014).

The use of adsorbents is an efficient way to isolate heavy metals and other pollutants from industrial, agricultural, and domestic effluents (Saleh *e*t *a*l., 2016; Gupta *e*t *a*l., 2013). It has become the most preferred method of heavy metals removal because it is inexpensive, versatile, simple, and highly effective. Despite its advantages over the conventional methods, the pursuit for more efficient, cheap and environmentally-friendly adsorbents has been the focus of researchers in recent years (Ngah *e*t *a*l., 2008; Hua *e*t *a*l., 2012). Biosorption is an emerging technique in this regard, possessing a tremendous scope, especially in the developing countries where potable water has limited accessibility. Biosorption is the technique of utilizing living and non-living biological materials specifically for the purpose of removing contaminants such as heavy metals from aqueous solutions and effluents (Salam *e*t *a*l., 2011; Feng *e*t *a*l., 2011; Demirbas 2008). This chapter, therefore, discusses the application of modified and non-modified biomaterials for efficient heavy metals removal.

The first section of the chapter reviews the pollution and toxicity of heavy metals. The second section of the chapter discusses the adsorbents in use for heavy metals isolation, including activated carbon, nano-materials, biomaterials, and low-cost adsorbents. The application of non-modified and modified biomaterials for the removal of heavy metals is also reviewed in this section. The last section, which is the heart of this chapter discusses the modification strategies associated with biosorbents for efficient adsorption, possible biosorption mechanisms and the factors affecting the biosorption process.

2. POLLUTION AND TOXICITY OF HEAVY METALS

Heavy metals pollution is caused by natural and artificial sources. The volcanic eruptions, erosion of metal deposits and unavoidable atmospheric pollution are the major points of entry of heavy metals naturally into the environment. Nevertheless, nature has an inherent capacity to curtail the impact of natural pollution. Artificial sources of heavy metal pollution are mainly from agricultural activities, tannery operations, mining operations, metal plating activities, production activities of commercial products (*e.g*.

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batteries, paints, pigments, glass, ceramics), leachates from landfills and contaminated groundwater, *etc*. (Förstner and Wittmann 2012). Since the survival and comfort of human beings are directly linked to the above activities, the continuous release of heavy metals into the environment is inevitable.

Cadmium, mercury, lead, arsenic and chromium (even at low concentrations) are regarded as the most toxic heavy metals due to their significant impact on the environment (Tchounwou *e*t *a*l., 2012). They are systemic toxicants classified by the international agency for research on cancer (IARC) and the US EPA as "known or probable" carcinogens with the potential of inducing organ damage. These heavy metals are very much denser than water and the water laden with these heavy metals turns very toxic. The microbial population, which grows on this toxic water also turns toxic. When the water bodies flow into the seas, the polluted microbial population accumulates in the sea bed through which the heavy metals largely enter into the overall food chain of many organisms.

It has been proven that heavy metals affect cellular components and organelles such as the mitochondria, nuclei, cell membrane, lysosomes and enzymes involved in detoxification, metabolism and damage them (Wang and Shi 2001). They interact with cell components such as nuclear proteins and DNA and introduce significant changes to cell cycle leading to carcinogenesis or programmed cell death (Beyersmann and Hartwig 2008). Heavy metals are directly linked to the increased production of reactive oxygen species (ROS) and oxidative stress affecting master regulatory protein and the guardian of the genome p53, thereby increasing susceptibility to cancer and other diseases (Patlolla *e*t *a*l., 2009).

2.1 Cadmium

Cadmium is a heavy metal with environmental and occupational concerns. The anthropogenic sources of cadmium into the environment include the production of nickel-cadmium batteries, pigments, nuclear reactors and alloys. The routes of exposure to cadmium are mainly inhalation and ingestion (ASTDR 2008). Cadmium is a severe gastrointestinal and pulmonary irritant, which can be toxic and poisonous when ingested or inhaled. Acute exposures to cadmium are associated with symptoms such as abdominal pain, pulmonary, hepatic or renal injury, muscle cramps, vertigo, convulsions, shock, burning sensation, and nausea (Baselt and Cravey 1995). The chronic exposure to cadmium is associated with hormonal imbalance and pulmonary adenocarcinomas (Waalkes *e*t *a*l., 1996).

2.2 Mercury

Mercury exists in three different forms in the environment (elemental, organic and inorganic) having varying degrees of toxicity. The most frequently encountered organic species in the environment are the methyl mercury formed by the microbial methylation of the inorganic mercury in soil and water (Dopp *e*t *a*l., 2004). Mercury is a widespread environmental pollutant which causes severe alterations in body tissues and induces a range of adverse health effects. The major routes of exposure to mercury are inhalation, skin absorption, ingestion, skin/eye contact. Mercury is a carcinogen that affects the kidney, eye, nervous and reproductive systems (Leaner *e*t *a*l., 2007). The anthropogenic activities leading to the release of mercury into the environment include the industrial production of electrodes, thermometers, barometers, fluorescent lamps and amalgams (Tchounwou *e*t *a*l., 2003).

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2.3 Lead

Lead occurs naturally in the environment, but the anthropogenic activities such as mining, burning of fossil fuels and manufacturing of pigments, lead acid accumulators and antiknocks in petrol contribute significantly to the release of lead into the environment. The routes of exposure are mainly inhalation, ingestion, and skin/eye contact (ATSDR 1999). Lead is the most systemic toxicant that affects several organs in the body, including the liver, kidney, central nervous system, haematopoietic system, reproductive system and endocrine system. Children are the most vulnerable to lead poisoning and are prone to nervous system breakdown and mental retardation. The reason is that children absorb lead from contaminated water significantly higher than adults (ATSDR 1999). Decreased sperm count in men and spontaneous abortions are the major effects of lead exposure in the adult population (Hertz-Piccioto 2000).

2.4 Arsenic

Arsenic is found in low concentrations in almost all environmental matrices (ATSDR 2000). It exists in organic form as methylated metabolites and in inorganic form as trivalent arsenite and pentavalent arsenate respectively. Arsenic compounds have a wide application in the medical field for the eradication of many diseases (Centeno *e*t *a*l., 2005). However, the anthropogenic sources of arsenic have serious health consequences. The route of exposure of arsenic compounds to our body system includes inhalation, ingestion, skin and eye contact. Arsenic targets organs such as skin, kidneys, liver, gastrointestinal tract and lungs. It affects our respiratory, nervous and reproductive systems (Tchounwou *e*t *a*l., 2003). The major anthropogenic sources of arsenic into the environment include the industrial production of herbicides, insecticides, fungicides and algicides for agricultural purposes.

2.5 Arsenic

The chemistry and toxicology of chromium are complex and interesting. For example, chromium poses detrimental as well as beneficial properties. It exists in two different states in the environment, Cr (III) and Cr (VI) with contrasting toxicities, bioavailability, and mobility. Cr (III) is not mobile and is required for the normal functioning of our body system. Chromium released into the environment from anthropogenic sources is mainly in hexavalent form. It is a toxic pollutant classified as a human carcinogen by many agencies (USEPA 1992). It moves readily through the soil and aquatic environment and is a strong oxidizing agent capable of being absorbed into our body tissues (Park and Jung 2001). The industries with the largest contributions to chromium release into the environment include tannery facilities, metal processing, chromate production, welding, and pigment production.

3. ADSORBENTS

The increase in the density of a fluid within the vicinity of an interphase is termed as adsorption. Adsorption is mainly controlled by physical forces (such as dipole, dispersive forces, or polarization forces) and chemical forces (such as the interaction of electrons between solid particles and the atoms of the liquid or vapour phase) (F. Rouquerol *e*t *a*l 2014). Adsorption on commercial and industrial scale depends solely on the type, quantity, the economic cost and effectiveness of the adsorbent material. The

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substances used as adsorbents can either be of organic or inorganic origin. Regardless of the origins, each adsorbent material should be: mechanically and thermally stable, highly porous, possessing a high surface area with the balance between the micro and macro-pores, easily regenerative, and high affinity for the adsorbate (Czaja *e*t *a*l 2009).

In recent years, adsorptive removal of heavy metals from effluents primarily uses conventional adsorbents such as activated carbon, polymers, activated alumina, silica and zeolite (Mouni *e*t *a*l., 2011; Haladu *e*t *a*l., 2016; Aguado *et al.*, 2009; Motsi *e*t *a*l., 2009). However, of late, the use of modified and non-modified carbon nanotubes (CNT), magnetic nanoparticles (MNP) and metal organic frameworks (MOFs) has received increasing attention for the removal of heavy metals from contaminated water (Gupta *e*t *a*l., 2011; Zagoosh *e*t *a*l., 2013; Khan *e*t *a*l., 2013). The fibrous shape, large external surface area and established mesopores of CNTs are offering higher adsorbing capacity for them. MNPs are very effective and easy to operate; hence they are widely used for the removal of heavy metals. On the other hand, MOFs offer a great potential as their porous surfaces can be easily modified which ultimately leads to the improved selectivity of certain functional groups.

3.1 Activated Carbon

The large surface area and microporous nature of activated carbon, which can be modified by sulfuration, ammonification, oxidation, and coordinated ligand anchorage, has made it a suitable adsorbent for the removal of heavy metals from aqueous solutions (Rivera-Utrilla *e*t *a*l., 2011). Activated carbon produced by carbonizing organic materials is the most widely used adsorbent. Yet, the high cost of the activation process limits its use in wastewater treatment applications. Numerous studies have focused on enhancing the oxygen-containing functional groups on the surface of activated carbon by physical and chemical treatment (Saleh and Danmaliki 2016 [a,b]; Danmaliki and Saleh 2016). Activated carbon is less specific and ineffective in isolating heavy metals from solution when the concentration of heavy metals is too high.

3.2 Nanomaterials

Development of cost-effective and novel nanomaterials for heavy metals treatment is gaining wide interest in recent years. Nanocarbon materials, nanometal particles, and polymer-supported nanoparticles have unique properties that provide high adsorption capacities and selectivity. Nanosized metal oxides, including nanosized cerium oxides, manganese oxides, magnesium oxides, ferric oxides, zinc oxides, aluminium oxides, and titanium oxides provide high surface area and specific affinity for heavy metal removal from aqueous solutions (Hua *e*t *a*l., 2012). Iron oxide nanoparticle based nanomaterials are widely used adsorbents for the remediation of contaminated water due to their favourable physiochemical properties. The removal of chromium was monitored using polypyrrole/Fe_3O_4 magnetic Nano composite. The magnetic nanocomposite was prepared by in situ polymerization of pyrrole monomer and it was tested for its effectiveness in the removal of toxic Cr (VI). The initial concentration of chromium was 200 ppm and there was 100% removal efficiency at pH of 2. Ion exchange and the reduction of the surface of the adsorbent were proposed as the possible mechanism of adsorption (Bhaumika *e*t *a*l., 2011).

The removal of Cd^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+} was monitored using a polymer modified magnetic nanoparticles. Fe_3O_4 magnetic nanoparticles modified with 3-aminopropyltriethoxysilane and copolymers of acrylic acid and crotonic acid were evaluated for the removal of heavy metals from aqueous solution.

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The magnetic nanoparticles removed the metal ions efficiently with high maximum adsorption capacity at pH 5.5 (Ge *e*t *a*l., 2012). Nano zerovalent iron particles have been used as an effective adsorbent for the removal of cadmium in the concentration range of 25-450 ppm. The maximum adsorption capacity and activation energy of the adsorbent were 769.2 mg/g and 54.8 kJ/mol at 297 K respectively (Boparai *e*t *a*l., 2011). The major drawback with nanomaterials is that they are expensive and they require a considerable amount of time for their preparation and functionalization. Additionally, for treating large quantities of waste water an enormous amount of nanomaterials is required.

3.3 Low Cost Adsorbents

Apart from industrial by-products and natural materials, agricultural residues or wastes can also serve as the sustainable source for low-cost adsorbents. Some agricultural residues such as rice husk, wheat bran, sawdust and peanut shell are discarded into the environment as they are available in plenty and having little commercial value (Abdel *et al,*. 2011). Hence, these residues were attempted by researchers as an absorbent for the removal of heavy metals from effluents. Ricordel *et al.* (2001) successfully sequestrated heavy metals from aqueous solutions using activated carbon made from peanut husk and rice husk. The work by Periasamy and Namasivayam (1996) studied employing peanut shell carbon (PHC) for the removal of Cu (II) from waste water. It was interesting to note that PHC exhibited 18 times greater adsorption capacity than commercially available granulated activated carbon (GAC).

Examples of Low-Cost Adsorbent

Activated carbon, Algae, Aragonite shells, Bagasse, Blast furnace slag, Bone chars, Charcoal, Clinopyrrhotite, Coconut coir, Cow-dung ash, Eggshell, Geothite, Immobilised biomass, Lignite, Natural zeolites, Olive stones, Orange juice residue, Peanut husk, Peat, Rice husk, Saw dust, Sepiolite (Orera), Waste straw dust, Waste tea leaves, Bacteria and Fungi.

3.4 Biomaterials

With the advent of adsorption as a waste water treatment technique, the need to match water treatment efficiency with cost effectiveness and environmental sustainability became paramount. Although a variety of adsorbents are already in use, the lookout for novel adsorbents that meet the above three requirements has resulted in enormous research works. Most commercially available adsorbents are either of coal origin or artificially synthesized. The sudden needs to be environmentally conscious have pushed most of these adsorbents unfit for use. It was in the wake of these needs that the application of biological materials as adsorbents was thought of.

The use of biomaterials as adsorbents is a new, but promising and alternative concept, especially in the removal of heavy metals from water. Biosorption and bioaccumulation have sometimes been used interchangeably to describe the removal of contaminants using materials of biological origin. However, while biosorbents involves the use of passive biomaterials, bioaccumulation describes the removal of the contaminants by metabolically active organisms. Phytoremediation and bioremediation also involve treatment of contaminants using biological organisms. Phytoremediation describes living plants ability to sequester contaminants and degrade them to less toxic elements during their metabolic activity. Conversely, bio-remediation is the process of introducing a microorganism into an effluent as to remove its pollutants.

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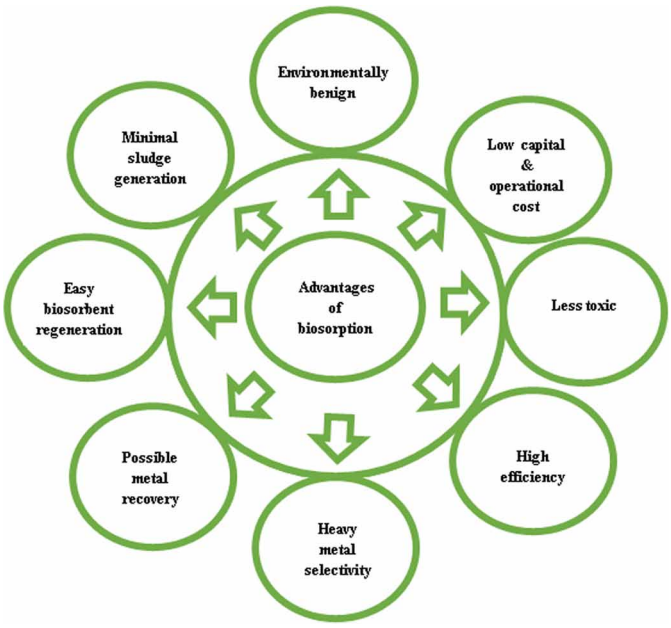
The scope of this write-up will be limited to the use of biosorbents in the sequestration of heavy metals from water non-metabolically. Biosorption has shown high efficiency in the removal of heavy metals from water especially at low concentrations. The use of readily available, inexpensive biological materials has made it widely accepted. It also results in the generation of low quantity biological sludge. Biosorbents can also be regenerated. The advantages of the use of biomaterials for heavy metals treatment are illustrated in Figure 1.

Similar to any adsorption process, the use of biosorbents in the adsorption of heavy metals requires a solid phase and a liquid phase. The liquid phase is made up of the contaminants to be sequestered unto the biosorbents. The passive removal of metals from water by biomaterials requires that the substrate shows high metal uptake, suitable mechanical properties, and selectivity (Davis *et al.*, 2003). Biosorbents removal of heavy metals also depends on its composition of proteins, lignin and carbohydrates that make functional groups such as carboxyl, hydroxyl, and amines available for metal sorption (Kuyucak and Volesky, 1988). In recent times, efforts have been directed towards screening efficient biomaterials, investigating different preparation/modification possibilities and the mechanisms involved in the adsorption of heavy metals on biomaterials and the application of biomaterials in water treatment at large scale (Wang and Chen, 2006). Biosorbents can be used directly or after modification. The following section explains the use of biosorbents with and without modification.

Examples of some biomaterials:

Aloe, Bagasse, Beat sugar sludge, Chitosan, Coconut shell, Coconut coir, Coffee, Corn cobs, Cottonseed hulls, Distillery waste, Green tea, Japanese coarse tea, Jute stick, Kelp and seaweed, Molasses, Newspaper, Nutshells, Palm tree cobs, Pulp-mill waste, Rice hulls, Sunflower seeds, Tea, Wheat straw and Yuzu.

Figure 1. Advantages of biomaterial for heavy water removal



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4. APPLICATION OF BIOMATERIALS IN THE REMOVAL OF HEAVY METALS

4.1 Non-Modified Biomaterials

Biomaterials used with little or no further treatment, alteration or change in their physical or chemical properties is referred to as 'non-modified biomaterials'. It is important to reduce the size of the biomaterials before they can be used as sorbents. As such, within these contexts, grinding biomaterials to powdered form is not referred to as modification because it does not affect its chemical structure. Non-modified biomaterials have been given a particular interest because of their easy availability and application. Despite being untreated, they have adsorption capacities suitable for the removal of different heavy metals. Non-modified biomaterials can be further classified into cellulose or plant materials and animal wastes.

4.2 Plant Waste

Plant cells are made up of cellulose, lignin, hemicellulose, protein, pectic substances, lipids, proteins and other chemical materials (Heredia *et al.,* 1995). These materials provide functional groups that have a high affinity for heavy metals and form chelates or metal complexes, useful for heavy metal adsorption. Cellulosic materials are the most abundant and renewable organic resource on earth (O'Connell, *et al.,* 2008). They are considered inexhaustible because of the huge quantity produced. Photosynthesis aids the production of 10^{11} -10^{12} tons of pure cellulose materials, yearly (O'Connell, *et al.,* 2008). The properties and reactions of cellulose are influenced by factors such as intermolecular interactions, the isolation process employed, chain lengths, cross-linking reactions, crystallinity, distribution of chain-length, functional groups along polymer chains and repeating glucose units (Klemm *et al.,* 2005, Poletto and Zattera, 2013). These factors contribute to the uniqueness of cellulose materials. Cellulose is poly-functional possessing high chain stiffness and is very sensitive to hydrolysis and oxidation of acetal groups (Klemm *et al.,* 2005). This determines its chemistry and method of handling (Klemm *et al.,* 2005). Different cellulosic materials have been used for the removal of heavy metals from aqueous mediums with less modification. In most cases, applying washed, dried and ground wastes of these cellulose materials can be effective enough for the treatment process.

Even micro-organisms such as algae, bacteria, and fungi have been found to adsorb metal ions from solution, forming metal complex effluents. The removal of heavy metals using biomass of dead microorganisms has been given much research attention because of their chemical composition. The sequestration of chromium, lead, and copper from industrial effluents using microorganisms was studied by Illhan *et.al* (Illhan *et al.*, 2004). The influence of pH, temperature and initial concentration on the removal of metal was studied. It was reported that the bacteria *Staphylococcus saprophytics* effectively removed lead and chromium from the effluent. The investigation on the removal of heavy metal from aqueous solution employing *Schizosaccharomyces pombe* (Fission yeast) in free and alginate immobilized cells was performed by Subhashini *et al*. (Subhashini *et al.*, 2011). The parameters such as pH, temperature, and initial concentration were studied. 73% heavy metals removal were achieved using this fungus. The study reported that immobilized cells remove heavy metals better than free cells.

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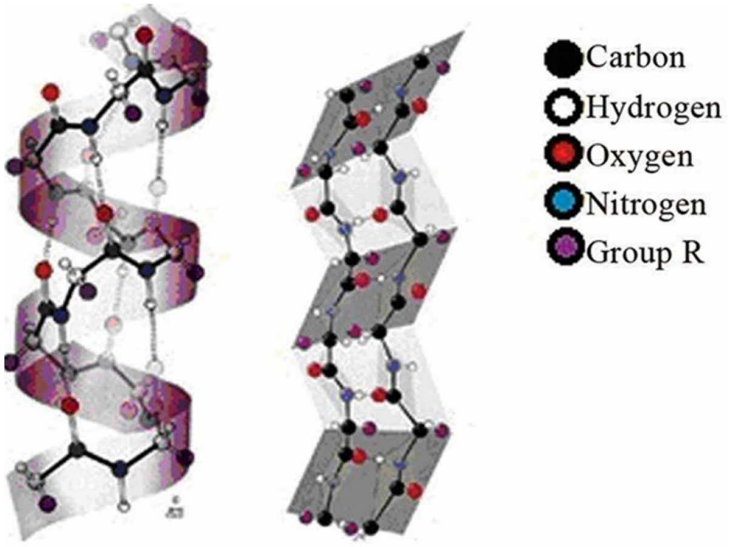
4.3 Animal Waste Biosorption

Animal waste adsorbents are a low-cost option for the removal of heavy metals from solution. The use of animal waste for heavy metal removal from water presents an alternative waste management opportunity. Animal bones (Al-Asheh *et al.,* 2002, Banat *et al.,* 2002, Al-Asheh *et al.,* 1999), chicken feathers (Al-Asheh *et al.,* 2003, Aguayo-Villarreal *et al.,* 2011) and animal horns (Banat *et al.,* 2002) have been successfully applied in removing different heavy metal from aqueous solution. For instance, chicken feathers with minimal treatment were used in the removal of Pb from water (Rosa *et al.,* 2008). Water and ethanol mixed in the ratio of (5:1) were used to rinse the chicken feather and was subsequently dried. When applied in the heavy metal adsorption process, it yielded about 8.3mg/g adsorption capacity at optimal treatment conditions.

The huge generation of animal wastes makes them readily available sorbent for water treatment. Chicken feather for instance constitute about six percent of a bird's total weight (Mittal *et al.,* 2007) while egg shell represents about 11% of an egg's total weight (Ishikawa *et al.,* 2004). They are thus largely generated as waste in poultry industries. The high heavy metal sorption capabilities demonstrated by these materials have been attributed to their keratin content (Banat *et al.,* 2002). They are also hydrophobic as a result of the presence of sterol and biomolecular triphosphate ester layers (Gao *et al.,* 2007). Keratin is a fibrous protein material that forms the main structural components of animal parts such as hooves, teeth, bones, and hair. The structure of Keratin and their corresponding elements that make up the functional groups are shown in Figure 2. Keratin monomers are arranged in bundles forming intermediate, tough filaments. They have high tensile strength, high surface area and are insoluble (Suyama *et al.,* 1996). They are particularly rich in carboxyl, hydroxyl and amines functional group which make them readily made for use as an adsorbent in water treatment. Avian keratin fiber; a keratin protein type contained in bird feathers showed high stability and removal efficiency over a wide pH range in the removal of copper, chromium, lead, uranium and mercury from water (Kar *et al.,* 2004).

Figure 2. The α-helix and β-pleated sheet structure of Keratin and their corresponding elements (Belamino et al., 2012)



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4.4 Modified Biomaterials

Numerous factors affect the suitability for use and adsorption capacity of unmodified biomaterials. The presence of the different functional group, heterogeneous/irregular surface areas, pore size distribution and other physical or chemical factors may influence the removal efficiency of a biosorbent (Gautam *et al.,* 2014). In order to increase their sorption properties and enhance their metal selectivity, biomaterials irrespective of their source (plant or animals) are modified (Gautam *et al.,* 2014). Several adsorbents are derived from the modification of biomaterials. This involves the treatment and subsequent alteration in the physical or chemical structure of the materials.

The reason for biomaterial modification has been supported by different researchers that compare the removal efficiency of modified and non-modified biomaterials in heavy metal sorption. For instance, in the removal of copper and zinc from waste water, chicken feathers treated with alkaline solutions showed higher adsorption capacities than those treated with anionic surfactant and untreated chicken feathers (Al-Asheh *et al.,* 2003). The findings of the work are illustrated in Figure 3. and 4 respectively.

Modified and non-modified (native) sugar beet pulp showed similar results in the removal of nickel and copper from water (Reddad *et al.,* 2002). Raw sugar beet pulp was modified by saponification and acid-base extraction. An evaluation of the resulting effect of these modifications on the biosorbents binding properties revealed that that base extracted pulp and saponified pulb displayed higher metal sequestration compared to the raw pulp. The study also showed that the functional group contained in the biomaterials has a tremendous impact on their sorption capacity. The above fact suggests that when biomaterials are modified, different functional groups are added which in turn increases the number of active sites available for metal binding (Lu *et al.,* 2009).

Figure 3. Sorption capacities of alkaline treated, anionic surfactant treated and untreated chicken feather in the removal of Cu from waste water (Al-Asheh et al., 2003)

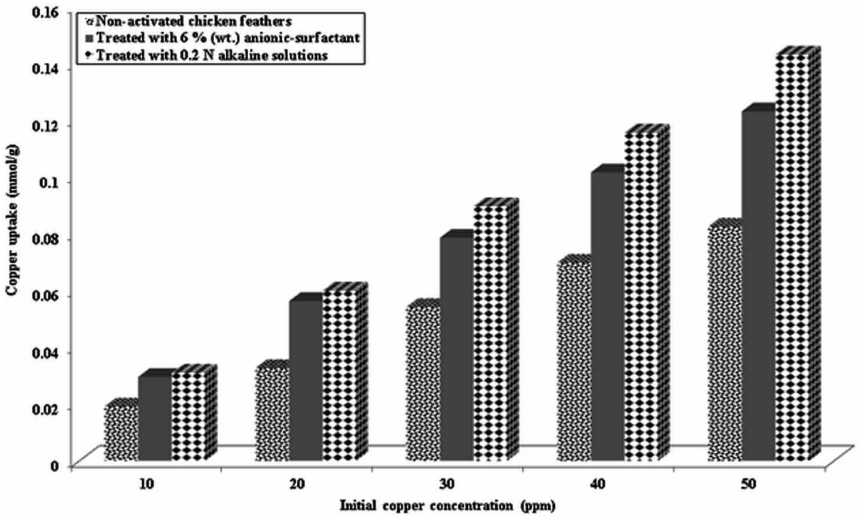

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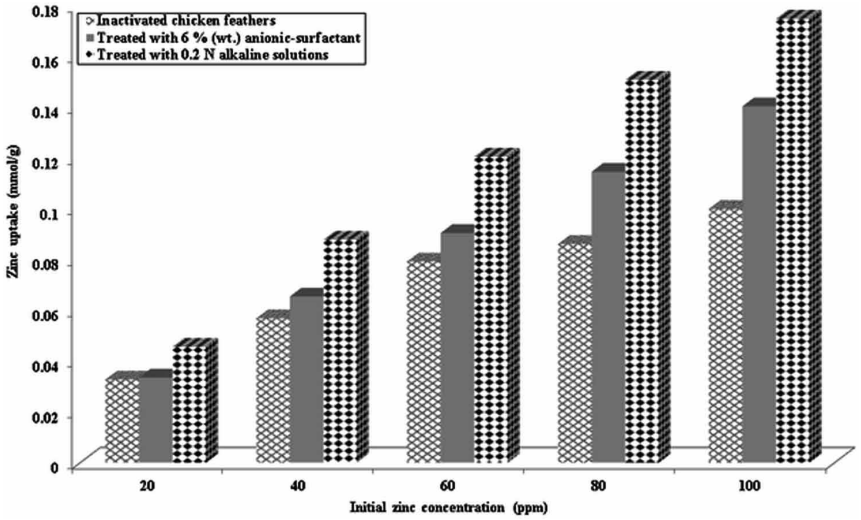
Figure 4. Sorption capacities of alkaline treated, anionic surfactant treated and untreated chicken feather in the removal of Zn from waste water (Al-Asheh et al., 2003)



5. MODIFICATION OF BIO-SORBENTS

The objective of the modification is to improve the surface area of biosorbents thereby increasing its sorption capacity. Modification is a kind of pre-treatment on bio sorbents. The modification discards the impurities on the surface of the biosorbents thus converting the surface into active sites readily available for sorption (Huang and Huang, 1996). It also imparts adequate structural stability and improves the adsorption potential of bio-sorbents. Modification can be accomplished either by physical or chemical methods. However, before going for any modification it is necessary to understand the parameters which influence the adsorption capacity of biosorbents.

5.1 Physical Modification

Physical modification of biosorbents involves the activation of the sorbent capability or increase in the adsorption capacity of biosorbents by heating or drying at optimum temperature.

5.2 Chemical Modification

Chemical modification of biosorbents can be broadly classified into two categories. The first one is monomer-grafting, in which specific groups are attached to the substrate. The grafting is again classified into, photografting, high energy radiation grafting and chemical initiation grafting. The other one is a direct modification where the functional groups are attached to the hydroxyl groups of substrate through chemical reactions. The chemical reactions involved in the modification are esterification, etherification, halogenations, oxidation, alkali treatment and silynation (Hokkanen, *et al*., 2016).

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5.3 Surface Functionalization

Surface modification is the process of modifying the surface of biomaterials such that its physical, chemical and biological characteristics are entirely different from its original state. The surface characteristics such as roughness, hydrophilicity, surface charge, surface energy, biocompatibility, and reactivity are altered on the surface of the biomaterials. Surface functionalization is a kind of surface modification. It is the phenomenon of introducing specific functional groups onto the surface of biosorbents to increase the removal efficiency of metal ions (Ihsanullah *et al.*, 2015)

5.4 Nanoparticle Functionalized Biosorbents

Nanoparticles are nano-sized particle possessing very large surface area. The atoms on the nanoparticles are unsaturated and can attach to any atoms (Farnad *et al*., 2012). Nano-particles due to their surface functionality and high surface area to volume ratio display very high adsorption capacity and efficiency (Fei *et al*., 2012). It's because of that there is a widespread interest among the researchers to employ nanoparticles in the adsorption of heavy metals from effluents. Of late, the surface of nanoparticles is functionalised to improve their selectivity of metal ions from effluents. Since the selectivity and efficiency are extremely high, there is a growing need for nanoparticle functionalised biosorbents for heavy metals sequestration in aqueous solution.

6. FACTORS INFLUENCING BIOSORPTION

The predominant factors that affect the biosorption processes are pH, temperature, initial metal ion concentration, biomass concentration, contact time and particle size.

6.1 pH

pH is the most important parameter that can significantly influence the biosorption process. It affects the solution chemistry of the metals and disturbs the functional group of the biomass (Das *et al.*, 2008). pH should be neither too high nor too low. It has been found that at a high acidic medium of pH close to 2, the adsorption of metal ions is almost nil. Therefore, the pH should be close to neutral (Ojedokun and Bello, 2016).

6.2 Temperature

The increase in temperature increases the adsorption potential of biomaterials. This could be due to the diffusion of metal ions through the solution as the viscosity of the solution reduces owing to the increase in temperature. It has been reported that at a temperature range of 25-35˚C, temperature does not have an influence on biosorption process (Das *et al*., 2008).

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6.3 Adsorbent Concentration

The binding sites for the metal ions are offered by the adsorbent. Hence, the concentration of absorbent has a profound influence on adsorption. Adsorbent concentration in the solution influences the specific uptake. The increase in adsorbent concentration can either increase or decrease the adsorption of metal ions. For some metal ions increase in the biomass favors adsorption whilst for other metal ions decrease in adsorbent concentration supports adsorption (Ihsanullah *et al*., 2015).

6.4 Ionic Strength of Metal Ions

The Ionic strength of metal ions also can affect the adsorption of heavy metal ions onto the biomass substrate. In general, an increase in ionic strength of metal ions has a negative effect on the sorption process. The detrimental effect could be due to two facts. Firstly, increasing ionic strength reduces the activity coefficients of metal ions, thereby reducing the transfer of metal ions onto the biomaterials. Secondly, at the high ionic strength (metal ions) formation of electrical double layer occurs between cations and biomass substrate hindering adsorption. The adsorption process is also affected by the contention of different metal ions which are trying to accommodate the limited active sites of the substrate (Ihsanullah *et al*., 2015).

6.5 Contact Time

The contact time also can affect the adsorption of metal ions onto the biomass. For batch adsorption process, it is very important to define the optimum contact time to attain maximum removal of heavy metal ions (Ojedokun and Bello, 2016). At large, longer contact time increases the chances of removal of metal ions from the effluents. However, this holds good until an equilibrium is achieved. The equilibrium is highly determined by the initial concentration of metal ions. By and large, when the initial strength of metal ions is low, the attainment of equilibrium is very rapid. Nonetheless, in few studies, it has also been reported that concentration of metal ions has no effect on adsorption.

6.6 Particle Size

The decrease in particle size of biomaterials increases its adsorption capacity as a reduction in particle size increases the surface area of the substrate (Somasani, 2012).

7. MECHANISM OF HEAVY METAL ADSORPTION BY BIOMATERIALS

Biosorption is the process of removal of metal ions from aqueous solutions by employing certain biomass. The metal biosorption by biomass mainly depends on the functional groups it possesses.

The most important functional groups are carbonyl (ketone), carboxyl, sulfhydryl (thiol), sulfonate, thioether, amine, secondary amine, amide, imine imidazole, phosphonate, and phosphodiester. The possible binding combination between functional groups and heavy metal ions is presented in Figure 5 (Zhang, 2014). Biomass involved in the biosorption can be living or non-living (Prabhakaran, 2006). The use of living organisms is called bio-accumulation. There are some operational difficulties while

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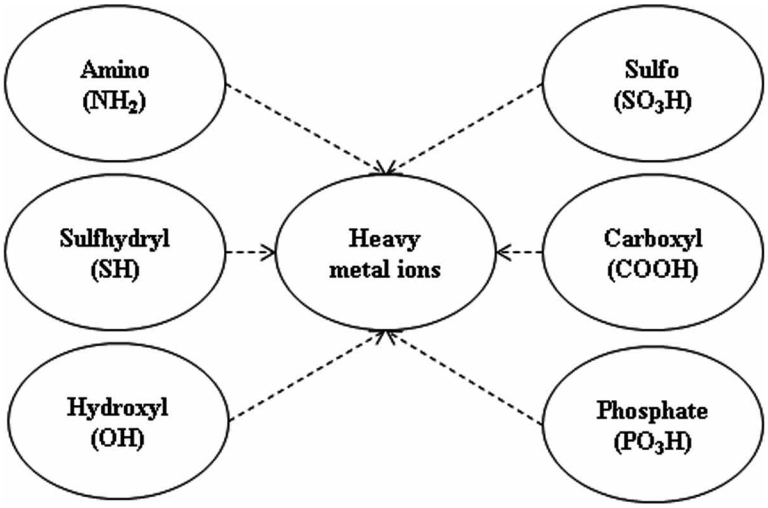
Figure 5. The possible binding combination between functional groups and heavy metal ions



using live biomass. The industrial effluents, in general, carry toxic metals of high concentration. The pH of the effluents is either too high or low where living organisms cannot sustain. Also, living cells require nutrients and increase the BOC and COD of effluents. Hence, bioaccumulation is not viable for all cases of adsorption of heavy metals. On the other hand, the non-living organisms are not affected by the concentration of heavy metals ions or by the pH of the effluents (Al-Qodah, 2006). Further, dead cells are inexpensive and need less maintenance. Above all, dead cells can be easily regenerated and reused. However, it is a developing technique and is seen as a potential process of removal of heavy metals from industrial effluents.

It is well known that the biosorption is an interaction between a sorbent and sorbate. The sorbent also termed as bio-sorbent or bio-material or substrate is in the solid phase. The sorbate, which is metal ions, in this case, is dissolved in the liquid phase. The liquid phase solvent is water here. The sorbate gets attracted to the sorbent due to the higher affinity between them when they come into contact with each other. The sorption process continues till an equilibrium reaches between sorbent and sorbate. The extent of sorbent affinity for the sorbate decides the sorbate distribution between solid and liquid phases (Das *et al.*, 2008).

The process of metal biosorption in living cells (bio-accumulation) is a two-step phenomenon. In the first step, the metals ions are adsorbed onto the surface of cells by interactions between metal ions and functional groups present on the surface of cells. The metal ion comes across the cell walls. The cell comprises of a wide range of polysaccharides and proteins and hence offers a number of active sites capable of attaching metal ions. Microorganisms *viz.* algae, bacteria, fungi display different adsorption capacity. The variance in the adsorption potential of microorganism is due to the variance in the cell wall composition of them. Algal cells are cellulosic. The metal binding groups in the microbe are carboxylates, amines, imidazoles, phosphates, sulfhydryls, sulfates and hydroxyls. Among them, amines and imidazoles are positively charged, when protonated they show an affinity towards negatively charged metal ions. The cell walls of bacteria are mainly comprised of peptidoglycans. Chiton and chitosan make up the cell walls of fungi. Of the two steps, the first step passive biosorption is independent of metabolism. The step takes place rapidly by a single or a combination of the below binding mechanism: coordination,

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complexation, ion exchange, physical adsorption (*e.g.* electrostatic) or inorganic micro precipitation. The second step is the active biosorption, where the metal ions penetrate the cell wall and enter into the cells.

Metal uptake by non-living cells is mainly in passive mode. The metal uptake takes place in two steps; passive uptake which takes place rapidly and active uptake which happens slowly. The first stage is more of physical adsorption where adsorption is at the surface of the cell. The adsorption reaches equilibrium within 30-40 min. The passive step is mainly due to the functional groups on the surface of the cell walls. The active mode is dependent on the metabolism and is associated with metal transport and deposition.

8. SUMMARY AND OUTLOOK

Thus, the chapter elaborated on the scope of biomaterials in the context of heavy metals removal from waste water or effluents. The chapter also discussed the modification of biosorbents and parameters influencing the biosorption process. The conventional method of heavy metal removal from effluents is inefficient, non-selective, expensive and time-consuming. On the other hand, the non-conventional techniques are highly efficient and selective. There are numerous non-conventional modes of heavy water removal from effluents. Biosorption is one such alternative method which has been gaining interest recently because of its simple operation, high efficiency, and economics. Also, biosorption offers the flexibility of trying out with different biomass as there is a wide variety of biomaterials availability. Further, a number of modification techniques are available to improve the adsorption capacity of biomaterials. As stated in the article, biosorption is a developing technology and a lot of augmentations are underway to make the technique more dependable. There is no doubt that the technology would be more established in the near future.

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Section 4
Utilization and Application

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Chapter 38
Waste Disposal:
Sustainable Waste Treatments and Facility Siting Concerns

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ABSTRACT

Through the human municipality growing and industrialization process, productions of municipal solid waste have been growing in parallel line. The properties and composition of municipal solid waste as the main solid waste produced by human has cultural, regional, social habits and behavior, beside the economic condition, influences the properties and compositions of waste disposal, which contains process that start after collecting and transporting MSW to landfill site. After site selection, the process of recycling, waste composting and incineration will be assessed as intermediate disposal methods. Our final goal in waste disposal focused on environmental protection. This chapter will have a review on recycling merits and as effective ecofriendly methods for disposing municipal solid waste (MSW) for saving greenhouse gases (GHGs). Incineration as a commercial waste disposal will also be reviewed. Making decision about waste disposal is a multi-criteria issue because of MSW mixture, climacteric of area, cultural and economic condition, technical support, and environmental impact.

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INTRODUCTION

Civilization and industrialization cause to produce of municipal solid waste (Parfitt, Barthel et al. 2010, Lim, Chen et al. 2013). Global solid waste production was 1636 million tons per year(Robinson 2009), meanwhile (Soltani, Hewage et al. 2015) indicate that ten years ago global MSW production was 0.6 billion tones /year, so it equal 0.64 kg of MSW / person /day and nowadays MSW generation had been reached to 1.3 billion tones /year which is equal to 1.2 kg /person/day. For the year of 2025 municipal solid waste production is estimated to reach 2.2 billion tons per year (Soltani, Hewage et al. 2015). Most common waste disposal methods are incineration, composting, recycling and landfilling (Magrinho, Didelet et al. 2006, Narayana 2009).Nevertheless some literatures indicate to recycling and landfilling as final waste disposal(Demirbas 2011). As a matter of fact, municipal solid waste (MSW) has mutable composition, with the main ingredients being; (40–60%) edible waste Products; (20%) paper and cardboard; and up to 40% glass plastic and metal (Costa, García et al. 1991). Meanwhile, Zhang et al. (2015) presented their waste disposal research on long term manned spacecraft and(Tanabe & Hoshino 2015)concentrated on secondary waste generated from wastewater treatment and as well as these issues should be added to our waste disposal subject, but we will concentrate on the ground side of waste disposal . With considering specification and characteristic of MSW, process of waste disposal should be planned. A fundamental activity, which should be in the first level of importance, is the site selection. Following siting process is another critical basic; managing recycling metals (mostly iron), plastic, paper and glass will be carried out. Other disposal methods that are the same as incineration and composting, decrease the volume of MSW and increase the suitability of application in other industry such as filler in construction (incineration ash) or agricultural nutrient (compost). Based on the local, national, and global limitation, merit of this chain of managing waste system may be arranged in different respect. Managing system for waste disposal mainly depends on the composition of MSW and the rate of development has the most critical effect on mixture of solid waste as well as social and regional factors (Denafas, Ruzgas et al. 2014).

SITE SELECTION

One of the most important parts of waste disposal process is site selection, which nowadays going on to be converted as critical factors by countries such as China(Zheng, Song et al. 2014), Brazil (Kannan, de Sousa Jabbour et al. 2014) and India(Suthar & Sajwan 2014) These countries are improving their standards to tackle this issue. Also Swartzbaugh (1993) mentioned that site selection is one of the three major phases in his presented method in USA, and the strategy and planning of waste disposal starts after site selection .

Critical Factors

There are many effective elements, which normally considered for site selection. Ekmekçioğlu et al. (2010) compared four alternative locations in Turkey for selection of best site for waste disposal. They carried out the study considering elements such as hydrology, topography and soils, adjacent land use, climate, flora and fauna, site capacity, road access and cost of the land. Some of the related elements and their relationship is presented based on obtained data from researches. The following points are related researchers on above-mentioned factors in siting issues:

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- Generally, sites with slopes exceeding 1:5 are not considered good, as there might be a risk of soil erosion (Tadros 2009).
- The leaching process has critical impact on the environment, depends on two factors: The landfill hydrology and, the geochemistry of landfill material (Johnson, Richner et al. 1998). Hydrological factor is the major factor that should be considered for subsequent treatment of leachates beside the leachate quantity data (Tatsi & Zouboulis 2002).
- Site capacity is considered as the key in deciding factor in fuzzy method of Turkey (Ekmekçioğlu, Kaya et al. 2010), for selecting waste disposal site between four nominated locations.
- The efficiency of municipal solid waste (MSW), depends on two major factors, transport capacity and manpower availability(Sharholy, Ahmad et al. 2008).
- Public health and environmental protection are the fundamental consideration for site selection (Önüt and Soner 2008).
- Flora and fauna and human health are reported as most important environmental risk in recycling solid waste (Pappu, Saxena et al. 2007).

Software and Analyzing Technique Application in Site Selection

During recent decades, there has been a rapid growth of attention in the application of computer base program for managing environmental problems (Ijäs, Kuitunen et al. 2010). As previously mentioned, many factors affect site selection. Furthermore, these elements also have internal and external correlation and limitation so application of mathematical and technical software will be suitable in the selection process. Recently, a mixture of these techniques have been used in various researches to show a more clear and trustworthy picture. Önüt and Soner (2008) used AHP, TOPSIS and MCDA, Şener et al. (2011) applied GIS and AHP, Shahabi et al. (2014) used from AHP and GIS. These techniques are notused specifically only for waste disposal method or site selection but also are widely applied in many sides of knowledge body. Some of these techniques are mathematical and usually subjective considerations or may ignore qualitative. Decision maker can easily use linguistic terms to describe a value as an alternative. Some of the well-known methods (abbreviation) are presented and defined As follows (Soltani, Hewage et al. 2015); AHP (analytical hierarchy process)

- TOPSIS (technique for order preference by similarity to ideal solution)
- MCDA (multiple criteria decision analysis)
- MILP (mixed integer linear programming)
- RIAM (rapid Impact Assessment Matrix)
- WLC (weighted linear combination)
- GIS (geographic information system)

Fuzzy Multiple Criteria Analysis (FMCA)

Based on the fundamental of this method, user should find the main criterion and then assess multi criteria through proposed methodology. The weights for selection criteria can be determined by fuzzy pairwise comparison matrices of Analytic Hierarchy Process (AHP). Furthermore, relative importance of the selection criteria could be determined by a fuzzy AHP procedure. This method had been used

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successfully by Önüt and Soner (2008), and Ekmekçioğlu et al. (2010) in Turkey .They reported that MCA method is a suitable assessment system for both site selection and disposal method.

Geographic Information System (GIS)

In a general sense, Geographic Information System (GIS) or spatial management of risk (Brugnot 2010), is a computer base information system, which designed to relate unrelated information of which key index variable is location. GIS had been applied to the water management, land researches and environmental risk assessment. GIS is also considered powerful decision supportive tools capable of performing spatial engineering analysis in different environmental modeling applications(Lukasheh, Droste et al. 2001). GIS had been used successfully in landfill siting by using vehicle routing and scheduling in the collection of solid waste(Chang, Lu et al. 1997).Nowadays, GIS is also being used at biogas plant sites in Finland(Höhn, Lehtonen et al. 2014), landfill site at Saqqez city in Iran(Shahabi, Keihanfard et al. 2014), and air pollution mapping in urban area(Kumar, Mohan et al. 2015).

Mixed Integer Linear Programming (MILP)

This is an optimizing program that is used for subjects, in which all or some of the variables are integers only (Sawik 2011). After collecting all related information about feasibility or optimization of linearly varying single or multiple variables, it can be applied as an engineering tool for waste disposal (Balaman & Selim 2014., Vadenbo, Hellweg et al. 2014). The adaptability of this system makes it suitable for various researches such as determining optimal recycling program (Baetz and Neebe 1994), environmental impacts(Chang, Yang et al. 1996), recycling waste(Louis and Shih 2007) rivers logistic activities.

Rapid Impact Assessment Matrix (RIAM)

Many traditional methods, which are usually applied for environmental impact assessment (EIA), produce a lot of data and information (quantitative and qualitative). Judgment on the same basis and giving a clear picture for permanent judgment are the main objectives in these issues. The computerized rapid impact assessment matrix (RIAM) can show enhanced graphical and clear pictures of matrix information. Furthermore, it gives the opportunity to evaluate development options(Pastakia & Jensen 1998). The original rapid impact assessment matrix has five evaluation criteria(Pastakia & Jensen 1998) contain: A1: Impact importance, A2: Magnitude, B1: Permanence, B2: Reversibility, and B3: Cumulatively .Depending on the environmental impact assessment(EIA) the matrix can be adjusted. Some of the real studies, which were carried out with above mentioned computer base method, are presented in Table 1.

MUNICIPAL SOLID WASTE RECYCLING

According to the report of Ang (2008), which was carried out about economic development, in the long run, of energy consumption and pollutant emission in Malaysia. Pollution and energy usage have positive relation. Malaysia as a leading country in tropical tourism have more than 261 active landfills (Kamaruddin, Yusoff et al. 2014)and previous report showed that the number of landfills was 230(Alkassasbeh, Heng et al. 2009). In five years there was 11.87 percent of growth, which gives a clear picture

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Table 1. Some real experiences with applied method for siting projects

Year/Authors	Country	Methods	Objective	Result
(Batarseh, Reinhart, & Berge, 2010)	India	RIAM	Select new site for waste disposal	Suitable methods for establishing the waste disposal facility in any urban center
(Ghose, Dikshit, & Sharma, 2006)	India	GIS	planning an effective solid waste management system	Proposed model have high efficiency in any kind of waste management
(Ijäs et al., 2010)	Finland	RIAM	1-possibilities of enlarging the scoring system 2-adjustability in different situations	This method is a conservative in character for judgment.
(Visvanathan, Visvanthan, Yin, & Karthikeyan, 2010)	Finland	GIS	1-spatial distribution 2-amount of potential biomass for biogas	GIS gives the most suitable location identification
(Ekmekçioğlu et al., 2010)	Turkey	Fuzzy multi criteria	disposal method and site selection	Suitable method for siting and disposal method
(Onüt & Soner, 2008)	Turkey	Fuzzy multi criteria	Solid waste transshipment site selection	Mathematical models can be combined with the existing method
(Shahabi et al., 2013)	Malaysia	GIS,AHP,WLC and Boolean logic	Waste disposal site locating in Saqqez	AHP and WLChad better decision making powers for locating landfill site
(De Feo & De Gisi, 2014)	Italy	MCDA,GIS	Minimizes the wasting of space for the siting	Better results in Combination model

about the future scenario of waste disposal. Increasing maintenance cost on one hand and lack of land on the other hand are the factors for finding another alternative method for waste disposal(Zia, Bhatti et al. 2007). Waste disposal together with in homogenous nature of municipal solid waste puts more pressure on effective disposal methods, when considering socio-economic criteria is a multi-environmental project(Soltani, Hewage et al. 2015).Installation of incineration facilities is surrounded by serious challenge. Meanwhile, recycling opportunities and organic material treatment are available as replacements. Furthermore, recycling contain GHGs saving merit(Mohareb, Warith et al. 2008).

Literature Review

Waste disposal is considered as a social and political issue all around the globe . Recycling is a major section of waste disposal and could be considered as a valid response to a critically catastrophic environmental crisis (Beal 2012). More than 90% of municipal solid waste (MSW) in Indian cities, disposed of, unscientifically in open damp and landfilling method (Sharholy, Ahmad et al. 2008).In order to earn sustainable conversion of MSW to useful products, improving recycling process is the key (Read 1999). Also for most municipalities, recycling had been proved costly in compare with landfilling(Lave, Hendrickson et al. 1999). Meanwhile, in economic assessment of literature, cost of landfill disposal is lower than recycling. However, after considering the externalities, recycling could be presented as economically efficient(Lavee 2007). Affluent countries (mostly developed countries) provide substantial financial and supervisory capitals for recycling waste fractions, such as metals, glass, plastics, and paper. In contrast,

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for developing economies, recycling is an economic activity in certain sectors of the society(Sanneh, Hu et al. 2011).Survey results for population estimation of the cyclists in various slums shows that, in 90,000 population area 1500 cyclists are there(Agarwal, Singhmar et al. 2005) and their income is sufficient for food and accommodation for a day. In developed countries or some parts of developing countries, social charity groups are working on recycling in living complex(Council & Hawkins 2014). To sum it up, social aspect of waste disposal is highly correlated to economic condition and developing rate of civilization area. On the other hand, land availability for waste disposal plays a critical role in waste disposal policy. Currently, zero waste strategy is reviewed by(Cole, Osmani et al. 2014). England (Read 1999) and Japan (Sakai 1996, Lim, Chen et al. 2013) are suitable samples for recycling care, methods and strategies . There are different reports on recyclable percentage of municipal solid waste such as 25%(Metin, Eröztürk et al. 2003), 50%(Holloway 1989) and based on a questioner study carried out by (Lavee 2007) shows that recycling ranges from 10% to 80%. In the light of this, prediction of the recyclable component should be made by studying the percentage composition of each material in MSW, such as plastic, paper, metals and glasses (Saeed, Hassan et al. 2009). Normally, Volume % of recyclable material in MSW is many times higher than weight %. This could be a fundamental reason of importance for recycling in waste disposal especially on the medium and large sized municipalities(Lavee 2007). Electricity consumption in material recovery facility ranges from 4.7 to 7.8 kWh for each metric ton of solid waste impute (Pressley, Levis et al. 2015). Consequently, in any site with comparing global price of raw materials and recovery cost, efficiency of recycling can be calculated. International standard organization (ISO) published two specific environmental standard (Standardization 1997, Standardization 2006) for life cycle assessment, which are widely applied for MSW management process(Diaz & Warith 2006). Environmental justifications of recycling are mentioned by Daskalopoulos et al. (1997) are as follows:

- Move towards sustainable economies by conservation of non-renewable resources
- Energy consumption due to production process will decrease
- Significant decrease in cost of waste management
- Increasing the landfill life
- Pollutant emissions due to production and waste disposal will decrease
- Benefits of participation in environmental education

Recyclable materials are divided into sub materials, which depend on industrialization rate and packaging in food industry. Sub materials for plastic, paper, glass and Aluminum presented by Agarwal et al. (2005). According to Palmer et al. (1997) the least expensive of the policies for waste disposal (aluminum, paper plastic and steel) is deposit/refund.

Recyclable Plastic Materials

Plastics are widely used in humankind's life. Furthermore, plastic production in society is higher than steel, and is increasing year by year(Yoshioka & Grause 2015). Percentage of plastic solid waste in MSW is also increasing (Al-Salem, Lettieri et al. 2009). Recycling is the best method for treatment of plastic materials considering stable chemical and physical characteristic(Li, Wu et al. 2015) . Specially assessment case study in Spain shows that high-density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET), polyvinylchloride (PVC), expanded polystyrene (EPS), poly-

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styrene (PS), liquid packaging board (LPB), and material recover facility(MRF) are detected in MSW (Bovea, Ibáñez-Forés et al. 2010). Major plastic sources are PVC and PET(Yoshioka & Grause 2015). According to Holloway (1989), steam separation method in municipal solid waste recycling have higher efficiency in recycling of plastic materials. Quality of recycled plastic vary widely in terms of color, mixed materials and density meanwhile, through the different types of plastic materials, PET recycling framework can also be considered as an acceptable method for preparation of raw material. High quality recycled PET cab be used as a raw material in different industries (Yoshioka & Grause 2015). According to Scheirs and Kaminsky (2006)and Al-Salem et al. (2009), higher quality and process of separation in recycling plastic such as tertiary and quaternary treatment scheme following primary and secondary treatment technologies and schedules, could be considered as a robust, worse scientific and traditional investigation. Preliminary researches such as (Yoshioka, Sato et al. 1994, Paszun and Spychaj 1997) tried chemical treatment for recycling. Manufacturing high quality carbon for phenol adsorption was carried out by Parra, Ania et al. (2004). Recent researches are focused on hydrocyclonis separation (Yuan, Fu et al. 2015), froth flotation as recycling technology (Wang, Wang et al. 2015), and using waste PETs as filler in phenolic resin mold (İyim & Orbay 2015) . Worldwide plastic production and power application for producing in plastic manufactories consumes 8 percent of total oil production. In Europe and USA, plastic recycling has reached to 26% and 9% respectively, which clearly shows that recycling industry have great scope for improvement (http://www.worldwatch.org 2012).

Recyclable Paper Materials

The domestic per capita consumption of board and paper in South Asia and India is 53kg,11kg and 6.5 kg respectively (Pati, Vrat et al. 2008). Paper as a renewable source material, is the major part of municipal solid waste such as white paper, mixed shredded paper, fresh newspaper, carton and brown packing paper, tetrapack (Agarwal, Singhmar et al. 2005). Based on the three years case study carried out by Metin et al. (2003) on 60 municipalities,in Turkey ;paper including cardboard is recognised as the main constituent in MSW. The savings of recycling for the paper products are smaller than non-renewable materials in the case of GHGs emission (Björklund and Finnveden 2005). On the other hand, paper quality, energy source at the mill and energy avoided by incineration process are the most effective elements in ranking between incineration and recycling method selection for paper (Figure 1).

Recyclable Aluminium and Glass

Aluminium production process consumes a majority source of power in society. In commercial area, aluminium and paper are the most recyclable solid waste. Nevertheless, in tourism area, putrescible material, such as aluminium and paper should be recycled(Diamadopoulos, Koutsantonakis et al. 1995). In municipal solid waste incineration, more than 90% of the aluminium and cooper is transferred to slag(Wäger, Eugster et al. 2005). This slag cab be used for cement production (Kikuchi 2001, Ferreira, Ribeiro et al. 2003). In many countries, zeolite is recognized as suitable absorbent for pollutant removal in environmental treatment process. However, this natural absorbent is not available in some countries. Therefor production of zeolite through the recycling process could be an acceptable opportunity for a win-win term. Zeolite synthesis (Yang and Yang 1998, Penilla, Bustos et al. 2003, Terzano, D'Alessandro et al. 2015), when compared to energy application and GHGs saving, the recycling is highly recommended. Bear and cold drink cans, deodorant scent cans and aluminium foils are the most commontypes of alu-

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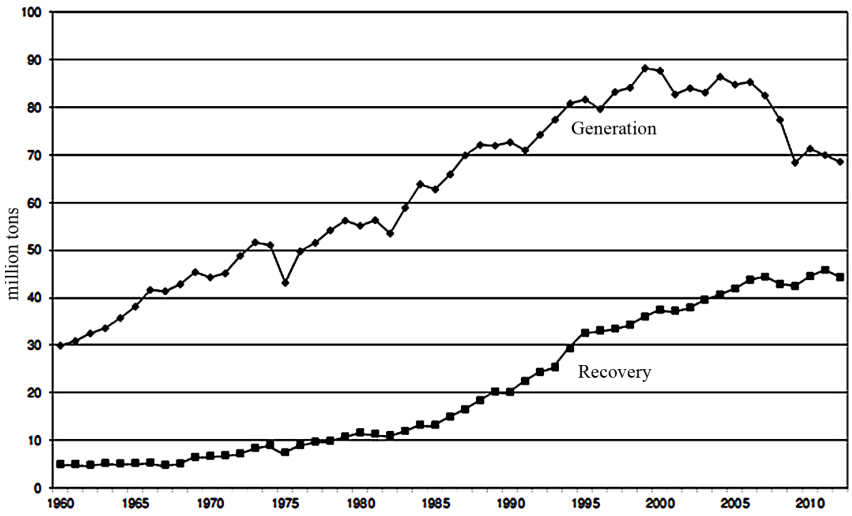
Figure 1. Paper and Paperboard generation and recovery, 1960-2012 (Paper and Paperboard generation and recovery, 1960-2012. [report] (2012))



minium products in MSW (Agarwal, Singhmar et al. 2005, Wäger, Eugster et al. 2005). Glass recycling in material refinery facilities(MRF) consumes a much larger fraction of electricity (28%) when compared to other material recycling, which only consumes 10% of total electricity (Pressley, Levis et al. 2015). Amortized cost for each metric tone of waste input to MRF in ranges from 19.8 to 24.9 USD(Pressley, Levis et al. 2015) (Figure 2).

Recycling, Greenhouse Gas (GHG) and Global Warming

Greenhouse Gases

Greenhouse gases (GHG) contain carbon dioxide (CO_2), methane (CH_4),nitrous oxide(N_2O) and fluorinated gases. USA total emission of greenhouse gases in 2013 reach to 6.673 mllion tones CO_2 equivalent (USEPA 2013).

- **CO_2:** Coal, natural gas and oil burning, waste and cement manufactoring are some major sources for Carbone dioxide emission to atmosphere. Absorbtion by plant is the main removal mechanism for CO_2.
- **CH_4:** Production and transporting process of natural gas, coal and oil causes the emission of CH_4. Municipal solid waste landfilling and agricultural activities are other two major sources of CH_4.
- **N_2O:** Agricultural livestock, combustion of solid waste and fossil fuels are main sources of N_2O.
- **Fluorinated Gases:** The smallest quantity in emission but still is a powerful greenhouse gas that is emitted from industrial process. Figure 3 present main sources of GHGs emissions. Industrial processes, transportation and electricity consumption can be considered as the main sources of GHGs emission through various waste disposal methods.

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Figure 2. Worldwide evaluation of recycled and primary Aluminium (http://www.world-aluminium.org 2010)

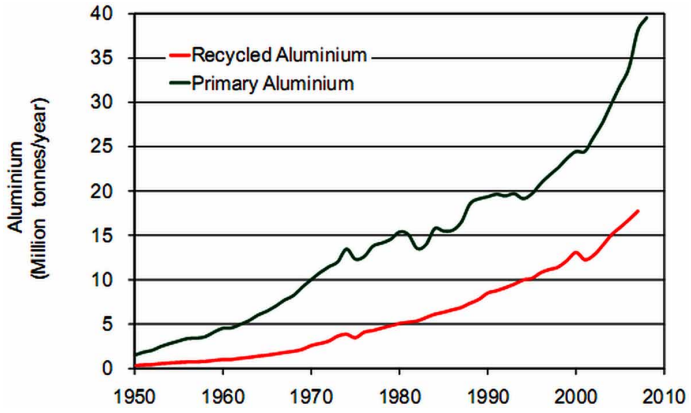
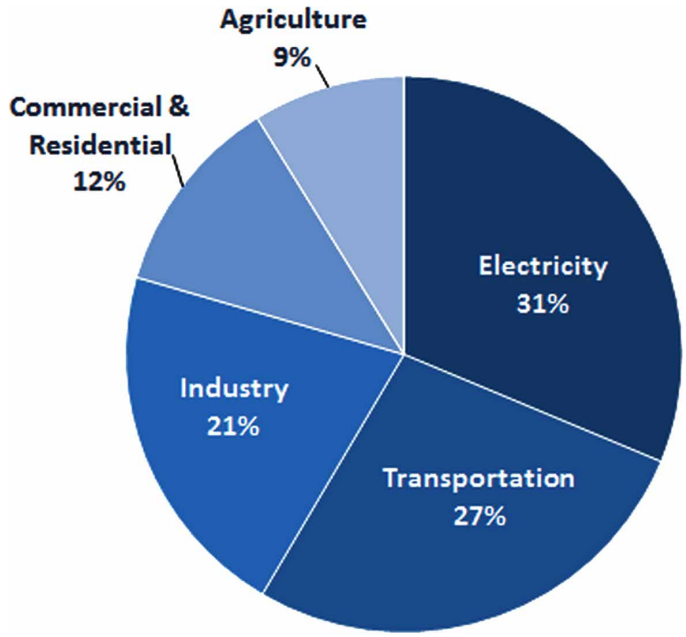


Figure 3. Sources of Greenhouse Gas Emissions (USEPA 2013)



Some of the important researches related to GHG, global warming and recycling indicate that recycling is an effective method for decreasing CO_2 gas emission and hence reducing global warming. Other researches were carried out by Astrup et al. (2009) on plastic recycling, Larsen et al. (2009) on glass recycling,Damgaard et al. (2009) on metals recycling, Laurijssen et al. (2010) on paper recycling and Kim and Song (2014) on wood recycling. Nowadays, most of the developing countries are not setting their municipal solid waste management system with specific view on energy recovery from waste in different process of MSW management, especially in disposing methods. This policy does not only allow us to produce energy, but also we can follow green technology in waste disposal, which saves us from greenhouse gases(Kothari, Tyagi et al. 2010, Nakata, Rodionov et al. 2010). Greenhouse gases

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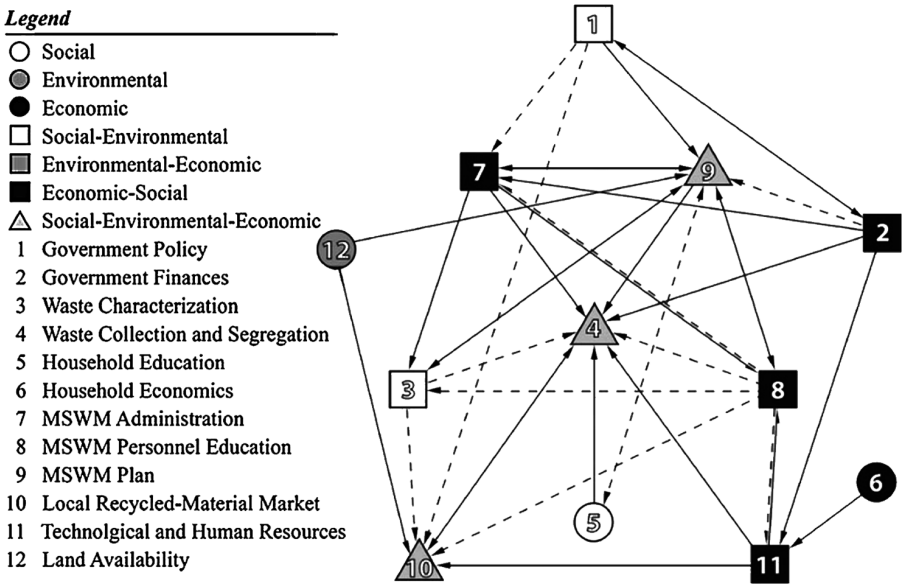
contain carbon dioxide(76.7%), methane(14.37%) and nitroxide (7.9%), which are normally produced from anaerobic biodegradation of disposed wastes in landfill(Zuberi & Ali 2015). Based on Fotovat et al. (2015) and Yoshioka and Grause (2015), concentration on refuse drive fuel (RDF) production from landfill disposal system, incineration facilities or recycling process can be considered as suitable GHGs reduction method. Furthermore, Tan et al. (2014) researches show that integration landfill gas recovery as major waste-to-energy strategy and incineration as the minor WTE strategy could reach to comfortable GHGs reduction and energy potential. Another research carried out in African weather by Oyoo et al. (2014) also suggested that integrating resource recovery, anaerobic digesting, sewerage and landfilling is the best method for all environmental impact categories in comparison to traditional methods, maximizing landfilling and finally combining composting, landfilling, sewerage and resource recovery. In other words, recycling gives new life to material as well as save GHGs. According to Schott and Andersson (2015), 35% of food waste in municipal solid waste are avoidable. Consequently, this amount of food waste avoidance can help in reduction of GHGs. Based on the report ofVergara et al. (2015), textile informal reuse save largest GHGs and landfilling leads to highest emission of GHGs. Municipal Solid Waste disposal is not only a multi-complex process including MSW collection, transfer station locations, treatment policy, location of treatment plants, and recovering energy by waste to energy (WTE) system (Consonni, Giugliano et al. 2005), but also an effective ecofriendly sustainable GHGs reduction method (Cheng & Hu 2010). Global attention to air pollution and GHG caused establishment of national and continental regulars for prohibiting environmental impacts of incineration plants. Recently, Cheng and Hu (2010) presented emission limits of air pollutant materials from municipal solid waste incineration system in USA, EU and China in their review paper. Municipal solid waste disposal is a multi-complex process including MSW collection, transfer station locations, treatment policy, location of treatment plants, and recovering energy by waste to energy (WTE) system (Dewi, Koerner et al. 2010).This issue presented in **Figure 4** as a schematic plan of management.

Figure 4. Collaboration web illustrating relationships among the 12 factors influencing sustainable recycling in developing countries (Troschinetz & Mihelcic 2009)



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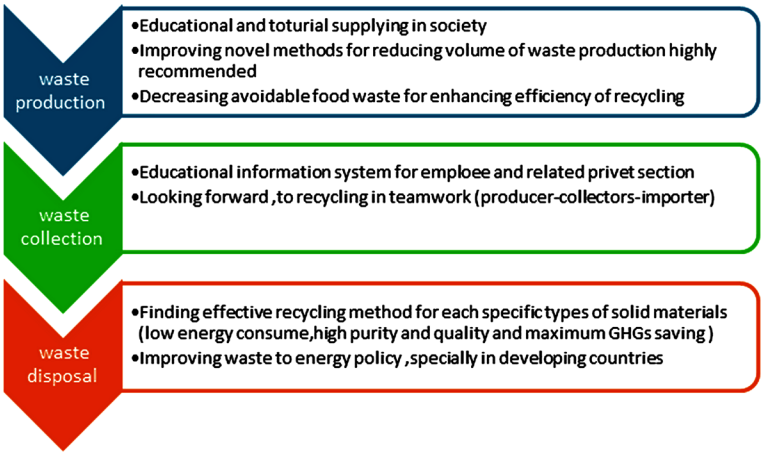
Recycling Efficiency

As opposed of the agricultural or industrial homogenous waste, municipal solid waste is the most complex stream (Wang & Nie 2001). For avoiding counterproductive results, establishing the new formal recycling method should have a clear picture from drawback and merits of informal recycling methods which already exist (Wilson, Velis et al. 2006). Informal recycling environmental impact as GHGs had been assessed in compare with industrialized and modernized formal recycling by Vergara et al. (2015) and their results indicate that informal recycling emit far fewer GHGs than formal system. A questioner study carried out by Lavee (2007) shows that recycling ranges from 10% to 80% . Other efficiency study carried out on 23 cases by Troschinetz and Mihelcic (2009) shows that average of recycling recovery in developing countries are 5% - 40%, in this research the average of MSW generation rate was 0.77 kg per person per day. Consequently, between about 40-300 grams of daily MSW could be recycled (Figure 5).

WASTE INCINERATION

One of major process of waste management is waste incineration, which can reduce approximately 90% of waste volume. Japan, Germany, France, Sweden, Switzerland and Denmark are the countries in which 50% or more of the un-recycled waste goes to incineration process (Hjelmar 1996). This kind of waste disposal is carried out in developed countries. Furthermore, limited available and cost effective land for landfill or transporting system are critical elements in waste disposal by incineration method (Hjelmar 1996, Quina, Bordado et al. 2011). Developing countries are also going to be major operators of incineration. In China, there were 109 MSW incinerators till 2011 and treatment capacity of these plants reaches to 94414 (Yao, Kong et al. 2015). Taiwan as a developing country combined sanitary landfilling of MSW with incinerated residuals as a specific method (Gau & Chow, 1998). On one hand, based on the world bank report by Daniel and Perinaz (2012), MSW production will reach 2.2 billion tones in 2025. On the other hand, incineration technology is going to be the second most important means of MSW management strategy because of increasing MSW and merits of this method of waste disposal (YAN & WU 2003).

Figure 5. Diagram of critical effective elements in waste disposal (recycling)



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Incineration Drawback and Solution

Some kind of hazardous residues that are produced by incineration systems are boiler ash, fly ash, air pollution control (APC) and bottom ash. Heavy metals (Zn, Cr, Pb, Ni, As, Hg and Cu) and high amounts of soluble salts (K, Na, Ca and Cl) are specific characteristic of incinerated residues, which normally form leaching solutions. Incineration residues should also be considered as an air pollution source (Tu, Yu et al. 2010). Air pollution control (APC) residues, generated from municipal solid waste incinerator(MSWI), are classified as hazardous waste since they contain a lot of leachable metallic elements, soluble salts and organic compounds, hence should be disposed carefully (Reijnders 2005, Quina, Bordado et al. 2010). Furthermore, as a thermal treatment, incineration may produce polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, which are highly toxic compounds(Fiedler 1996). MSW residues obtained from waste incineration should also be categorized as a hazardous waste and waste management in this part of waste disposal should be properly carried out (Li, Xiang et al. 2004). Based on the report of (Quina, Santos et al. 2008), solubility of APC in water is 24% higher than in 1/10 ratio of solid to liquid ratio which is the cause for its reduced utilization. For metal carbonation of APC residues which originate through natural aging from MSW incinerator, water content plays a critical role (He, Cao et al. 2006). There was a positive effect of pre-washing in chemical stabilization of MSW incineration by-products (APC) as reported by Quina et al. (2010). Also, water washing presented by Lin et al. (2011) as a suitable way for removing odor and environmentally apprehensive organic materials. Due to high content of soluble salts air pollutant control (APC) residues have been classified as "not allowed as building material" (Quina, Bordado et al. 2011). Therefore, pretreatment for removing soluble salts absolutely should be carried out. Aerobization of metallic elements which reach residues is possible, furthermore it doesn't lead to much dramatic increase of metallic elements in the leachate (Inanc, Inoue et al. 2007). Presence of high quantity of nitrite in municipal solid waste incinerator (MSWI) bottom ash was reported by Belevi and Moench (2000). Nowadays, Islam and Patel (2011) and Yang et al. (2014) have indicated that high concentration of metallic (Fe and Al) hydroxides and layered double hydroxides, which have high capacity for nitrite absorption, can solve the problem of nitrite in MSWI. Controlling pH will be an effective factor in removing organic matter but it has the disadvantage of nitrite reduction. Hence, using additive assistance (PO_4^{-3}), will be suitable for nitrite retention by formation of apatite(Yao, Kong et al. 2015). Dioxin contained in MSWI residue is another drawback, which makes it a hazardous potential waste. Humification of municipal solid waste incineration residue has high positive effect in decreasing dioxin content and it can be carried out through biological activities(Kim & Osako 2004).

Incineration Bottom and Fly ash Application

- Road construction in Denmark(Birgisdottir, Bhander et al. 2007).
- Ceramic tile body(Andreola, Barbieri et al. 2001).
- Incineration ash can use as co landfilling with cellulose for alkaline degradation of cellulose(Svensson, Berg et al. 2007).
- Geotechnical or construction offered by Tu et al. (2010) for incineration slag since structure of slag can immobilized heavy metals .
- Residual carbon of incinerator used for formation of dibenzofurans by using $Na^{37}Cl$ in USA(Addink & Altwicker 2001).

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- Suitable for use as secondary constructional issue or applied in landfill disposal process with MSW(Youcai, Lijie et al. 2002).
- Applied as the liner, leachate drainage layer and protection layer in place of natural mineral such as till, gravel, sand and clay(Travar, Lidelöw et al. 2009, Su, Guo et al. 2013).
- Prohibitory application for nitrite immigration in the landfill(Yao, Kong et al. 2015).

There have been some researches, such as Lisk (1988), Durlak et al. (1997, and Hellweg (2001) on optimum operation management system and technical supplying through incineration process in thermal plants for decreasing hazardous emission. Nevertheless, environmental impact of fly/bottom ash is a concern for many researches. Table 2 presents related studies to environmental impact through incineration ash application.

Heavy Metals

Batteries are the main source for zinc, cadmium and nickel. Meanwhile, mercury content in batteries is nearly zero. So they could be found in sludge and incinerator ashes (Lemann, Walder et al. 1995). In the process of waste incineration, rare metals like Ag, Ga, Bi, In, Sb, Te, Sb, Pd and TI are volatilized in gaseous and/or chloride form. In the next step at melting furnace, fly ash goes to condensing while, Zr, Cr, Ni, Ta and V remain in the molten sludge (Jung & Osako 2007). Based on the report of Jung et al. (2004), a considerable amount of heavy metals have been distinguished to be lost as waste material in the land-filling of incineration residues. Due to the volatility of Pb and Zn, these low metallic elements are found in the bottom ash up to a third amount of these metals in the incinerator. Cd will be found in the fly ash, where as Fe, Cu, Al, and Cr will be found in the bottom ash (Jung, Matsuto et al. 2004). Shimaoka et al. (2007) researched on determining the alterations due to weathering in 2-10 years old landfill site in which MSW incineration residues have been applied as landfill. Based on the research, not only did Al, Mn and Fe increased by depth of landfill, but also in 8-10 years old landfill, concentration of Al, Zn, Pb and Fe in pH 6-10 was lower than the fresh residues. Hydration was presented as the reason for stabilization of these elements. Figure 6 show the XRF composition of MSWI residues in fresh and land-filled residues.

Table 2. Related studies to environmental impact through incineration ash application

Location	Effective impact	Reference
China	Incineration ash application in asphalt	(Xue, Hou et al. 2009)
France	Incineration ash application in cement	(Aubert, Husson et al. 2007)
Brazil	Comparing incineration and landfilling environmental impact	(Mendes, Aramaki et al. 2004)
Italy	Comparing incineration and landfilling and sorting strategy	(Cherubini, Bargigli et al. 2009)
Denmark	Road constructed with incineration ash	(Birgisdottir, Pihl et al. 2006)
Spain	Toxic organic compounds reminding in soil and grown plants	(Domingo, Schuhmacher et al. 2000)

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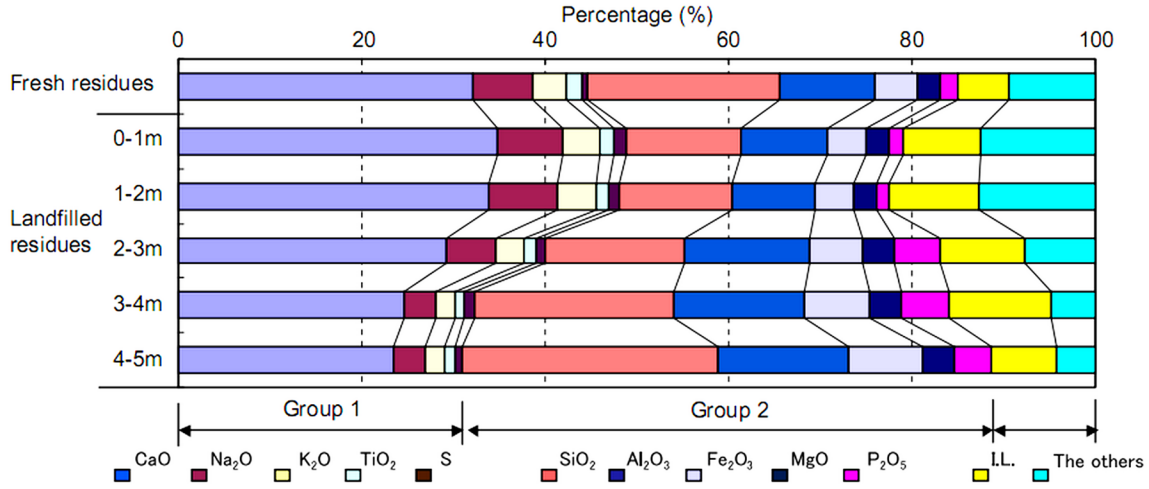
Figure 6. Major compositions (>1%)in the fresh and landfilled MSWI residues determined by XRF (Shimaoka, Zhang et al. 2007)



Dissolved Organic Matter

Organic carbon in waste incineration process is converted to CO_2 (98-99%) or transferred to bottom ash (1-2%) or (0.1-0.4%) to boiler ash APC residues(Ferrari, Belevi et al. 2002). Based on the research of (Seo, Kim et al. 2007) fluorophores, an aromatic amino acid in dissolved organic matter fraction, could be considered as an important effective factor in the complexation process with the pollutant materials. Residual organics have received far less attention in comparison to metallic elements as counterpart. Aromatic amines, antrhracene, carboxylic acid diethylamide, bromo–N-(4-bromo-2-chlorophenyl)-propanamide) and other aromatic compound are major odorous compounds in incinerator bottom ash (Lin, Yen et al. 2010; Ferrari, Belevi et al. 2002).

MUNICIPAL SOLID WASTE COMPOSTING PROCESS

Municipal solid waste is by far the largest source of human made organic waste, which has the capacity of composting, based on the document presented by (Epstein 2011). According to the research, there was a publication of report on compost application in year of 1888. Composting process is a natural process in our environment. In fact, industrial composting is an expert of advanced copy of natural biodegradation of organic material, which is specialized by mechanical and electronic equipments. After recycling process, edible waste which has high quantity of organic matter, could be used in the composting system; an intermediate disposal method, which converts high quality of organic manure. Furthermore, this process could decrease the volume of MSW (Stentiford 1996, Epstein 2011).

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Microbial and Thermal Characterization

Composting is a microbiological singularity that highly depends on temperature fluctuation within the windrows. The temperature through a composting mass regulates the rate at which many of the biological procedures, play a specific selective role on the advancement and the succession of the composting microbiological communities (Hassen, Belguith et al. 2001, Epstein 2011). Controlling the process of composting fundamentally depends on the Oxygen rate, which has to be kept at optimum level. Generally in biological terms, operating temperature should be more than 55 ° C for highest sanitation, 45 to 55 ° C for achieving maximum biodegradation ratio and 34 to 40 ° C for the lowest diversity of microbial communities (Stentiford 1996) . Three major steps, which can be distinguished in a schematic aerobic composting process, are: (i) mesophilic phase, (ii) thermophilic phase and finally (iii) a cooling phase. Thermophilic and mesophilic are basically effective temperature regime throughout the composting process. Thermophilic condition could control herb seeds and pathogen. Mesophilic situation is prepared to finally reach mature stable compost. Mesophilic condition provides optimum temperature for rapid and suitable biological decomposition of organic materials(Epstein 2011). Nowadays, compost plant construction and management are well developed and there are many advanced composting system for operation and application. The future of this technique was presented as organic fiber production from unsorted MSW (Quirós, Gabarrell et al. 2014),producing higher agronomic value compost (Awasthi, Pandey, & Khan, 2014). Meanwhile, composition of municipal solid waste plays a major role in the management of waste. In **Table 3** composition of MSW in some parts of the world, USA, China, Malaysia, and Gambia are presented.

Organic Fertilizer Production for Agricultural Application

Composting is growing as a green technology and the application of MSW compost as organic manure in different agricultural system has a historical background, same as the composting of municipal solid waste. These two parallel lines are going fast together. The quality of municipal solid waste compost highly depends on the waste composition, which usually correlated to the economy and developing factors of the production origin. **Figure 7** shows the composition of MSW in developed countries and average of 19 developing countries.

Table 3. MSW composition in New York (MacBride 2014), Hangzhou China (Chi, Dong et al. 2014), (Sanneh, Hu et al. 2011) and Kuala Lumpur Malaysia (Saeed, Hassan et al. 2009)

Component	New York USA	Hangzhou China	Greater Banjul Area Gambia	Kuala Lumpur Malaysia
Food waste	26.54%	58.15%	32.44%	57%
Paper	23.32%	13.27%	9.19%	17%
Plastics	15.01%	18.81%	-----	15%
Textiles	8.42%	1.47%	2.25%	1%
Glass	2.6%	2.73%	1.48%	1%
Metals	4.06%	0.96%	1.40%	2%
Wood	4.35%	2.61%	2.35%	2.61%
Slag/Sand	-----	-----	48.44%	2%
Electronic	0.97%	-----	-----	-----
Fine, organic	10.4%	1+5%	-----	-----
Other	4.26%	-----	-----	-----
Total/average	100%	100%	100%	100%

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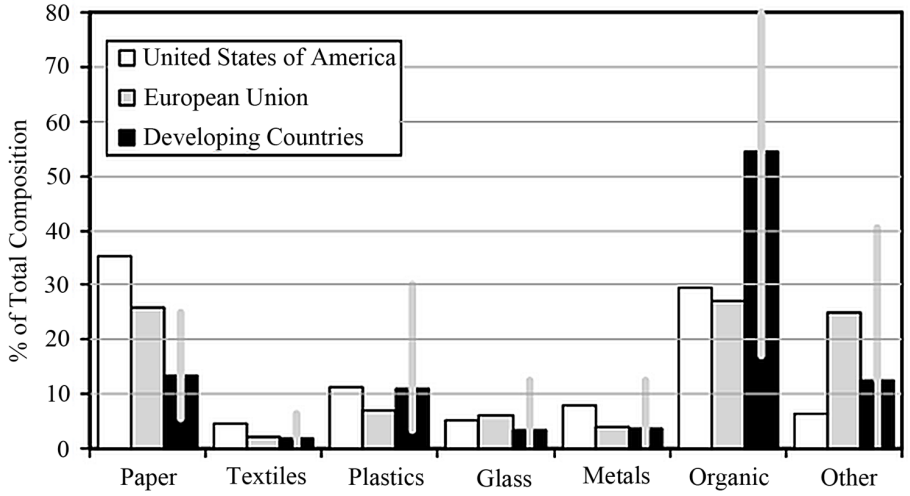
Figure 7. Comparison of MSW composition of United States and European Union in compare with the average of 19 developing countries (Troschinetz & Mihelcic 2009)



Horticulture science is a well-known part of agriculture, which has many operations and applications in human society and environment such as landscaping, floriculture parks, grass area for playground and countryside vegetable and fruit garden. This could be considered as the main applier of municipal solid waste compost. Different kinds of compost application in horticulture are presented by (Stoffella & Kahn 2001). (Hargreaves, Adl et al. 2008) present a review on agricultural application of MSW compost. Based on the research of (Garcıa-Gil, Plaza et al. 2000), for long term application of MSW compost, heavy metal content and other toxic material should be considered as an aspect of quality control. Some of the positive effects of MSW compost are mentioned in the following points:

- Improving soil biochemical and biological properties (Garcıa-Gil, Plaza et al. 2000)
- Increasing total N and C, furthermore enhancing nitrate reeducates and de-hydrogenase activities in soil (Crecchio, Curci et al. 2001)
- Improving physical and chemical properties of soil (Shiralipour, McConnell et al. 1992, Giannakis, Kourgialas et al. 2014)
- Increasing yield of vegetables comparing chemical fertilizers (Mkhabela & Warman 2005).
- Better seedling emergence for tomato, pepper and cucumber comparing commercial peat (Roe, Stoffella et al. 1997)
- Suitable effect on adjusting plant hormones for cultivation of some forage species (Ouni, Albacete et al. 2014)

In fact, due to the materials departure and waste string as well as lack of nutrients and high level heavy metals, composting dropped to <4% in present time from 17% in 2001(YAN & WU, 2003). Composting of municipal solid waste has some drawback as follows:

- This kind of waste disposal needs size reduction and waste separation before starting
- Volume of produced organic manure is disproportionately large and quality is low

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- This organic fertilizer may cause many pathogens and heavy metals in soil(Ayari, Hamdi et al. 2010).
- Since compost is bio manure so application in public area of cities and landscape may cause to odor and bioaerosol problem
- A product should be marketed (Epstein 2011).

ENVIRONMENTAL IMPACT

Waste disposal is one of the most important parts of waste management, which has a critical effect on our environment. On one hand, waste disposal methods reduce the volume and hazardous effects of our municipality (agricultural, industrial and municipal) waste, on the other hands, this part of waste disposing will produce other byproducts which are hazardous or may cause higher environmental impacts(Smith, Brown et al. 2001). Some of the environmental impacts of waste disposal are presented in GHG emission explained in (Palmer, Sigman et al. 1997, Williams 2005). It reports odor, noise, traffic congestion, emission of carbon dioxide and other pollutions from all kinds of waste disposal. Report of (Hjelmar 1996) indicates that landfilling incineration bottom ash is less problematic in comparison to air pollution control residues. Based on the researches of Japanese team (Mendes, Aramaki et al. 2004) in Brazil, landfilling have higher environmental impact in comparison to incineration.

During Waste Incineration

- A complete overview carried out on incineration environmental impact by scientist team from Denmark, Australia, Germany, and Italy (Sabbas, Polettini et al. 2003) and they concentrated on salts, metals and greenhouse gases emissions in their studying.
- Odor, litter and dust problem during discharge, handling and transportation.
- Sub-micron particles contain heavy metals and metallic compounds.
- Nitrogen oxide which can form at the flame temperature.
- Incompletely combusted pyrolysis products may produce volatile organic compounds and carbon monoxide (Daskalopoulos, Badr et al. 1997).

During Waste Composting

As an organic fertilizer, municipal solid waste compost is usually applicable manure for enhancing soil's physicochemical properties. According to Hargreaves et al. (2008), MSW compost could be applied in agriculture as a safe fertilizer. Meanwhile, application of urban waste compost for humans and its environment hazards, were reviewed by Déportes et al. (1995) .Furthermore Lou and Nair (2009) reviewed the effect on greenhouse gases emission in application of MSW compost. Following notes are some of the specific researches on environmental impacts through composting MSW:

- Dust and aerosol particles, some microbes and odor to air (Iranpour, Cox et al. 2005)
- Leachate, from high content of moisture (60%- 65%) in compost, to water resources (Daskalopoulos, Badr et al. 1997).

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- Volatile organic compounds (VOC) production in composting process(Brinton 1998).
- Emission of NH_4-N through the composting process(Komilis & Ham 2006, Pagans, Barrena et al. 2006).

During Waste Recycling

Recycling process take a place by construction, transportation, washing, chapping all of which needs electrical energy application and causes production of GHG as a specific industrial activity. Among all environmental impacts of recycling, one of the most important issues is direct human hazard or injury as following:

- Health risks for sorting and recycling process and de-inking recycled materials (Rigamonti, Grosso et al. 2009).
- Hepatitis B and C prevalence during the separation process (Tsovili, Rachiotis et al. 2014).
- Respiratory disorders throughthe recycling MSW (Abou-ElWafa, El-Bestar et al. 2014).
- Gastrointestinal, skin, musculoskeletal and respiratory problems observed in Municipality operators worker (El-Wahab, Eassa et al. 2014).

SOLUTIONS AND RECOMMENDATIONS

Civilization and industrialization are related and correlated to waste production in municipals. Waste disposal has many aspects and relationships to other parts of waste management. The processes of waste management start withthe waste generation and end with final landfilling. On one hand, municipalize going on to produce higher volumes of waste; while on the other hand, industrialization has another effective point in waste composition. Selecting an effective method for treatment or disposing MSW could give novel improvement in saving energy and reducing the drawbacks of produced waste. Meanwhile, concentration on decreasing volume of waste production with the educational system and promoting on the cultural background of any society will assist the sustainable environment. Not only, the economic circumstances, but also cost effective properties will have a significant effect on selecting favorite waste disposal method. Protecting the environment in green way method needs to avoid the production of hazardous waste or environmental impacts. Governmental policy is the most effective element as well as private section cooperation could lead us to eco-friendly methods of waste disposal. In other words, recycling is a major concern of waste disposal and is an important requirement for today. Nevertheless, in the next decades, there will be critical imperative activity. To sum it up, our future worlds are mostly going to incineration of municipal solid waste and land filling disposal method, so eco-friendly aspects of these methods will be the key to reaching green way of waste disposal. Meanwhile, professionally engineered, cost effective green technologies for specific recycling method have high value in researches.

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Chapter 39
Assessment of Available Technologies for Hospital Waste Management:
A Need for Society

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ABSTRACT

Modern hospital practices with galloping growth in medical technology facilitate increase human life span, decrease mortality rate and increase natality rate. Life supporting health services generates potentially hazardous and infectious hospital wastes like pharmaceuticals, cottons, food, paper, plastics, radionuclide, sharps, and anatomical parts etc. These wastes are complex in nature with maximum part of municipal solid waste and small part of biomedical waste (anatomical parts, body parts etc.). Improper conduct and management of hospital waste create several problems and nosocomial diseases to human beings and harms environment. Traditional practices included for management are open burning, mixing waste, liquid discharge and waste disposal without treatment normally. Hence, this issue comes in lime light and several guidelines come to sort out this problem. Thus, challenges associated with traditional hospital waste management techniques and modern techniques for management are assessed in general and association with human society in particular in this chapter.

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INTRODUCTION

With rapid growth of human population and urbanization there is increase in quantity of waste generation. Most developing and develop part of the world is facing challenges of waste. Waste is the substances which have resource but not value. Waste is classified by their source of generation, process by the wastes is produced, and also by its composition. According to literature, there are several attempts to define waste, enlisted in Table 1. Similarly, source of generation, compositional structures, and regulatory framework also supports and defines waste, given in Table 2, in Indian context only.

Among the varieties of waste, as listed in Table 2, Bio-medical waste (BMW) has a serious thought, because inappropriate treatment and final disposal of the wastes directly shows the negative impact on human health and local environment. Thus, bio-medical waste, which consists of pathological and hazardous healthcare wastes, included as a major part of study in this chapter. In general wastes generated from

Table 1. Definitions of Waste

Agency	Definition	Reference
BASEL Convention	"Wastes" are substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law.	BASEL Convention, 1989
OECD	Wastes are materials other than radioactive materials intended for disposal, for reasons specified.	OECD, 1994
World Bank	Unwanted materials left over from any human activity. or, Refuse from places of human or animal habitation. Waste may be generically defined as heterogeneous mixture of material which is discarded as superfluous and has no further use or value to its owner.	World Bank, 2000
EU	Any substance or object which the holder discards or intends or is required to discard.	European Commission, 2012

Table 2. Different type of wastes according to Indian regulatory framework

Rules	Definition
Hazardous Wastes (Management and Handling) Rules- 1989	Hazardous waste means any waste by reason of its physical, chemical, reactive, toxic, flammable, explosive or corrosive characteristics causes danger or is likely to cause danger to health or environment, whether alone or when in contact with other wastes or substances.
Bio-Medical Waste (Management and Handling) Rules - 1998	Bio-Medical Waste (BMW) means any waste, which is generated during the diagnosis, treatment or immunization of human beings or animals or in research activities pertaining thereto or in the production or testing of biological.
Municipal Solid Wastes (Management and Handling) Rules- 2000	Municipal Solid Waste (MSW) includes commercial and residential wastes generated in municipal or notified areas in either solid or semi solid form excluding industrial hazardous wastes but including treated bio-medical wastes.
E-Waste (Management and Handling) Rules- 2011	E-Waste means waste electrical and electronic equipment whole or in part or rejects from their manufacturing, refurbishment and repair process which are intended to be discarded as waste.
Plastic Waste (Management and Handling) Rules- 2011	Plastic waste means any plastic products such as carry bags, pouches or multilayered packaging, which have been discarded after use or intended life is over.
Solid Waste Management Rules-2015*	Solid Waste means and includes solid or semi-solid domestic waste including sanitary waste, commercial waste, institutional waste, catering and market waste and other non-residential wastes, street sweepings, silt removed or collected from the surface drains, horticulture waste, construction and demolition waste and treated bio-medical waste and e-waste generated in an area under urban local body.

*(It is in draft stage. It will come into force on the date of their final publication in the Gazette of India.)

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households and industries can be managed through using conventional and advanced treatment methods. But, bio-medical waste technically not ease to handle, it requires relatively adequate managing skilled workers for proper management. Often, it has been noticed that the management and handling of these types of wastes is taken over by poorly educated or untrained workers, who perform the management steps without proper guidance and self-protection. Hence, the objective of this article was to study the document existing resources, management practices related to bio-medical waste in general and a city specific study in particular.

Patient and hospital staffs during the service of humanity release large quantity of waste which is rising in its quantity and composition, due to advances in scientific knowledge its impact is also increasing. We are unaware about the bad effects of the waste generated by hospitals on human body and environment (Sharma et al., 2013; Sanjeev et al., 2014; Patil et al., 2013). Cleanup costs for medical wastes are extremely high (Johnson et al., 2013; Brichard, 2002), so hospitals avoid following BMW management practices. It is complex type of waste hence, there is not a particular method of BMW treatment or disposal that completely eliminates all risks to humans and environment. Untreated Bio-medical waste deposits have health risk to the public due to potential for pathogen release to harm human beings epidemically or endemically; acutely or chronically. Main target of this waste are:

- Doctors,
- Nurses,
- Paramedical personals,
- Hospital workers,
- Waste management workers,
- Transporters,
- Hospital visitors etc. And this type of infection is known as noscomial or hospital acquired infections (HAI).

Some time it has been also seen that staffs dealing with BMW and rag pickers are badly affected, because unknowingly or unwittingly, they search through all kinds of hazardous material while trying to recover items which they can sell for reuse. Some hospitals and laboratory waste may contain hazardous chemicals, biohazards, radioactive materials, papers, metals as well as sharps like (hypodermic needles, knives, scalpels, etc.). About 75-80% of the waste produced in hospitals is non-risk waste and comparable to domestic waste and usually called “non-hazardous” or “general health-care waste” (Mosquera et al., 2014). The remaining 10–25% of health-care waste is considered as “hazardous” and may cause a variety of environmental and health risks (Chartier et al., 2014). There is temporal and spatial variation in BMW generation during different parts of world (Table 3). Mixing of BMW to general waste contaminate the general waste also.

There is not adequate public understanding of BMW management (Singh & Nath, 2013; Yong et al., 2009). There is no segregation of waste starting from generation to disposal, need of awareness among the sweepers and cart drivers about personal protection, no separate committee for the management of the hospital waste, and no proper cover during transportation of waste, incinerated ash is found thrown on the area nearby the incinerator (Kungu et al., 2016; Athvale et al., 2010), polychlorinated dibenzo-p-dioxins and furans (PCCD/Fs) in the fly ash and air (Chen et al., 2015) and concerned people are explored to the danger of such wastes (Hassan et al., 2008). Handling and proper disposal of BMW have very high risk to cause injury or infections in healthcare personnel and there are also risk to general public through the

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Table 3. Amount and composition of hospital waste generated from different countries

Country	Infectious waste Quantity(Kg/bed/day)	Total waste Quantity (Kg/bed/day)	Reported by
United States	2.79	10.7	Compendium (2012)
South Africa	1.24	-	Compendium (2012)
Vietnam	0.3	-	Compendium (2012)
Tanzania	0.08	0.14	Compendium (2012)
Iran	6.67	-	Askarian et al. (2010)
Taiwan	0.6	3.26	Cheng et al. (2009)
Algeria	0.7-1-22	-	Benzoudi et al. (2008)
Mongolia	0.16-3.23	-	Diaz et al. (2008)
Jordan	0.5-2.2	-	Abdulla et al. (2007)
Jordan		6.10	Compendium (2012)
Brazil	0.57	3.25	Da Silva et al. (2005)
Turkey	1.25-2.6	-	Altin et al. (2003)
Turkey		1.39	Akbolat et al. (2011)
Bulgaria	0.40	-	Spasov (2003)
India	0.5-2.0	-	Patil et al. (2001)

spread of pathogenic micro-organisms from healthcare facilities to the environment (Babanyara et al., 2013; Hossain et al., 2013; Brichard, 2002; Mohee, 2005). To minimize these problems many efforts have been done at international level but proper management of BMW is still infancy all over the world (Athvale et al., 2010; Altin et al., 2003). There is lots of confusion among generators and operators about the safe management of BMW (Athvale et al., 2010). For scientific and secure management of BMW, handling, segregation, mutilation, disinfection, storage, transportation, and final disposal are essential steps for any health care institution (Isaacs & Dhakkal, 2015; Altin et al., 2003). In developed countries these vital steps are in process of adopt. While in India and other developing and poor countries it is an intractable problem. The management of BMW has received little attention despite their potential environmental hazards and public risks (Thakur and Ramesh, 2015; Hassan et al., 2008).

WHO stated that 85% of hospital wastes are comes under the category of non-hazardous, approximately 10% is infectious and only 5% is non-infectious but hazardous wastes. In USA, only 15% of the hospital waste comes under the category of infectious waste. Whereas, in India this could range from 15% to 5% of the total quantity of hospital waste generated (Chandra et al., 1999). Table 3 summarizes the amount of hospital waste generated from different countries, according to data available, while Table 4, enlists the different sources of BMW generation, its treatment options and harmful effects associated with the sources in general.

There are several technological options available for handling and treatment of BMW at traditional and modern scale (Thakur and Ramesh, 2015).

- Autoclaves are generally used for sterilization of infectious reusable materials such as sharps, surgical instruments, surgical gloves, aprons *etc.*

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Table 4. Sources of bio medical waste generation, treatment options and harmful effects

Waste category	Source of generation	Color code bins	Treatment options	Harmful effects
Human Anatomical Waste	Human tissues, organs, body parts	Yellow	Incineration/ deep burial	Foil smell, enhance microbiological activity, risk to diseases
Animal Waste	Animal tissues, organs, body parts carcasses, bleeding parts, fluid, blood and experimental animals used in research, waste generated by veterinary hospitals, colleges, discharge from hospitals, animal houses	Yellow	Incineration/ deep burial	Bad odor, enhance microbiological activity, risk to disease
Microbiology & Biotechnology Wastes	Wastes from laboratory cultures, stocks or specimens of micro-organisms live or attenuated vaccines, human and animal cell culture used in research and infectious agents from research and industrial laboratories, wastes from production of biological, toxins, dishes and devices used for transfer of cultures	Yellow	Local autoclaving/ microwaving/ incineration	Risk to allergy, skin and other infections, Biochemical, anatomical, and Physiological alterations, Capable to reach inner part of body through inhalation
Waste sharps	Needles, syringes, scalpels, blades, glass etc. that may cause puncture and cuts. This includes both used and unused sharps	Blue/White	Disinfection (chemical treatment/ autoclaving/ microwaving and mutilation/shredding	Physical damage, Subcutaneous infections, Virus associated blood infections such as HIV, Hepatitis B and C, etc.
Discarded Medicines and Cytotoxic drugs	Wastes comprising of outdated, contaminated and discarded medicines	Black	Incineration/destruction and drugs disposal in secured landfills	Potential carcinogens, Abortions, water contaminations, Antibiotic resistant
Solid Waste (Infectious)	Items contaminated with blood, and body fluids including cotton, dressings, soiled plaster casts, lines beddings, other material contaminated with blood	Yellow	Incineration autoclaving/ microwaving	Communicable Diseases such as: Cholera, Tuberculosis, Diphtheria, Flue, etc.
Solid Waste	Wastes generated from disposable items other than the waste (sharps) such as tubing, catheters, intravenous sets etc.	Red	Disinfection by chemical treatment, autoclaving/ microwaving & mutilation/shredding	Physical damage, environmental pollution
Liquid Waste	Waste generated from laboratory and washing, cleaning, house-keeping and disinfecting activities, dialysis		Disinfection by chemical treatment and discharge into drains	Water and land contamination
Incineration Ash	Ash from incineration of any bio-medical waste	Black	Disposal in municipal landfill	Hazardous
Chemical Waste	Chemicals used in production of biological, chemicals used in disinfection, as insecticides *etc*.	Black	Chemical treatment and discharge into drains for liquids and secured landfill for solids	Children malformation, Abortions, Antibiotic resistant, Reaches through inhalation in lungs and other body parts
Radioactive waste	Radiotherapy Units of Cancer ward	Special containers	Send to Atomic labs	Headache, dizziness and vomiting, Tissue destruction, fatal

(Source: Modified from Schedule I and II of Bio-Medical Waste Management and Handling Rules, 1998, India; Pruss et al., 1999; Chartier et al., 2014)

- Incineration is considered as a best alternative for treatment with high temperature for burning of BMW.
- Chemical disinfection and sterilization has been done generally with iodine-povodine solution, 1% Sodium hypochlorite solution etc., whereas, floors and bins are cleaned with phenol and bleaching powder with other many more market based chemicals.
- Sharps and needles are shredded onsite with shredder.

Some places where modern technologies are not available for BMW treatment due to limitations to reach to remote areas or absence of proper skilled manpower, encapsulation and deep burial is suggested by researchers and policy makers. Some other technological options are also available in literature, properly discussed in next section of chapter.

TREATMENT OPTIONS FOR HOSPITAL WASTE MANAGEMENT

Among the different treatment options, according to source of generation, some common methods utilized for management of infectious wastes at worldwide level (Table 4), are:

Physical Methods

In physical processes, autoclave, hydroclave, incineration are frequently used and suggested technologies, discussed here as:

Autoclave

Autoclaves are mainly of two types-

- Gravity flow and
- Vacuum, Gravity flow autoclave.

Gravity flow autoclaves operated at 121ºC temperature, 15 psi pressure for 60 minutes or 135ºC temperature, 31 psi pressure for 45 minutes or 149ºC temperature, 52 psi pressure for 30 minutes. While, vacuum autoclaves are operated at 121 ºC temperature, 15 psi pressure for 45 minutes or 135ºC temperature, 31 psi of pressure for 30 minutes. Steam is used for temperature and pressure.

Hydroclave

Another steam based technology is hydroclave, it has a double walled container, inner chamber contains waste and steam is injected to outer jacket which transfer heat to inner chamber. Moisture content of waste creates pressure of about 35- 36 psi (if waste is dry then steam is injected) at 132°C with residence time of 20 minutes. To process one complete cycle, it takes time of 50-60 minutes including start up, heat up, sterilization, venting, depressurization and dehydration. These mentioned technologies have chances to little infection and not minimizes waste.

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Incinerator

Complete destruction of waste is done by incinerators only at high temperature, mainly two chambered incinerators are preferred, primary chamber have about temperature of 800 ±50 ºC while secondary chamber have temperature of 1050 ±50ºC.

Others

Other technologies like microwave and plasma pyrolysis are still in infancy stage used for BMW treatment. Microwave is also steam based technology in which water contained waste is rapidly heated by microwave energy at frequency of about 2450 MHz. (Emmanuel, 2001). While, plasma pyrolysis uses extremely high temperature of about 1200ºC, in this technology, BMW is converted into simpler forms like CO, Hydrogen and hydrocarbons. It is better than incinerator because of there is no need to segregation of chlorinated compounds.

Chemical Methods

Mainly reusable and recyclable BMW like used gloves, instruments, masks etc. needs chemical treatment before disposing. These types of materials are generally treated with 1% -Sodium hypochlorite solution for minimum one hour. Use of super critical water with hydrogen peroxide is a good stabilizer of metals in incinerated ash (Bo et al., 2009). Cement has capacity to immobilize incinerated ash in form of bricks (Anastasiadou et al., 2012) which stable in buildings and roads. Use of super critical fluids like CO_2 (SF-CO_2) is also a good option for sterilization of wastes (Goddu et al., 2007) and make process easier for waste handlers. For the treatment of liquid wastes Effluent Treatment Plants, Microbial Fuel Cells (MFCs) are good option of liquid waste treatment. Fenton Treatment also a very good option for BOD_5 and COD and bacteria removal (Berto et al., 2009).

Biological Methods

There are not well developed methods available for BMW, but a very few documented in literature. Cotton, bandage and other degradable matter when soiled or inoculated with white rot fungus such as *Periconiella sp.* are capable to degrade them (Pandey et al., 2008). Vermi composting is also a good method for it use of epigenic earthworms is a good alternative. Dinesh et. al., (2010) used polycultures of three earthworms, *Eisenia fetida*, *Eudrilus eugeniae*, and *Perionyx excavates,* and reported that union of several earthworms is better way due to hazardous environment.

Therefore, all the above said categories for biomedical waste can be managed through below enlisted options:

- Autoclaves and retorts;
- Microwave disinfection systems;
- Chemical disinfection;
- Combustion, and
- Disposal on and beneath the land.

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Whereas, residues of syringes and needles also a major part of this wastes, and generally managed through:

- Burial in covered pits;
- Encapsulation by cement/concrete materials;
- Point-of-use needle destruction technologies and size reduction with mechanical type destruction appliances.

Each treatment options for medical waste from hospitals have its limitations in different respects, which were highlighted in Table 5.

HOSPITAL WASTES IN VARANASI (UTTAR PRADESH), INDIA

With increasing awareness in public regarding hazards of hospital waste, a survey based study was conducted including questionnaire as a tool to support the findings of observations regarding process route of waste from generation to its disposal. The study area selected was the most populous city of eastern Uttar Pradesh i.e. Varanasi, with a population density of 2,395 people per square kilometre. Therefore,

Table 5. Comparisons of treatment technologies for medical wastes

Treatment systems	Autoclave	Hydroclave	Microwave	Incinerator	Chemical
Description	Steam sterilization (Direct heating)	Steam Sterilization (indirect heating) simultaneous shredding and dehydration	Microwave heating of Pre-shredded waste	High temperature waste incineration	Mixing pre-ground waste with chemicals, such as chlorine
Sterilization efficacy	Medium	Medium	Medium	High (total destruction of micro-organisms)	Dependent on chlorine strength and dispersement through the waste
Capital cost	Low	Low	High	High	Moderate
Operating cost	Low	Low	High	High	Low
Operator maintenance skills	Low skill level required	Low skill level required	Automated, but highly complex and high level maintenance skill required	High level operator and maintenance skills required	High level required for chemical control and grinder
Air emissions	Odorous but non-toxic	Somewhat odorous but non-toxic	Somewhat odorous but non-toxic	Can be highly toxic	Some chlorine emissions
Water emissions	Odorous, may contain live micro-organisms	Odorous but sterile	Negligible	None	None
Treated waste characteristics	Wet waste, all material recognizable	Dehydrated shredded waste, unrecognizable material	Shredded but wet waste	Mostly ash, may contain toxic substances	Shredded wet waste, containing chemicals used as disinfectants

Source: (Babu et al., 2009)

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to evaluate the actual scenario of hospital/bio-medical waste in Varanasi (Uttar Pradesh), three specific funding partners i.e. Central, State, and Private hospitals taken as a study site, enlisted in Table 6, with coded abbreviations used for them.

This figure of population density is higher than national (382 people per square Km) and state level (Uttar Pradesh, 829) of population density. Gender wise population distribution indicates to have 1, 921,857 male and 1,754,984 female populations. Varanasi seems to be centralized place for various facilities such as commercial, education, health etc. with wider coverage area including eastern Uttar Pradesh and neighbor state (Bihar). Varanasi is identified as zone for centralized treatment facility from out of the ten selected zone under the World Bank (2011) funded project (Uttar Pradesh Health Systems Strengthening Project). Hospitals from Varanasi district were selected by following a pre short survey of health care facilities present in the city. Six healthcare facilities and one Common Bio-Medical Waste Treatment Facility (CBMWTF), Varanasi were selected to assess the waste as given in Table 6.

After selecting hospitals for waste management study, a questionnaire was developed for cross sectional study and given to key personals of hospitals (Table 7). A structured questionnaire was developed to ask the questions from respondents/stakeholders. The questionnaire was designed to obtain respondents awareness towards the waste management and to know the practices being implemented in those hospitals. Thus, a simple framework of questionnaire having binomial variables with a scale of either 1 or 2 (Yes or No) was used to conduct interview in selected hospitals. Whereas, on qualitative scale, a descriptive study was designed to explore the current hospital waste management practices by interviewing with key personals like directors, medical superintendent, deputy medical superintendent, chief matrons, housekeeping in-charges, medical officer and persons related to waste management processes. Focus was done on:

- National rules,
- Internal policies,
- Monitoring and awareness,
- Personal protective equipment's,
- Solid and liquid waste,
- Handling practices,
- storage facilities,
- training of hospital staff related to hospital waste management, and
- new technologies using by them.

Table 6. Study sites for assessment of BMW at Varanasi city (U.P.)

Type of Funding Hospitals	Name of Study site (Code)	Remarks
Central Government	Sir Sunderlal Hospital (SS1)	Tertiary care Hospital
	Central Hospital DLW (SS4)	Railway Hospital
	Indian Railways Cancer Institute and Research Centre (SS5)	Railway hospital for cancer patients
Private	Heritage Hospital (SS2)	Specialty care Hospital
	Apex Hospital (SS3)	With charitable blood bank
State Government	Pt. Deen Dayal Upadhyay Rajkiya Hospital (SS6)	Super specialty Hospital

(SS means survey site)

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After questionnaire survey study, only 2 out of 6 selected hospitals were found to have data related to waste generation and management practices. Hence, these 2 hospitals were finalized for the detailed survey study plan i.e. SS1 and SS5 with CBMWTF.

Major Observations and Findings

Before detailed study plan, it has been observed that all the six study sites of Varanasi are required to handle hospital waste in a specified manner or in general way. Thus, total findings of the study are divided into different subsections, to easily understand the way to waste management practices and awareness among workers to officials at three major funding partners in Indian context i.e. Central, State and Private Hospitals.

Table 7. Questionnaire and key findings of survey sites

S. No.	Questions	SS1	SS2	SS3	SS4	SS5	SS6
A. Solid Waste							
1	Do you properly segregate your waste?	Y	Y	Y	Y	Y	Y
2.	Does your hospital has color coded waste containers and they are properly labeled? (Biomedical Waste & accumulation start date)	Y	Y	Y	Y	Y	N
3	Do departments have waste accumulation areas away from reach of peoples?	Y	Y	Y	Y	Y	Y
4	Does your hospital have a separate waste collection area for BMW?	Y	Y	Y	Y	Y	Y
5	Do your staffs who handling with waste receive BMW management training?	Y	Y	Y	Y	Y	Y
6	Do your staffs use Personal Protective Equipments for waste handling?	Y	Y	Y	Y	Y	Y
7	Does your hospital keep record of the amounts of BMW generated per month?	Y	N	N	N	Y	N
8	Does your hospital use a CBMWTF, for transport, & dispose of BMW?	Y	Y	Y	Y	Y	N
9	Does your hospital follow which of the following						
A	Off- site incineration	Y	Y	Y	Y	Y	NC
B	Through on- site incineration	N	N	N	N	N	N
C	Through autoclave	N	N	N	N	N	N
D	Through Chemical Disinfection						
E	By other processes	N	N	N	N	N	N
B. Liquid Waste							
1	Do you discharge wastewater in followings:						
A	Sewer	Y	Y	Y	NC	Y	Y
B	Septic system.	N	N	N	NC	N	N
C	Surface water.	N	N	N	NC	N	N
2	Does your Hospital keep records about amount of waste water discharge per day?	N	N	N	N	N	N
4	Have you ever sampled your waste water for water quality analysis?	N	N	N	N	N	N
5	Do you have a diagram of your waste water discharge system to sewer?	N	N	N	N	N	N

*SS means survey site, Y=Yes, N=No and NC=No Comments

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Questionnaire Based Findings

Here, questions were clustered into two major divisions i.e. solid waste generated from hospitals and liquid waste generated from the source sites, which were further categorised into different questions. It has been found that a significant portion of solid waste including bio-medical waste generated from study sites in hazardous in nature. Similarly, there is also a difference noticed between data from questionnaire and self-observations during site visits i.e., SS4 and SS6 claiming that they have well labelled coloured containers with biohazard symbols/category wise labelling but these all findings were missing during self-visits. On the other hand, SS1 and SS2 show the match between claims and practical awareness.

The awareness for The Bio-medical Waste Management rule, 1998 and status of policy implementations among study sites also followed through question items. The status of management was alarming at state funded hospital (SS6) in comparison to central and private funded hospitals, because of no segregation facility and biomedical and general waste were. Thus, this indicates a requirement of major inputs for the improvement in segregation facilities, whereas, SS6 has a well separated accumulation area away from main building for collection of waste from several departments. While, SS2, SS4 and SS5 were found better in position for management of waste generated.

It has also been noticed that all the staff and working professionals have training on handling of BMW, but only two study sites have the data records on BMW generation i.e. SS1 and SS5 and other study site's members shows unawareness regarding to the records on data generation. Although, use of CBMWTF for waste treatment and disposal has been declared by 5 study sites i.e. SS1 to SS5 except SS6 (State government funded hospital).

Assessment of Solid and Liquid Waste from Study Sites: Generation and Treatment Strategies

Solid and liquid waste treatment systems were also not showed a promising for clean environment during study sites. In the case of solid waste treatment, all the study sites depend upon the CBMWTF, which is the only unit, managing the BMW of about 260 health care centres of city nearby districts of Uttar Pradesh. Collection and transportation of waste from different sites was done on daily basis from Varanasi and on alternate days from other districts. It is established by a private firm and charges for treatment and disposal of BMW is decided on the basis of beds present in hospitals. This unit have a treatment options i.e. Incineration, Autoclave and Shredders. Ash forms of BMW go to secure landfills or common Hazardous Waste Treatment Facility at Kanpur. Mixed waste is the biggest problem here, which increases the cost of treatment plant and rest of the study sites discharging wastewater directly into sewer system. Lack of proper wastewater management is also noticed during the study of sites.

SS1 and SS5 showed an awareness for treatment of BMW. Survey site 1, one of the biggest tertiary care hospital of city and eastern, U.P. There were about 1,181 beds, on which 47, 610 indoor patients, admitted with 1,027,134 out patients, 84,966 emergency outpatients investigated in year 2011 (according to data from hospital records of 2011). During treatment and caring of patient there were about 101167 Kg BMW generated. Hence, there were about 0.2346 kg/bed/day and about 0.0058 kg/patient/day BMW generated (Figure 1 and Figure 2). Similarly, survey site-5, biggest cancer hospital and research centre of eastern U.P., of about 107 beds, from which 8308 Kg of BMW generated. So, there was ratio of waste generation is 0.1945 Kg/bed/day (Figure 2). Collection of these waste materials was done accordingly

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to colour codes declare by the policy framework i.e. yellow, red, blue/white translucent and black. Segregation of waste materials generated at source, and reducing the risks for contamination and cost of handling waste segregation according to colour coding was found in both study sites.

Cleaning practices were also found appropriate and according to the regulations at both sites (SS1 and SS5). Personal Protective Equipment (PPE) was also used by waste handlers, which shows the awareness towards safety and handling practices.

Lack of resources and poor processes were noticed due to rotation working policy of waste handlers is noticed. Similarly, on-site treatments of BMW in premises of both study sites were absent. All the treatment of waste was compiled at CBMWTF only, with daily transport to the facility centre. Thus, BMWM is a serious sector among various waste management practices. Improper procedures and lack

Figure 1. Generation of bio-medical waste (Kg) on yearly basis and their collection in colour coded bins for study site -SS1

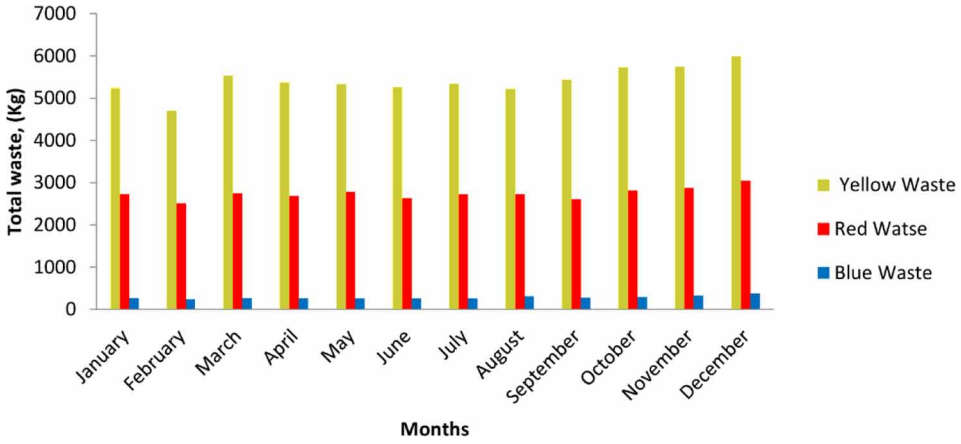
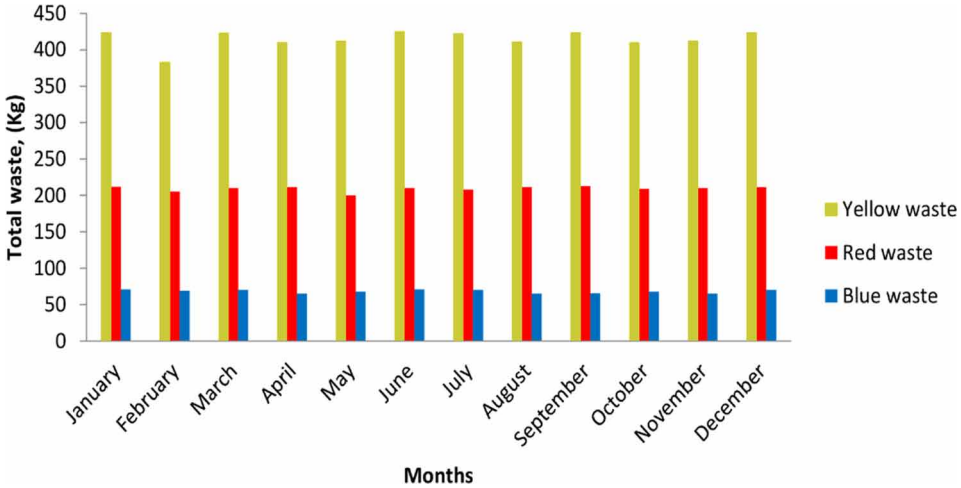


Figure 2. Generation of bio-medical waste (Kg) on yearly basis and their collection in colour coded bins for study site -SS5



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of awareness among officers-in-charge of BMW management at hospitals and nodal district officers at SPCB and CPCB requires an urgent need to solve the problem of BMW. Among all study sites, provides a bad picture of BMW management/ hospital waste management in general central, state or private funded in nature. Although various alternative options for BMW also noticed i.e. replacement of traditional BMW containers, trolleys, etc., use of microwave, hydroclave and biological agents (Thakur & Ramesh, 2015; Pandey & Gundevia., 2008; Dinesh et al., 2010) for clean-up of bio-medical waste provides a new insight for such type of waste practices. Similarly, Plasma pyrolysis with high temperature provides an energy recovery options and reduces the volume of organic matter (Tanksali, 2013; Nema & Ganesh Prasad, 2002). Many authors described the reasons for bad system/improper management as lack of sensitivity and awareness, concerning human health risks of BMW and economic constraints (Da-Silva et al., 2005). Other studies from India have also reported similar situations (Pandit & Choudhary, 2008; Shafee et al., 2010).

CONCLUSION

Hospitals are the place where humanity is serving from birth to last breath including treating several fatal diseases, abnormalities, immunization and rehabilitations etc. Its gives society to healthy life and maintain human population. During this process lot of several types of waste generated which are infectious in nature which has great potential hazard to human beings as well as natural environment. These waste creating several diseases, soil, air and water pollution also. Complex natures of Bio-medical waste are creating several problems during waste management. There is no single cleaner technology present to handle this complex type of waste so there is need to adopt good segregation practices. Hence, in concluding remark we can say that biomedical waste management is lacking proper implementation way in Indian context. Thus, handling, disposal and treatment options needs urgent involvements to improve the systems at all the three sectors-central, state and private funding hospitals, with specific focusing on awareness, policy reformation with responsive governance.

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Chapter 40
Mystery of Recycling:
Glass and Aluminum Examples

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ABSTRACT

Recycling is a key component of modern waste reduction and is the third component of the "Reduce, Reuse and Recycle" waste hierarchy. Recycling and/or waste minimization is a prerequisite for sustainable value and green environment. Recyclable materials include many kinds of glass, paper, metal, plastic, textiles, and electronics. The composting or other reuse of food is also considered recycling. This chapter starts with an expanded definition of recycling; afterwards, the recycling processes of glass and aluminum are examined in detail. Besides recycling, for a green environment the necessity for reducing and reusing of waste is also considered. Another topic will be the myths of recycling-unknown realities about recycling process. Furthermore, types of recycling and cost-benefit analysis will be explained. Ultimately, the chapter will be concluded by criticisms about recycling, and potential areas for further discussion.

RECYCLING

Definition and Scope

Recycling and/or waste minimization is a prerequisite for sustainable value and green environment. This chapter starts with an expanded definition of recycling; afterwards, the recycling processes of glass and aluminum are examined in detail. Besides recycling, for a green environment the necessity for reducing and reusing of waste is also considered. Another topic will be the myths of recycling-unknown or misknown realities about recycling process. Furthermore, types of recycling and cost-benefit analysis will be explained. Ultimately, the chapter will be concluded by criticisms about recycling, and potential areas for further discussion.

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Recycling, mainly driven by economic and regulatory factors, is performed to retrieve the material content of used and nonfunctioning products (Srivastava, 2007). Recyclable materials include many kinds of glass, paper, metal, plastic, textiles, and electronics. The composting or other reuse of food is also considered recycling. Materials to be recycled are either brought to a collection center or picked up from the curbside, then sorted, cleaned, and reprocessed into new materials bound for manufacturing. Recycling can also be defined as a process to change waste materials into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution and water pollution by reducing the need for conventional waste disposal, and lower greenhouse gas emissions as compared to plastic production.

Many types of waste can be retrieved by recycling material. Among the diverse types of waste, glass is one of the most valuable recycling materials because it can be revived and recycled completely and hardly decomposes. Recycled glass can be used for porcelain, building material, sidewalks, and asphalt roads. Glass recycling has many advantages such as the preservation of natural resources and minerals, reduction in energy consumption, and reduction in air pollution. If glass can be recycled effectively, the environment can be greatly improved (Furlani et al., 2010; Ismail & Al-Hashmi, 2009).

Recycling is a key component of modern waste reduction and is the third component of the "Reduce, Reuse and Recycle" waste hierarchy. Aluminum is also another product that is mostly recycled and reused. Aluminum recycling has a number of key environmental and economic benefits. Compared to other high volume materials, aluminum production has one of the largest energy differences between primary and secondary production: 186 MJ/kg for primary compared to 10–20 MJ/kg for secondary (Green, 2007). With energy and cost savings in mind, many producers now have targets of increasing their usage of secondary materials (2002; Alcoa, 2006). However, the accumulation of impurities in these recycled material streams provides a significant, long-term compositional barrier to these goals (Liu, 2003).

On the other hand, these processes have also important quality standards. The examples for such standards related to recycling are ISO 15270:2008 for plastics waste and ISO 14001:2004 for environmental management control of recycling practice. These standards are needed for more efficient and effective processes in terms of recycling.

Continuously increase in world population and changes on the habits of consumption demand on the materials leads to rapid decrease on natural resources. It ıs inevitable that these resources will be run out shortly by the high consumer demand. In order to use effectively the limited resources, some of countries have taken a number of decisions, contributing the effective consumption on the resources. One of the most important ways of preserving the resources has been recycling, which is a process of reusing the materials used before and waste materials which have no use. In order to preserve the resources for the future generations and crises on energy leads the countries to take some radical action on energy and resources consumptions. All the material which can be reused such as asphalt, concrete, timber, paper, glass etc. has been reused for the same purposes or different. Especially construction industry has been a major resource for recycling to preserve and protect the environment. Unfortunately all this kind of preservation policy has no effective implementation. This chapter will underline the preservation policies and recycling carried out around the world.

Waste management has received in the last decades increasing attention. This is mainly due to the growing volume of waste produced, the scarcity of disposal areas and environmental protection. Lately, due to the harmful environmental effects of disposal, the emphasis has been shifting towards recycling. (Barros et al., 1998) Recycling is the process of remaking materials from ones that have already been

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used. It also means using the used materials as raw material. If a product is described as "recycled", it means that it contains material that has been reprocessed. Most common materials recycled are paper, aluminum, plastic and glass (Go Facts Environmental Issues, 2006).

There is increasing pressure on waste managers, planners and waste regulators to deliver a sustainable approach to waste management and to integrate strategies that will produce the best practicable option for the environment. To aid evaluation and selection of the "best option(s)" for the management of wastes, guidelines were produced by the EC in 1989. These highlighted the potential resource conservation and pollution benefits available through developing solutions that focused on minimizing waste, on reusing and recycling unavoidable waste and rendering unusable wastes and residues safe for disposal. This so-called "waste hierarchy" has become the bedrock of strategy development for waste management throughout Europe. (Barton et al., 1996)

Recycling reduces waste, reduces consumption of new raw materials, reduces energy utilization, reduces air pollution (from incineration) and water pollution (from landfill) and reduces greenhouse gas emissions from the production of new goods from raw materials. Recycling is a key part of modern waste management and the third component of the "Reduction of waste, Reuse, Recycle "waste hierarchy (Lyons & Burford, 1993). The material can be recycled, including most types of glass, paper, metal, plastic, textiles, and electronics.

Life Cycle Assessment (LCA) has been defined by SETAC as "an objective process to evaluate the environmental burdens associated with a product, process or activity, by identifying and quantifying energy and materials used and waste released to the environment, and to evaluate and implement opportunities to effect environmental improvements". LCA is normally considered to involve the following stages:

- Goal definition (i.e. study objectives) and scope.
- Preparing the inventory of burdens (e.g. resources used, pollutants emitted).
- Assessment of the environmental impact of these burdens.
- Improvement analysis.

In practice the process is iterative as the results from subsequent stages will often require previous assumptions about system boundaries, required data, data quality, etc. to be modified. Approaches to setting the goal and scope of a LCA study and developing the inventory of burdens have been subject to much debate and a consensus has been reached within the LCA community. The inventory procedure provides a fingerprint for the defined activity by quantifying the mass of raw materials and consumption of energy. This encompasses the extraction from the earth of all raw materials used both directly by the activity and indirectly through provision of raw materials used to supply energy and finished/semi-finished products demanded by the system. It includes emissions to air, discharges to water and generation of solid waste. (Barton et al., 1996)

People are producing more waste. Developed countries mostly in Europe and North America produce far more waste than most other countries. The least amount of waste is produced in several countries as Zimbabwe, Sudan and Gambia in Africa. In back, people were more likely to repair something rather than throw it away, and therefore goods lasted much longer. Nowadays, people tend to throw something away when it goes wrong, frequently because it is cheaper to buy something new than to have repairs done. This brings the increase in the amount of waste material and at the same time the increase in the potential for recycling them.

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A report by Imperial College London concluded that recycling one tonne of steel saved 970 kg of carbon emissions, however recycling one tonne of aluminum saved 3.54 tonnes (Grimes S. et al., 2008). Recycling aluminum is much more critical than many other products because of its environmental effects. This reality is shown by many reports in academic literature.

There is a report of OECD. Some of the outcomes of the report are that:

- Global extraction of material resources goes on to grow, in spite of significant improvements in countries' resource productivity, i.e. the amount of material resources that is used per unit of output.
- Per capita consumption in G8 and OECD countries remains at high levels and is about three times that of the rest of the world.
- Within the G8, Canada, Germany, Italy and Japan have succeeded in decoupling material consumption from economic growth in absolute terms, i.e. to make smaller the amount of material resources that they use.
- If indirect material flows associated with trade are taken into account, i.e. material flows that are not incorporated into traded products such as materials for resource extraction and processing, progress in countries that are net resource importers is more modest.
- While G8 countries offer a mixed picture on all annual waste generation, with some countries indicating a decrease and others an increase, a generally not negative trend can be observed in municipal waste management (representing roughly 10% of total waste).
- Further progress can only be achieved through more integrated policy approaches that take account of the full life-cycle of materials and are designed according to the principles of Sustainable Materials Management developed by the OECD.

Comprehensive efforts towards increasing recycling combined with the relatively stable waste generation observed after 2008 across Europe have led to an upsurge in combustion Waste-to-Energy (WtE) overcapacity in countries like Austria, Germany, the Netherlands, Belgium, Sweden and Denmark (Friege & Fendel 2011; Sora, 2013).

As we mentioned, the generation of waste is increasing within the European Union. The 2008 EU Waste Framework Directive (WFD) introduced some important changes to the European waste market. Most importantly, the evaluation of needs for incineration capacity can now be assessed at the European level, as non-hazardous combustible waste can be traded between countries more freely. As a result, shipments of combustible waste from countries with treatment under-capacity towards countries with treatment over-capacity have increased significantly in the last few years and are expected to continue increasing, especially if fuelled by favorable economic conditions created by national authorities. (e.g. the UK) (Dubois, 2013) It has therefore become of prime importance to specify basic notions such as recovery and disposal, so as to better organize waste management activities. It is also essential to reinforce measures to be taken with regard to prevention as well as the reduction of the impacts of waste generation and waste management on the environment. Finally, the recovery of waste should be encouraged so as to preserve natural resources.

This Directive also establishes a legal framework for the treatment of waste within the Community. It aims at protecting the environment and human health through the prevention of the harmful effects of waste generation and waste management. It applies to waste other than: gaseous effluents; radioactive elements; decommissioned explosives; faecal matter; waste waters; animal by-products; carcasses of

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animals that have died other than by being slaughtered; elements resulting from mineral resources. In order to better protect the environment, the Member States should take measures for the treatment of their waste in line with the following hierarchy which is listed in order of priority: prevention; preparing for reuse; recycling; other recovery; notably energy recovery; disposal. Member States can implement legislative measures with a view to reinforcing this waste treatment hierarchy. Furthermore, they should ensure that waste management does not endanger human health and is not harmful to the environment.

Any producer or holder of waste must carry out their treatment themselves or else must have treatment carried out by a broker, establishment or undertaking. Member States may cooperate, if necessary, to establish a network of waste disposal facilities. This network must allow for the independence of the European Union with regard to the treatment of waste. Dangerous waste must be stored and treated in conditions that ensure the protection of health and the environment. They must not, in any case be mixed with other dangerous waste and must be packaged or labelled in line with international or Community regulations.

On the other hand, any establishment or undertaking intending to carry out waste treatment must obtain a permit from the competent authorities who determine notably the quantity and type of treated waste, the method used as well as monitoring and control operations. Besides, any incineration or co-incineration method aimed at energy recovery must only be carried out if this recovery takes place with a high level of energy efficiency.

Lastly, the competent authorities must establish one or more management plans to cover the whole territory of the Member State concerned. These plans contain, notably, the type, quantity and source of waste, existing collection systems and location criteria. Prevention programs must also be drawn up, with a view to breaking the link between economic growth and the environmental impacts associated with the generation of waste.

Benefits of Recycling

Reusing of materials minimizes the need of raw material and this inherently prevents the damage to the environment and the deterioration of the natural balance by consumption which is rising up in line with population. Moreover, using recycled materials provides a large amount of energy savings. For instance, reusing aluminum materials instead of producing from raw provides 35% energy saving which is very advantageous for all parties including the producer and the end-user.

There is a limit to the amount of oil in the Earth from which we can make plastic, and a limit to the amount of aluminum ore to make cans. Resources that will run out eventually are called finite resources. Recycling reduces our consumption of finite resources. Also, when recycled materials are used to make new products, they don't go into dumps or landfills, so land is conserved. Producing products from recycled materials constantly uses much less energy than producing the same products from raw materials. Less energy consumed means less greenhouse gases, such as carbon dioxide and methane. These aids prevent global warming. Recycling one plastic bottle can save the amount of energy needed to run an average light bulb for six hours.

Glass was an expensive material until the 1800s when the mass-production of glass container started. Nowadays, the raw materials are more readily available so it is fairly cheap to make. Glass is made from three main ingredients: sand, soda ash and limestone. The ingredients are added together in a furnace and then heated until they melt. The molten glass is poured into moulds or blown to make bottles or other containers. Glass making needs a source of heat, which is usually produced by burning fossil fuels.

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Interests on reusing of the limited resources and produced products is increasing with the rapid population growth, whether changes, consumption of natural resources and increasing environmental awareness (Sengül, 2009). Recycling aids to protect the environment. Recycling significantly decreases the amount of waste in waste incineration plants or amount of waste deposited in landfill areas. A lot of landfill areas in the world have been designed with considering the situation of infiltrating water system of the toxic chemicals from the decomposing solid waste. In spite of this reality, in the contemporary world, there are a lot of examples of contaminations hazardous chemicals that cause pollution of water resources.

Incineration of solid waste is efficient for electricity need but this creates an additional cost for carbon dioxide and other greenhouse gases. Therefore, recycling rate must be increased as much as possible before incineration. Recycling prevents the abandonment of wastes to the nature. Recycling of plastic, metal, glass and paper provides electricity saving. For instance, if it is assumed that 100 unit electricity is used in producing a metal box from raw material, the electricity consumed will fall to 5 units for producing new metal box from reused metal box (Ayvaz et al., 2013).

Recycling facilitates the preservation of restricted resources. Let's look at the example down for scrutinizing this benefit in an appropriate perspective;

Recycling 1 ton steel eliminates the requirement for approximately 1.2 ton iron substance, eliminates the energy requirement derived from burning 800 kg coal and approximately eliminates the requirement for 70 kg lime stone (calcareous). By means of recycling of all sort of paper excessively requirement for cutting millions of trees may be eliminated. Precious metal (gold, silver, tantalum, titanium, rhodium etc), metal (copper, aluminum, nickel etc) oil (herbal oils, industrial oils) are termed as finite resources and will be consumed in anyway sooner or later. Mobile phone and computer manufacturers progressively report their raw material requirements, many of them launched to recycle their corrupted or obsolescent products by their own efforts.

Recycling intensifies energy productivity. It considerably reduces energy consumption for the manufacture of raw material which is going to be derived processing in the form of new kernel and energy cost. Operation of mines, kernel derivation, decomposition of derived kernel and its shaping, carriage etc., will not be needed anymore.

Recycling facilitates the establishment of strong economy. Reduction of costs for energy productivity, resource protection and professional development etc., are the efficient parameters for the nations for reaching to powerful economy. Usually, during economic recession periods recyclable products even though experiencing bottom price levels, shifting to pre-crisis periods is experienced much faster compare to remaining sectors. One of the sectors experiencing minimum impact from economic crisis is the recycling sector, most impactful factor for that reason is known as raw material provision availability in much more economic ways. Specialization in recycling by means of more advanced technological implementations intensifies as the time goes on. Public institutions directly or by means of sub-contractor firms create remarkable benefits of energy save in terms of storage and waste collection.

Recycling constitutes a profession. It constitutes a wider employment field compare to storage or waste burning operation. In a period experiencing high unemployment and in case of market deregulations such a benefit is not possible to consider unimportant. Recycling also ensure qualifications for unqualified individuals. Unqualified workers gained labor training are earned for public life earning a profession; such circumstance may be useful for the elimination of guilt rates. Even illiterate individuals may be ensured with a specialized skill following professional training and business applications.

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Recycling creates social structure. Fundamental fact for humans to come together and to constitute social gatherings remains on problems and related precautions. Recycling is not different than those. From diverse cities or countries individuals from diverse cultures, different educations, diverse age groups, diverse genders, political and life orientations by means of coming together behave in the same way for the well-being of environment and living creatures. Recycling is an important source for revenue. Infrastructure and investment are quite high costs while giving recycling services but the correct implementation of the waste materials (rubber, paper, plastic, glass, metal, electrical and electronics, accumulators, batteries, etc.)

Recycling makes natural resources protected. Natural resources minimize each day as a result of population increasing and the changing in the consumption habits of the world. Therefore, to reduce material consumption, with the means to recycle waste have to be considered qualified to use the world's natural resources efficiently. Whereas, recycling is an extremely significant process for the conservation and efficient use of our natural resources. For instance; with aid of recycling paper we can provide less cut trees in the forest. Similarly, oil can be saved by recycling of plastic waste.

Packaging which is used can be evaluated for use as a raw material source of waste, such as the protection of raw materials to be consumed or used instead of natural resources leads to significant savings. Our natural resources, because of the increase of the world population and consumption are decreasing every day. Hence, it is requisite to use of our natural resources in a more efficient manner. Recycling reduces the amount of waste. Reduction in the amount of waste going to recycling waste by applying a smaller amount of space for the transportation of waste and storage operations, and less energy is used. This reducing is not more weight to domestic waste. Referring constitute it is a significant proportion by volume. Recycling means less waste goes to landfill and, in addition to facilitating the transportation and storage of these wastes, because now less landfill and requires less energy.

Recycling Provide Benefits to Urban Ecology:

- Recycling leads to rise economic contribution to the municipality, especially in the quality of cleaning.
- Reducing the amount of waste to be collected every day is no need to collect recyclable waste every day, provide more progressive collection of these waste.
- Prevented the use of valuable land in the city as dump place. Fewer garbage, wrap around floating in less point, which means less obnoxious odors point.

Recycling and Environment

It is also important to reuse materials as raw materials for preventing environmental pollution. Recycling papers reduces the air pollution by around 74-94%, water pollution by 35%, water using 45%. It is possible to prevent cutting 8 trees with reusing 1 ton paper.

Simply recycling metal and glass could reduce the total cost of waste disposal by 66%, and save 147 kg of carbon emission per thousand cases. In 2009–2010, 9.7 million surgical interventions or procedures were performed; extrapolating our figures gives a sense of the annual potential for savings nationwide: approximately £1 million and 1350 tons of carbon (NHS, 2010)

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It could be argued that the U.S. environmental movement started with recycling. For old-school environmentalists, recycling is such an integral part of the movement that it's difficult to separate the two. And in those early days, back in the 1980s, the cause was noble and pure: Why throw away products that could be new again? Why not turn trash into raw materials?

At a certain point, though, recycling developed something of a dark side from an environmental perspective. On the surface, it's still a good idea both to recycle waste and to design products and packaging with the idea of recycling them in a closed loop. Unfortunately, in its modern-day incarnation, recycling has also given the manufacturers of disposable items a way to essentially market overconsumption as environmentalism. Every year, reports come out touting rising recycling rates and neglecting to mention the soaring consumption that goes along with them.

Trade groups representing different packaging interests–plastic, paper, glass–have become the largest proponents and financial sponsors of recycling. If you go to the Environmental Protection Agency's website looking for statistics on packaging recycling, the stats on plastics recycling come from the American Plastics Council and the Society of the Plastics Industries, Inc. (SPI), both trade associations representing the plastics industry.

The plastics industry's interest in recycling is two-fold of course–on the one hand, by supporting recycling and helping to establish infrastructure for plastic recycling, the industry ensures a steady supply of new materials. On the other hand, it aids consumer to justify the consumption of more disposable plastic goods and packaged items if they can comfort themselves with the idea that whatever they throw in the bin will be recycled.

The thing is, recycling isn't the small operation it once was, it's a commodity business that fluctuates with supply and demand. It's also a global market, with recyclables collected in the United States being shipped to wherever demand is highest (often China). A few years ago, when demand for recycled paper products dropped, recyclers all over the country where warehousing stacks of cardboard, waiting for the prices to turn around. "The hope is that eventually the markets turn around and that the material is sold, but I have heard of instances where it gets landfilled, because a community doesn't have the demand or the space or the company to deal with it," says Gene Jones, executive director of Southern Waste Information Exchange - a nonprofit center for information about recycling waste.

Moreover, not everything that's "recyclable" actually gets recycled. Even when you're dealing with easily recycled items like PET or HDPE plastic (the plastics commonly used for bottles), or glass or cardboard, first you've got to get consumers to dispose of the items properly, then you've got to have a collection system in place (just over half of U.S. cities have curbside recycling, keep in mind), and then recyclers typically need to have a buyer lined up to justify recycling anything (Uzir, A. et al., 2014)

Roughly 40 million metric tons of electronic waste(e-waste) are produced globally each year, and about 13 percent of that weight is recycled mostly in developing countries. About 9 million tons of this waste - discarded televisions, computers, cellphones, and other electronics - are produced by the European Union, according to the United Nations Environment Programme (UNEP). And UNEP notes that this estimate of waste is likely too low. Informal recycling markets in China, India, Pakistan, Vietnam, and the Philippines handle anywhere from 50 percent to 80 percent of this e-waste, often shredding, burning, and dismantling the products in "backyards." Emissions from these recycling practices are damaging human health and the environment (UNEP, 2005).

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"Developing countries with rapidly growing economies handle e-waste from developed countries, and from their own internal consumers. Currently, an estimated 70 percent of e-waste handled in India is from other nations, but the UNEP estimates that between 2007 and 2020, domestic television e-waste will double, computer e-waste will increase five times, and cell phones 18 times" says Lucy McAllister. She is a Ph.D. candidate in environmental studies at the University of Colorado Boulder.

The informal sector's recycling practices magnify health risks. For example, primary and secondary exposure to toxic metals, such as lead, results mainly from open-air burning used to retrieve valuable components such as gold. Combustion from burning e-waste creates fine particulate matter, which is linked to pulmonary and cardiovascular disease.

While the health implications of e-waste are difficult to isolate due to the informal working conditions, poverty, and poor sanitation, several studies in Guiyu, a city in southeastern China, offer insight. Guiyu is known as the largest e-waste recycling site in the world, and the city's residents exhibit substantial digestive, neurological, respiratory, and bone problems. For example, 80 percent of Guiyu's children experience respiratory ailments, and are especially at risk of lead poisoning (Leung et al., 2008).

Residents of Guiyu are not the only ones at risk. Researchers such as Brett Robinson, a professor of soil and physical sciences at Lincoln University in New Zealand, warn that wind patterns in Southeast China disperse toxic particles released by open-air burning across the Pearl River Delta Region, home to 45 million people (Robinson, 2009). In this way, toxic chemicals from e-waste enter the "soil-crop-food pathway," one of the most significant routes for heavy metals' exposure to humans. These chemicals are not biodegradable, they persist in the environment for long periods of time, increasing exposure risk.

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal bans the exchange of hazardous waste, including e-waste, between developed and developing countries. The United States is the largest generator of e-waste worldwide and the only industrialized nation not yet ratifying the Basel Convention.

E-waste is an important global environmental and health issue. Promising policy responses have arisen from the European Union, which is defining the source as responsible for e-waste. With this approach, manufacturers are required to eliminate dangerous toxins from production.

Types of Recycling Products

1. **Aluminum:** There may be a symbol, such as an alu mark, on the product to indicate what metal it is made from. Drink cans are usually made from aluminium and food cans are usually made from steel. Aluminum cans are 100 percent recyclable and can also be recycled over and over again. Even better, turning recycled cans into new cans takes 95 percent less energy than making brand-new ones.
2. **Steel:** Steel is also another metal which can be recycled, and you can separate steel from aluminum with a magnet. Just like aluminum, steel products can be recycled over again without compromising the quality of the steel. More than 80 million tons of steel are recycled each year in North America, and recycling steel saves the equivalent energy to power 18 million households a year. Aluminium metal is non-magnetic whereas steel is magnetic. Food cans are mainly made from steel. You have to be sure that drink and food cans are clean before recycling. Aerosol containers can also be recycled, but only when they are completely empty.

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3. **PET Plastic Bottles:** There are about 50 different types of plastic. Pet bottles are the most used ones. Americans buy about 25 billion single-serving bottles of water each year, according to the Container Recycling Institute. Worse yet, about 80 percent of those bottles will end up in a landfill. Making plastic out of recycled resources uses about two-thirds less energy than making new plastic. And because plastic bottles, more than any other type of plastic, are the most commonly used type, they are usually the easiest to recycle. HDPE is another type of plastic which stands for high-density polyethylene, a common and more intense plastic, which is used for detergents, bleach, shampoo, milk jugs. This type of plastic is also used in household daily life and should be recycled.
4. **Glass:** Glass is separated into 3 colors: green, brown and clear. Besides recycling reusing is another method for glass. You can reuse glass whenever possible. Jars can be used as small containers and bottles can be used as vases. Recycled glass saves 50 percent energy versus virgin glass, and recycling just one glass container saves enough energy to light a 100-watt bulb for four hours. Recycled glass generates 20 percent less air pollution and 50 percent less water pollution, and one ton of glass made from 50 percent recycled materials saves 250 pounds of mining waste.
5. **Paper:** Paper is separated into the following groups: magazines, newspapers, office paper, cardboard, phone directories. Besides recycling, you can reduce paper waste by cancelling unwanted deliveries, or read news online as opposed to buying newspapers. Also you can reuse paper around the home as scrap paper or packing material. Envelopes can also be reused. According to the Environmental Protection Agency, paper makes up about one-third of the all the municipal waste stream in the U.S. That's a whole lot of paper, and since we know that recycling all that paper conserves resources, saves energy, and doesn't clog up the landfills, there's no reason not to do it. Buying recycled paper whenever possible is another way for recycling paper. On the other hand, there are so many reasons to recycle all kinds of paper that it makes no sense not to. First, recycled paper saves 60 percent of energy versus virgin paper, and also generates 95 percent less air pollution. Recycling one ton of paper saves 17 trees and 7,000 gallons of water. Sadly, though, every year Americans throw away enough paper to make a 12-foot wall from New York to California.
6. **Batteries:** All waste batteries are classified as hazardous waste and recycling is always the best option. Ordinary household batteries do contain some hazardous chemicals so ideally should not be thrown out with the day to day rubbish. Rechargeable batteries contain harmful metals, so should never be thrown away with daily rubbish, they should be returned to manufacturer for disposal or recycled elsewhere. Ordinary batteries require a lot of energy to make, so in order to save energy, use rechargeable batteries and electricity mains instead of ordinary batteries. Rechargeable batteries are the most environmentally friendly option as can last for up to several hundred charging cycles resulting in less waste being produced.
7. **Paint/Oil:** Waste such as paint, paintbrushes, car oil and oil filters have to be carefully disposed of, as they can be very damaging to the environment. Mostly, there are disposal or recycling instructions on the packaging of the product. Buying products in bulk whenever possible to reduce packaging waste and using eco-friendly alternatives whenever possible are important steps for recycling. It is crucial to recycle the engine oil correctly as even a small amount of oil can cause damage to the environment as well as making a noticeable mess.

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8. **Building Materials:** Buildings are made from many materials, many of which are recyclable such as metal, wood, glass, etc. Recycling these materials accordingly is an important environmental solution. Architectural salvage yards may take some items for reselling and many building materials can be reused, such as bricks and wood.
9. **Clinical Waste:** Clinical waste such as nappies, sanitary waste and medical supplies have the potential to be infectious so must be disposed of using special methods. Households as an environmentally conscious people should be very careful when disposing of needles and syringes and look for doctors or manufacturer instructions of how to dispose of medical waste on the packaging containers. Medicine containers can be recycled accordingly once it is empty. Many local municipalities offer free medical waste collection. Some companies are also currently implementing clinical waste treatment schemes and make money from recycling.
10. **Textiles:** Most home recycling bins, provided by your local council, accept old clothes and textiles. Recycling banks may also accept old clothes. Donating old clothes that are still usable to charity shops or take them to a jumble sale will help recycling. If they are unusable, then old clothes can be used to make other textile items, such as cushion covers or cleaning cloths.
11. **Corrugated Cardboard:** Old corrugated cardboard (OCC) represents a significant percentage of the commercial solid waste stream. In 1996, the U.S. generated 29 million tons of OCC, or 13.8% of municipal waste stream. Approximately 90% of that comes from the commercial or non-residential sector.
12. **Computers:** Electronic rubbish, and computer equipment in particular, is a rapidly expanding stream of UK waste. Low prices allow consumers to replace "gadgets" often, and rapid technological change means there are always newer, better, more powerful products on the market. The result is a burgeoning computer waste mountain. Up to 20 million "obsolete" PCs are discarded annually in the USA alone. Computers can be recycled in a couple of ways, depending on the state of the machine (Molland, 2014). Also known as e-waste, discarded computer equipment comprises monitors, printers, hard drives and circuit boards. Such items should on no account be thrown out with your household rubbish because they contain toxic substances, and are effectively hazardous waste. E-waste often ends up in the developing world, and the UN's Environment Program is alarmed by the amount of electronic goods which is improperly disposed of overseas. There is increasing concern about the pollution caused by hazardous chemicals and heavy metals in Africa, Asia and South America. A single computer can contain up to 2kg of lead, and the complex mixture of materials make PCs very difficult to recycle. Increasingly, manufacturers of electronic goods incorporate e-waste management into their environmental policies and operate consumer recycling schemes. Dell, for example, covers the cost of home pick-up, shipping to the recycling centre, and recycling of any obsolete equipment. The goods are "de-manufactured", and sorted according to type or material. Materials like steel and aluminum are then re-cycled to make new products, from car parts to plastic toys. Meanwhile non-reusable substances are disposed of in an environmentally sound manner. Another big brand, Hewlett Packard, recycled over 74 million kilograms of electronics in 2005. Since beginning the program 20 years ago, HP has expanded recycling operations to more than 40 world regions. Another option is donating old computers to non-profit organizations. A number of non-profit organisations collect electronic equipment including computers and printers, either for reuse or for de-manufacture and recycling. Recipients pay nothing for the equipment or buy it at a heavily discounted rate. Developing countries benefit most from these schemes.

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13. **Printing Cartridges:** Recycling printer cartridges really is worthwhile as cartridges can be expensive and remanufactured printer cartridges can cost as little as 10% of what original cartridges do. By lessening the amount of cartridges ending up in landfill sites, you are being kinder to the environment too. 24 million homes in the UK have a personal computer and 90% of those homes have printers. The average household uses 2-3 inkjet cartridges a year and many offices use large numbers of laser cartridges. Only 15% of the 65 million printer cartridges that are sold in the UK are recycled which means the rest end up in landfill sites and this is major bad news as the plastic used in a typical cartridge is made of engineering grade polymers and is expected to take up to 1000 years to decompose.
14. **Mobile Phones:** Most people in the developed and developing countries now own a mobile phone and they can be recycled. The first way is donating old mobile phones to friends or family. Another option may be taking back old mobile phones to manufacturers for recycling, because some companies have set up mobile phone recycling schemes.
15. **Composting:** Composting is the decomposition of materials that originated from animals and plants. These organic materials can be things such as plant trimmings, vegetable cuttings, eggshells and teabags. The composting process produces a dark, crumbly matter that can be used as fertilizer in garden soil. Composting is an excellent way to recycle kitchen and garden waste. It is very easy to build your own compost bin and use the compost to help your garden grow.
16. **Vehicles:** Up to 80% of a vehicle can be recycled, first for a more green world try and fix your vehicle instead of throwing it away, but if you want to buy a new one, then sell unwanted vehicles instead leaving them to rot.
17. **Electrical Equipment:** Most electrical equipment can be reused or broken down into parts. If the electrical equipment is still in full working order, to help the environment, sell it in a car boot sale or donate it to a charity shop. Some retailers may take back old products to recycle. Also, some councils accept electrical equipment at their waste recycling centers. Always trying to repair items rather than throwing them away will be a better option, which will allow others to find a use for the item, when you no longer want it. Choosing electrical items that have a long life span will also help environment.
18. **Furniture and Wood:** Wood can often be reused to make other items, such as a bird table for garden. Recycled wood can be used to produce unique eco-friendly furniture. Recycling old or damaged pallets prevents unnecessary landfill and reduces the need to chop down trees for new wood to make new pallets. Donating usable furniture to charity shops, schools, community centers, friends or neighbors or selling furniture at garage sales or in auctions is another option. Clean and repair broken furniture before you sell/donate it.
19. **E-Waste:** The useful life of consumer electronic devices is relatively short, and decreasing as a result of rapid changes in equipment features and capabilities. This creates a large waste stream of obsolete electronic equipment, electronic waste (e-waste). Even though there are conventional disposal methods for e-waste, these methods have disadvantages from both the economic and environmental viewpoints. As a result, new e-waste management options need to be considered, for example, recycling. But electronic recycling has a short history, so there is not yet a solid infrastructure in place. (Kang, 2005)

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Aluminum

The industrial-scale production and use of aluminum is less than 150 years old. Yet in that time, the industry has grown until it is second only to the iron and steel industry among metal producers. The growth in aluminum usage was particularly rapid in the years following World War 2, and every sector of the industry can point to product that were never produce from aluminum a generation ago but are now primarily manufactured from aluminum alloy. Beverage cans, sports equipment, electrical bus work, window frames-all are now produced from aluminum, along with thousands of other product.

Books on the production of aluminum metal have previously focused on its recovery from naturally occurring raw materials. The principle natural ore for aluminum is bauxite, a mineral consisting primarily of hydrated aluminum oxides. Aluminum is recovered from bauxite by a selective leaching sequence known as Bayer process (Damgaard et al., 2009; OECD, 2010), which solves most of the aluminum while leaving impurities behind. The aluminum recovered from the leach solution by precipitating it as aluminum hydroxide. The hydroxide is the dried and calcined to generate purified alumina. The calcined alumina as in turn fed to electrolytic cells containing a molten salt electrolyte based on cryolite (Na3AIF6). The alumina this solves in the cryolite electrolyzed to generate molten aluminum metal and carbon dioxide gas. These process has been the sole approach for producing primary aluminum metal since the late 1800s and will likely continue in this role for decades to come (Schlesinger, 2013).

History of Aluminum Recycling

According to Mark A. Schlesinger from Yale, the successful recycling aluminum depends on several factors:

- A plentiful and recurring supply of the metal, concentrated sufficiently in one area to justify the cost of collecting it.
- An infrastructure for collecting the scrap metal, removing impurities, and delivering it to a recycling facility.
- A method for recycling metal that is economically competitive with the production of the metal from natural ores.
- A market for the recycled metal, should its composition or quality differ from that of primary metal.

Aluminum is recycled because it is inexpensive to turn into new aluminum products and because making new aluminum is expensive. On the other hand, it is not logical to recycle all the materials. For example, steel is much cheaper to produce from raw materials, so there is less reason to recycle it – although it can easily be recycled.

Aluminum is recycled through a variety of programs. The most generally recognized consumer programs are curbside and municipal. In these programs, items like beverage cans, aluminum foil, aluminum baking trays and pie pans are recycled. The aluminum industry actively supports the Curbside Value Partnership, which is a program dedicated to increasing participation in curbside recycling programs and to measure this growth using solid data. Within the industry, building and automotive parts are collected

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for recycling. More than 90 percent of the aluminum in building and automotive parts is recycled at the end of use. All of these items serve as a feedstock and are sent to aluminum recyclers to be melted down in the secondary production process.

Aluminum is one of the most recycled - and most recyclable - materials on the market nowadays. Nearly 75 percent of all aluminum produced in the U.S. is still in use today. Aluminum can be recycled over and over again without any loss to quality. In fact, an aluminum beverage container can be recycled and back on the shelf in 60 days.

The economics of aluminum also contributes to its position as one of the most-recycled metals in the U.S. Unlike many other materials, aluminum pays more than for its own recycling in the consumer and industrial waste stream. The reason: demand for aluminum continues to skyrocket and recycling aluminum saves more than 90 percent of the energy required versus producing new metal.

Glass

Glass was an expensive material until the 1800s when the mass production of glass containers began. Today, the raw materials are more easily available so it is fairly cheap to make. Glass is made from three main ingredients; sand, soda ash and limestone. The ingredients are added together in a furnace and then heated until they melt. The molten glass is then poured into moulds or blown to make bottles or other containers. Glass making needs a source of heat, which is usually produced by burning fossil fuels (Morgan, 2009).

When it comes to reducing and reusing glass, there are ways of reducing the amount of glass needed. For example, modern bottles are much lighter than in the past and this saves on manufacturing and transport costs. Just 5 years ago a small beer bottle weighted 260 grams, but this has now been reduced, by almost a third, to 170 grams. Once a bottle has been used, it can either be reused or recycled. From an environmental point of view, it is much better to reuse a bottle than to recycle it. Less energy is used in the collection, cleaning and refilling of a bottle than is needed to recycle it.

During the 1950s and 1960s it was quite common to take bottles back to shops from where they would be collected and taken back to the factory. As the manufacturing plants became larger and began to supply bottles to further-away places, it became too costly to take the bottles back to the factory so this practice slowly died away. In some countries, milk is still delivered to some homes in glass bottles. The average milk bottle is used about twenty times.

In the developing world, reusing glass bottles is more common and soft drinks often come in glass bottles that are collected and returned to the factory. Clear glass containers such as jam jars are frequently reused in homes for jam making and pickling amongst other things. However, a bottle or jar that is to be collected from homes or shops and reused many times has to be made from heavier, thicker glass, in order to withstand wear and tear. Because of this, more glass is used in its manufacture and more energy in its transportation. There are also additional costs of collection, transportation and cleaning (Go Facts Environmental Issues, 2006).

The great thing about glass is that it can be recycled very easily, and this can happen over and over again without any loss of quality. It was the first material to be progressively recycled and nowadays a large percentage of all glass is recycled. For example, in Finland and Switzerland, as much as 90 per cent of glass is recycled. Glass collected from factories and bottle banks is taken to recycling plants where it is monitored for purity –that is if it is all the same color with no foil or caps- and crushed to make cullet. Then the cullet is mixed in with the other raw materials and melted (Morgan, 2009).

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Another glass recycling type is CRT (cathode ray tube) glass waste. It includes the parts from TVs, PC monitors and other monitors used in special applications, and waste from the original assembly process. According to European Waste Catalogue and United States Environmental Protection Agency (EPA) CRTs are classified as hazardous household waste (Maschio et al., 2013).

Recycling Criticisms

Recycling is gaining increased acceptance worldwide, but not everyone agrees that it's the best way to deal with the environmental problems of garbage. There are several criticisms of recycling. Criticisms concerning the cost of recycling are mostly related to lack of market competition. (Tasaki, 2005)

The process of recycling an old product into something reusable uses energy and creates pollution. Critics claim that recycling is simply a zero-sum game, where the pollutants and waste from making new goods shift into the recycling industry. For some types of recycling, this may be true -- the trade-off between new products and some forms of recycled plastic, for example, are questionable. Nevertheless, there are at least as many ways to recycle that offer clear benefits in terms of energy used, natural resources consumed, pollutants released and landfill space used. There are those, though, who believe that recovering energy by incinerating waste is better, by and large, than recycling it. The Institute of Mechanical Engineers, for example, has recently urged the government to invest in heating and energy projects with local waste being used as the fuel resource, much like the schemes found in countries such as Germany and Austria. "The government should abandon its focus on recycling as the only way to rid us of landfills," it says, "as this is quite unachievable and is clearly deceiving the public about what is really happening to their waste. Recycling should only be for waste products that cannot be more sustainably converted into electricity, heat and/or transport fuels." Adam Read, a former professor of waste management at Northampton University, believes that the industry is still in the foothills when it comes to understanding the full environmental implications of each form of waste treatment. "We certainly need to understand our waste-flow better," he says. "We need a better grasp of the calorific values, water content, market values and the like of each waste source before pushing ahead. Yes, it sometimes will be more economical to burn waste, but the environmental impact is always going to be less when recycling. However, incineration will always be better environmentally than landfill because of the methane generated when organic waste rots underground."

Some claim that there's no "garbage crisis." They say there's plenty of landfill space - landfills are a safe and simple way to store as much garbage as we need to put there (EcoWorld). It's true that there's technically plenty of space in the United States and other countries in which to store our garbage, but the thought of filling valleys and fields with garbage doesn't appeal to many people, and certainly not those who live near those valleys and fields.

This criticism closely ties to the problem of recycling causing its own environmental impact. Because of this impact, recycling only represents a minor improvement over landfills or incineration of garbage. Yet, it makes people feel like they've accomplished something important in protecting the environment. Recycling can also enable an attitude of entitled consumerism - people feel that it's OK to purchase and use environmentally harmful products like bottled water or plastic diapers because they make up for it by recycling. These views point to the ultimate solution: buy less stuff. Purchasing reusable goods or simply buying fewer things we don't need is the best way to stop the garbage stream at the source (Grabianowski, 2015). Recycling is not the only way of thinking green. Reducing or reusing is also important concepts to be environmentally conscious.

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CONCLUSION

This chapter briefly talks about recycling, types of recycling and examines two important recycling materials, aluminum and glass in details. Recycling is the process of making or manufacturing new products from a product that has originally served its purpose. If these used products are disposed of in an appropriate, environmentally friendly way, the process of recycling has been set in motion. A large section of the community is beginning to realize the importance of recycling. However, there are many members of the population that remain unaware or simply think it is too much of a bother.

On the other hand, it is obvious that the world has limited resources and they are finite. Recycling, reusing or reducing are all increasing the potential of the world resources. This chapter covered all materials that an informed layman and consumer should be aware of regarding most commonly known recyclable materials. We also discussed some materials that are not widely known to be recyclable. There should be special attention given to materials that bring high savings when recycled which include glass and aluminum, and they are explained in this chapter.

Recycling, just as any other business concept, is also related with supply and demand concepts. The thing is, recycling isn't the small operation it once was, it's a commodity business that fluctuates with supply and demand. It's also a global market, with recyclables collected in the United States being shipped to wherever demand is highest (often China). Nowadays, there are many companies making high profits by integrating their business model, accordingly with recycling.

Green is not only a color anymore, it is a symbol for the environmental consciousness. Furthermore, recycling is highly related with environment and has a great importance. There are many ways for recycling. It is also important to reuse materials as raw materials for preventing environmental pollution. Recycling papers reduces the air pollution by around 74-94%, water pollution by 35%, water using 45%. It is possible to prevent cutting 8 trees with reusing 1 ton paper. Simply recycling metal and glass could reduce the total cost of waste disposal by 66%, and save 147 kg of carbon emission per thousand cases.

Thinking about recycling is not enough, action is required for a better world. Moreover, not everything that's "recyclable" actually gets recycled. As we mentioned, even when you're dealing with easily recycled items like PET or HDPE plastic, or glass or cardboard, first you've got to get consumers to dispose of the items properly, then you've got to have a collection system in place, and then recyclers typically need to have a buyer lined up to justify recycling anything (Uzir, A. et al., 2014) Roughly 40 million metric tons of electronic waste(e-waste) are produced globally each year, and about 13 percent of that weight is recycled mostly in developing countries. About 9 million tons of this waste - discarded televisions, computers, cellphones, and other electronics - are produced by the European Union, according to the United Nations Environment Programme (UNEP). And UNEP notes that this estimate of waste is likely too low. Although, recycling has high efficiency rates in some products, low collection and recycling rates decreases the ultimate report results.

Aluminum and Glass are the two important recycling products examined in this chapter. Aluminum is recycled because it is inexpensive to turn into new aluminum products and because making new aluminum is expensive. Aluminum is recycled through a variety of programs. The most generally recognized consumer programs are curbside and municipal. In these programs, items like beverage cans, aluminum foil, aluminum baking trays and pie pans are recycled. Aluminum is one of the most recycled - and most recyclable - materials on the market nowadays. Nearly 75 percent of all aluminum produced in the U.S. is still in use today. Aluminum can be recycled over and over again without any loss to quality. In fact,

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an aluminum beverage container can be recycled and back on the shelf in 60 days. These advantages make the aluminum product example of this chapter.

On the other hand, Glass was an expensive material until the 1800s when the mass production of glass containers began. Today, the raw materials are more easily available so it is fairly cheap to make. When it comes to reducing and reusing glass, there are ways of reducing the amount of glass needed. Once a bottle has been used, it can either be reused or recycled. From an environmental point of view, it is much better to reuse a bottle than to recycle it. Less energy is used in the collection, cleaning and refilling of a bottle than is needed to recycle it.

Like every concept in the world literature, recycling is also having criticisms, but these criticisms are much less than its advantages. Importance of recycling may change from one country to another, but nobody can argue that it is a useless activity. For a better environment and green future, recycling is a mandatory process.

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KEY TERMS AND DEFINITIONS

Composting: The decomposition of materials that originated from animals and plants.

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Quality Standards: Concise sets of prioritized statements designed to drive measurable quality improvements within a particular area of health or care.

Recyclable Products: The products that can be efficiently and effectively reused after serving its purpose.

Solid Waste: Any discarded or abandoned materials. Solid wastes can be solid, liquid, semi-solid or containerized gaseous material.

UNEP: The United Nations Environment Programme (UNEP) is the leading global environmental authority that sets the global environmental agenda, promotes the coherent implementation of the environmental dimension of sustainable development within the United Nations system and serves as an authoritative advocate for the global environment.

Waste Hierarchy: The evaluation of processes that protect the environment alongside resource and energy consumption to most favorable to least favorable actions.

Waste Reduction: The minimization of waste at its source to minimize the quantity required to be treated and disposed of, achieved usually through better product design and/or process management. Also called waste minimization.

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Chapter 41
Sustainable Environmental Service – Knowledge Management:
A Case of Bangkok MSW Management

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ABSTRACT

Knowledge management (KM) is a key factor to increase effectiveness of management system. There have been researches of KM on many environmental services. Unfortunately, only a few researches have focused on sustainable service for Municipal Solid Waste (MSW). There are evidences of ineffective waste management causing socio-economic and environmental problems, especially in urban areas of developing countries. Humans live in service economy and knowledge society. Waste management is one of the most important public services that all residents should receive while knowledge is needed to make service run smoothly and sustainably. This paper combines concepts of sustainable service and KM to clarify the importance and how these concepts have impacts on societal well-being. Literature reviews and questionnaire surveys are main analysis methods of this paper. Sustainable service with KM roles will be described and co-created values are identified.

INTRODUCTION

Waste has become one of the most important concerns of cities all over the world. It does not only cause socio-economic impacts, but also more vitally environmental problems. Although there has been a wide attention given to make waste management system more effective, there are many obstacles causing the system faraway from accomplishment. There are evidences that socio-economic and environmental

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problems are harmfully caused by ineffective waste management, especially in urban areas of developing countries, such as odor, leftover waste, or air pollution (Pires, 2011). Having an effective waste management is difficult; however, it is possible. The current ineffective municipal solid waste management (MSWM) is caused by many factors. A very important reason leading to performance of MSWM system is staff's knowledge and related stakeholders applied to each process of management system. It has been evidenced that in some processes, waste management staff do not technically know how to use machines whereas residents would like to be educated of suitable household waste management methods or how to sort waste for disposal correctly.

It is undeniable that humans live in service economy and at the same time in knowledge society. In service sector, environmental service has gained much recognition in recent years especially on a Payments for Environmental Service (PES) perspective (Kumar, 2013; Legrand et al., 2013). PES has rapidly developed all over the world. It is a mechanism of a new type of subsidy objects to protect the environment and ecosystem services based on provision of economic incentive. PES is considered as a new market-based initiative for conservation and environmental management (Fauzi & Anna, 2013). It encompasses a diversity of mechanisms ranging from voluntary compensation to non-voluntary one.

Unfortunately, there have been only a few studies related to municipal solid waste management (MSW). In those studies, PES was widely used in many applications; however, in MSWM, it was used in economical prospect such as willingness to pay for improving waste collection service, which finally contributes to a better waste management system or a public-private partnership for waste management system incentive. Despite the fact that PES schemes can improve waste collection service in some cases, it is insufficient to say that economic based incentive system can be applied to all cities, especially in developing ones. Thus, it is important to find alternative methods to increase the effectiveness of MSWM system, which this paper emphasizes on roles of KM that will eventually lead to value co-creation for a better society well-being.

Waste management is one of the most important basic public services that all residents should receive. Knowledge, in the same way, is needed to make service run smoothly, consistently, reliably, and sustainably. Every process of waste management needs different types of knowledge and different ways to exploit the knowledge. Thus a good management of knowledge is very essential for a successful waste management. The importance of effective KM has increasingly been recognized in both business viewpoint (Deng, 2010; An et al., 2013) and academic viewpoint (Nonaka & Takeuchi 1995). Knowledge is a form of capital where the main competitive advantage is an intangible asset in all types of organizations. In the past decades research on KM is fragmented across industries. Many factors are important to KM, for example, KM strategies (Shin & Chou, 2012), KM processes (Grover & Davenport, 2001), or KM enablers (Choi & Lee, 2002). On a perspective of MSWM, KM is needed in all processes. Since each process requires different knowledge to effectively manage waste, this is one of the most vital factors showing the performance of MSWM system. Moreover, to emphasize its importance, knowledge transfer and knowledge sharing are factors that should be taken into account to KM in order to avoid occurrence of knowledge gap and hidden knowledge.

As mentioned earlier, MSWM is a basic public service. It is in need that provided service should be sustainable and affordable by community. Applying a concept of sustainable environmental service is a key to increase performance of MSWM system in long-term. The concept of service sustainability is to satisfy the need of current providers and recipients to practice mutual value co-creation without decreasing the quality of future value co-creation. In other words, the provided service should meet society needs, conform to standards, and most importantly cause no harmful impacts to society, economy and the environment.

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This paper combines the two very important concepts which are sustainably environmental service and KM to clarify the importance and how these concepts have impacts on society well-being in a case of an environmental service perspective. In each process of MSWM, roles of knowledge are explained. MSWM in Bangkok is an example case of the environmental service. This paper describes how sustainable service with KM has roles on MSWM system and finally identifies what co-created values contribute to better provision of waste management system for a better society as a whole. In literature review section, situation of MSWM in Bangkok and roles of KM on waste management are explained. Methodology section discusses about methodology of conducting research and comprises of primary and secondary data collection and analysis. About the results, this section explains what and how results are by focusing on roles of KM for each process of waste management and co-created values when KM plays an important role. Discussion section describes implications of MSWM by applying KM concept.

LITERATURE REVIEW

An Overview of Bangkok Municipal Solid Waste Management

MSW is one of the anthropogenic natural results. Gradually accumulated, the enormous amount of waste has caused tremendous adverse impacts to the world. In developing countries, the impacts are more severe as lacks of effective management system. Not only do poorly managed waste streams generate a vast amount of MSW, but also MSW causes a remarkable environmental pollution that exposes risks to mankind's health (Batool & Chuadhry, 2009). As mentioned earlier, Bangkok, the most condensed and fastest growing city in Thailand is chosen as a representative of an urban city in developing countries that has coped with MSW related problems. Factors that obstruct effectiveness of MSWM are vast amount of generated waste, improper waste collection and transportation, and lack of collaboration among stakeholders. The successfulness of the MSWM system highly depends on effectiveness of management processes. Unfortunately, MSWM system in many developing countries is relatively ineffective despite of a relatively high proportion of budget spent. This causes an incomplete long-term planning which eventually impacts the effectiveness of the whole system (Dyson & Chang, 2005).

Bangkok, the capital city of Thailand, has continuously witnessed accumulating MSW management problems. Both economic development and the rapid growth of population increase sharply from 48 million in 1982 to 65 million in 2012 as they really enlarge MSW generation in Thailand. As of December 2012, population in Bangkok was 5,673,560, which was about 9% of the total population in Thailand (DOPA, 2012). Due to the growth of population and economic, the amount of collected MSW has rapidly increased from 8,988 tons a day to 9,748 tons a day in 2000 and 2013 respectively (PCD, 2011; BMA, 2012). In other words, on a 3-year average MSW has increased 4.31%. As a result, this generation amount represents 21% of the country total waste generation (PCD, 2011). Bangkok Metropolitan Administration (BMA) is responsible for city management and well-being of Bangkok residents. BMA has recognized the increasing problems related to MSW and its management. Therefore, BMA has been trying to alleviate and solve the problems by having a long-term plan and policies and launching MSWM schemes. BMA has spent an amount of budget trying to make the MSWM system effective and draw public participation. Unfortunately, the attempt has not successfully been implemented due to many obstacles which can be categorized into parties as service providers, service recipients and ecosystem based on a tripartite service concept (Shirahada & Fisk, 2013). No co-created value occurs even though

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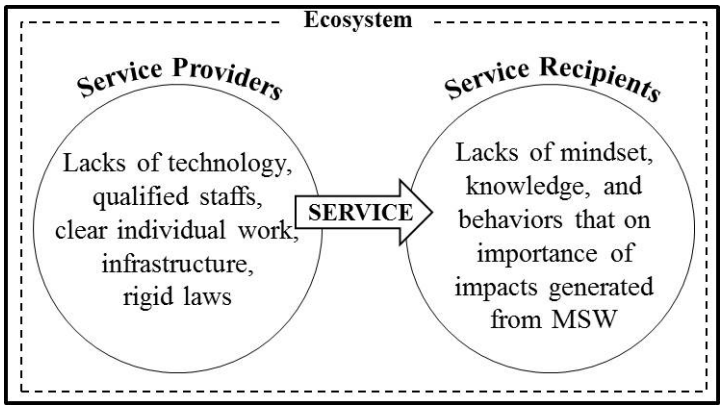
Figure 1. Ineffective waste management with no value co-creation



the tripartite concept aims to show co-created values created by resource integration among parties, due to the ineffective management system. The following demonstration shows an unsuccessful MSWM system as there are no interactions among service providers and recipients.

Bangkok MSWM is in need for involvement of related parties to have effective MSWM collaboration. The collaboration is based on an integrated MSWM that suits the city characteristics, works well with residents, conforms to standards and laws, provides economic benefits, and is environmentally friendly to the society.

Waste is defined as any residual materials from industrial and human activities and has no residual value (Ortiz et al., 2010). According to the Thailand Public Health Act 1992, MSW includes waste from community activities generated from residential households, commercial and business establishments, fresh markets, institutional facilities, and construction and demolition activities, excluding industrial waste. In Bangkok, there are four types of waste namely organic waste, general waste, recyclable waste, and hazardous waste (DEQP, 2011; DOE, 2013).

Department of Public Cleansing (DPC) and fifty Bangkok district offices are responsible for cleansing the city. MSW is collected from receptacles in front of houses, buildings, or designated locations on the specific dates and times. After being collected, waste is transported to three waste transfer stations located in three different city borders which are, Sai Mai, On Nut, and Nong Khaem. Then collected waste is put into trailer trucks by contracted private companies to be landfilled in two landfill sites in neighboring provinces, Nakon Pathom and Chachoengsao.

Ninety percent of the collected MSW is managed by disposing in sanitary landfills and 10% of the rest is composted (PCD, 2011; DOE, 2012). Waste composition is different based on economic growth, people behavior, and activities (Ogwueleka, 2013). However, MSW in Bangkok is homogenous in every district. Figure 2 demonstrates the composition of waste at transfer stations (Jungrungrueng, 2014).

MSW is one of the five critical issues of Bangkok, BMA's targets aim at having sustainable MSWM to reduce environmental impacts and global warming in Bangkok (Jungrungrueng, 2014). To achieve the targets, BMA organizes projects, for example, solid waste management at sources and community based solid waste management, these projects have been applied to promote public participation to create mutual benefits between communities and BMA in waste reduction and increase yields of recyclable materials from being contaminated.

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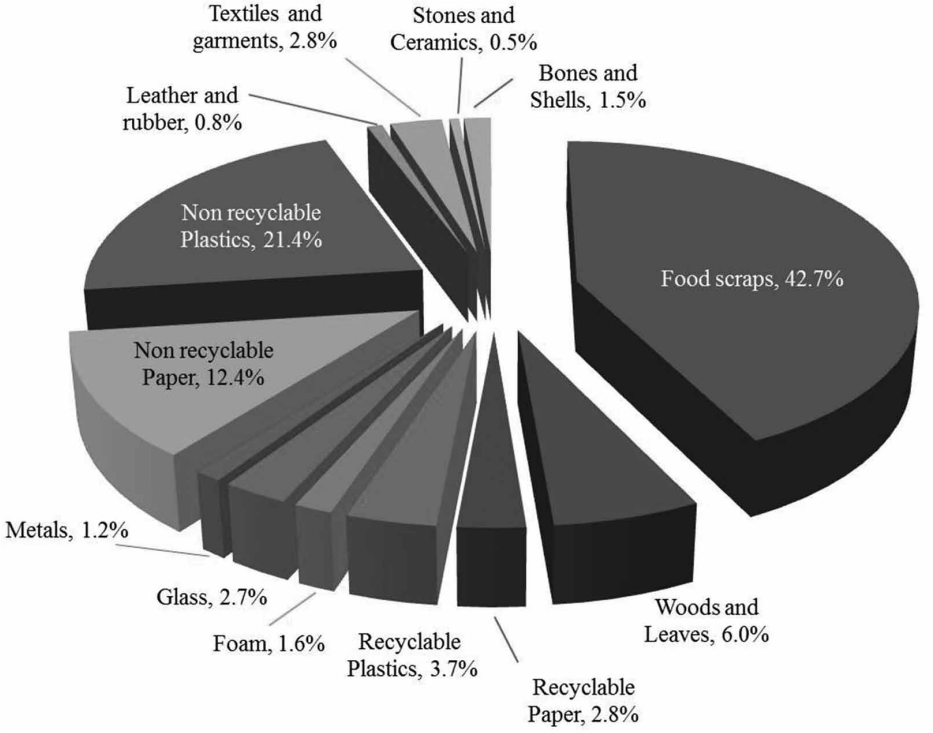
Figure 2. Waste composition at transfer stations in 2012



Municipal Solid Waste Management: An Environmental Service

According to the study of Garrod & Willis (1998), there are six functional elements of processes associated with MSWM, including waste generation, waste storage, waste collection, waste transfer, waste processing, and waste disposal. Re-categorizing those elements in terms of service recipients and providers, the first two elements are associated to waste generators which generally are the people who have demand for MSWM service. The latter four elements are more related to MSWM service providers, which is BMA in this case. However, all processes of MSWM should be received collaborative management from all related parties to create mutual benefits.

Although there have been many campaigns launched to encourage Bangkok residents to do waste reduction at source such as 3Rs programs and recycle bank programs, some of the programs were successfully implemented only for a short period. Reasons are because those programs were inconsistently promoted, lack of skills of residents, and mindset and behavior of people having less concern on the importance of the environment. Moreover, insufficient waste management infrastructure is another add-on factor that contributes to an inefficient MSWM. In other words, waste generation and waste storage are correctly done at some levels. In some cases, people do waste sorting but all sorted waste is mixed together when it is collected, this is because waste collecting trucks do not support to handle with different types of waste. In terms of waste storage, MSW is collected from the receptacles in front of houses, buildings, or designated locations on the specific dates and times. Unfortunately, in some area, people throw their waste into public places or do open air burning because of no waste management service in their areas.

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In the city environmental master plan, BMA has planned to have more waste transfer stations, but finding available lands to be transfer stations is not easy. Residents do not welcome and are not willing to live near waste dumping sites. For waste processing and disposal, there are two main concerns. First, diminishing landfill volume, the increasing generation of MSW is a major problem as there are signs of insufficient landfill capacities. The BMA has been unable to find a new land as a new landfill site. In the plan, there will be an incinerator with a pilot capacity of 300 tons per day and has expected to start operation in a few years. Second, it affects community and society, and the environment.

Waste collection policy states that all locations are to serve and make the city clean. Each district office gets support from the Department of Environment (DoE) in terms of machines, waste collection trucks, boats, and waste bins. The district offices collect waste based on the scheduled date, time, and location given by the BMA; and ensure of cleanliness that will be no leftover waste. All in all, Bangkok MSWM system seems to have all important infrastructures; however, looking into details of each process the infrastructure and resources do not suffice.

Knowledge Management on a Perspective of Waste Management

As aforementioned, KM has widely been recognized in both business and academic arrays. Having effective KM, it is important to be noted that knowledge transfer and knowledge sharing are important factors that propel created knowledge, which should be understood and accepted by all involved parties. Knowledge is a mix of framed experience, values, contextual information, and expert insights that provides a framework for evaluating and incorporating new experience and information (Davenport & Prusak, 1998).

Tacit and explicit knowledge are two types of knowledge having been suggested in Nonaka's work (Nonaka et. al., 1994). Tacit knowledge more or less related to personal knowledge. It is subjective and experienced based knowledge which cannot be expressed explicitly in words. It includes cognitive skills which are intuition, images or beliefs. On the other hand, explicit knowledge is easy to express in words. It is objective and rational knowledge. This type of knowledge includes theoretical approaches, databases, and problem solving. KM is a process of using knowledge to produce wealth for improving and developing organizations (Nonaka and Takeuchi, 1995). Moreover, it captures, develops, shares, and effectively uses organizational knowledge.

Transforming from one's tacit knowledge to be used as understandable explicit knowledge is a key for successful KM. Polanyi (1967) stated in his work that tacit knowledge is the fact that "we can know more than we can tell". He also emphasized the importance of dialogues among individuals to groups and finally to organizational levels (Polanyi, 1964). This is a way to share, transfer and transform personal tacit to explicit knowledge.

When it comes to reality, it is important that knowledge should be verified, justified, and accepted. Applying the KM concept to MSWM is a very new field of research. This paper focuses on roles of KM on each process of waste management. Before going into detail of those processes, it is inevitable to discuss about related actors in the provision of MSWM service. Starting from the very first to the last waste life cycle, MSW is generated by residents, collected by district offices, and processed and disposed of by BMA and designated companies. These four parties are main actors that directly contribute to the effectiveness of provided MSWM service. Indirect actors are also important to service performance. NGOs and private sectors act as a catalyst that makes MSWM system run correctly and transparently

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(Heap, 1998). Above all, ecosystem is one of the most important actors acting as a service provider and a service recipient. The only difference of ecosystem among other actors is that ecosystem does not have explicit roles or activities. Instead of that, it is the source of raw materials that are produced, used, and discarded as waste. And it is the end of waste management process where all waste is disposed to.

Gap of knowledge usually happens among theories, practices, and employees in different levels. Hidden knowledge is also a form of knowledge gap when knowledge is kept individually. Other than that, it is treasure hidden in employees' minds (Greiner, 2007). As tacit knowledge is a key of personalization strategy, it is important to share this hidden tacit knowledge. Sharing hidden knowledge can be done by socialization or sharing and creating knowledge among related members. Socialization can be easily done by many communication channels, such as face-to-face interactions, video conferences, or meetings.

Knowledge sharing distributes knowledge among people in an organization. Sharing of knowledge encompasses various kinds of technologies ranges from simple ones to advanced ones. People and business practices represent organization cultures which are driving factors that determine the success or failure of KM. Knowledge sharing can be done by participation in social networks, informal meetings, or group works (Teigland & Wasko, 2003). Knowledge transfer is a mechanism of selective knowledge exchanges. Not everybody in the company needs to know everything at all times. Related stakeholders should be aware of knowledge exchange opportunities during working. Knowledge transfer needs to be worthwhile for all related parties by applying it into their activities (Krogh et al., 2001).

Applying KM concept to MSWM, in all processes of MSWM system, involved stakeholders are automated to facilitate collaboration and learning by conduction knowledge transfer and knowledge sharing. Ultimately, as an intelligent support, KM is to increase the effectiveness of MSWM system and at the same time to create a sustainable waste management service.

METHODOLOGY

Data Collection

Acquiring primary data was done by conducting questionnaire surveys, which key parts are shown in the Appendix. The surveys primarily aimed to find human aspects on KM and perspective on current provided waste management service. Conducted between December 2013 and January 2014, population frame of the surveys was 422 people in Jatujak district, selected from eight community types namely, communities, department stores, schools, universities, companies, temples, markets, hospitals and hotels (BMA, 2012; DEQP, 2011).

The survey sample size was calculated with a 95% confidence level using Yamane's simplified formula (Yamane, 1983). All 422 surveys were done by employing random sampling method which target respondents were waste generators whose age ranged from 16 to more than 60 years. All surveys were conducted by direct interviewing. Therefore, there were no missing data. Apart from the questionnaire surveys, ten experts from business, academic, and private sectors were interviewed by employing semi-structured and open-ended interview methods. Practical information on KM and implications to waste management service were given. In-depth information obtained from the interviews was transcribed and incorporated into other analyzes of this paper.

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Besides, reliable data are crucial to have meaningful results which eventually are used in other researches or in Bangkok waste management system. Thus, data were collected mostly from government agencies, published journals, international databases managed by trustable organizations. Combining information from primary and secondary sources, results generated in this paper are more useful.

Data Analysis

The questionnaire consists of 105 queries from 20 questions. Out of these questions, the questionnaire is separated into four parts. The first part contains questions related to general information of respondents. The second part asks about household waste storage, disposal, and sorting behavior. The third part acquires information about human aspects on current waste management system and provided service. And for the fourth part, it relates to needed knowledge on waste management and values of applying KM concept. In this part, respondents freely expressed their opinion on waste management and what and how waste management system should be. Questions that were given to experts related to current situation of MSWM and how KM would affect the performance of waste management service. The interview aimed to obtain three topics of information which are roles of KM and how to lessen knowledge gap, impacts of KM on waste management, and their opinion on implications in combining two concepts – sustainable waste management service and KM.

All data from conducting questionnaire surveys were analyzed by a computer program which is SPSS Statistics version 17. Respondents' demographic profile and their concerns on MSWM provided service were analyzed by using descriptive statistics function, that allows precisely analyzed results by checking validity and computing univariate statistics. In terms of human aspects on needed knowledge for sustainable MSWM, a Likert five-point scale type was used for the answers, which were later grouped into the six MSWM processes. Based on these six processes, answers of aspects on value co-creation when applying KM concept are grouped and analyzed using descriptive statistics function.

Not only did questionnaire survey data obtain, but also the respondents gave insightful data while they were completing the questionnaire survey. The most useful data related to KM were data from respondents' knowledge and ideas on their aspects. Apart from quantitative data analysis, documentation, conceptualization, and examining relationships were analyzed qualitatively. Moreover, in the meantime during conducting questionnaire surveys and expert interviews, by observing surroundings and listening to what the respondents or experts spoke out, data were jotted down and recorded. After getting all required data, important factors, concepts, and relationships were identified. Examining these relationships of the concepts of KM and sustainable waste management service, personal tacit knowledge was categorized and transformed to a more understandable explicit knowledge (Adams et al., 2007).

All obtained data are analyzed and explained with mixed research methods. Increasing reliability of this paper, analyzed results are justified by theoretical support consisting of planned behavior theory, social exchange theory, and knowledge-based theory of the firm, which all details will be explained in discussion section. Moreover, practical implications of sustainable waste management service in MSWM system in Bangkok are explained which the implications were derived from the integration of quantitative SPSS data analysis and qualitative interview analysis.

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RESULTS

MSW generation shows an increasing trend parallel to the development of economic conditions, urbanization, and rapid growth of population (Beigl et al., 2008; Singh et al., 2011). MSW is a part of basic urban service and an imperative environmental service. Safe collection and disposal of MSW have been considered as one of the basic services gaining extensive attention from many countries especially developing ones (Seik, 1997). In this section, roles of KM on each process of MSWM are discussed and co-created values leading to sustainable waste management service are identified. Inefficient MSWM service has posed many serious challenges to responsible parties (BMA 2012; DOE, 2012). The significant reason causing inefficiencies is knowledge gap that should be disseminated to all related parties. Lack of proper knowledge transfer also impacts performance of MSWM. Therefore, to lessen the gap of knowledge and strengthen the quality of knowledge transfer, applying suitable KM strategies is needed. This paper provides those strategies based on analysis of human aspects.

Roles of Knowledge Management on Municipal Solid Waste Management

The results of questionnaire surveys show that there are 205 male and 217 female respondents. The majority of respondents have an average income of 10,001 to 20,000 baht or about $US300 to $US600. Average household size is 3 people per house. In terms of household waste management, 216 (51.2%) respondents do waste sorting. Putting waste in front of their houses for collection and putting waste in public waste bins are two main management methods as there are 96.7% of respondents doing these. Each household generates 1-3 kilograms of waste per day. In terms of attitudes on current waste management service, Table 1 below shows frequency results from all respondents. Table 2 shows concerns of waste management service and relationship of respondents' aspect on waste management performance and their concerns.

Table 2 shows that odor and leftover waste during collection process are the most two occurring problems that need to be urgently solved. These results go in line with information provided by Pollution Control Department (PCD). In 2013, there were 180 environmental pollution cases appealed, which 135 cases were problems related to MSW, odor, and hazardous waste (PCD, 2013). When asking about who should be major parties to be involved in MSWM for a better waste management system, majority of 368 respondents think that everyone from all sectors, including residents, NGOs, government, and private companies should be actors in the system. Almost 80% of all respondents are willing to join in waste management system for better management process.

In terms of KM, respondents think that knowledge on waste management should be consistently promoted to the public which refers to all residents, to schools which refers to lessons for students in a subject, to waste management providers which refers to direct and indirect staff. This aims mainly to

Table 1. Respondents' aspect on current performance of MSWM service

	Very good	Good	Acceptable	Bad	Very bad
Count	8	101	236	51	26
Percentage	1.9	23.9	55.9	12.1	6.2

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Table 2. Residents' concerns on MSWM service

Performance level	Concerns				
	Not on time	Leftover waste	Falling waste	Odor	No service
Very good	3	2	3	1	0
Good	31	40	33	57	4
Acceptable	97	130	77	169	14
Bad	25	30	22	42	8
Unacceptable	9	14	9	20	6
Total	165	216	134	289	32

ensure that both service recipients and service providers are aware of risks and impacts that are generated by improper waste management and the importance of the ecosystem which human runs on them. Table 3 below summarizes important types of knowledge for waste management.

As shown in Table 3, there are thirteen types of knowledge that residents think the types are needed for having sustainable waste management. The checked signs show the importance of needed knowledge for each process of MSWM based on residents' knowledge. The residents state that there should be collaboration among all related stakeholders in each process along waste management chain. They

Table 3. Residents' aspects on needed knowledge for sustainable waste management

Needed knowledge	Service recipients		Service providers			
	Waste generation	Waste storage	Waste collection	Waste transfer	Waste processing	Waste disposal
14. Waste sorting		✓	✓			
15. Types of waste	✓	✓	✓	✓	✓	✓
16. Waste minimization	✓					
17. 3Rs	✓				✓	
18. Education in schools	✓	✓	✓	✓	✓	✓
19. Laws and enforcement	✓	✓	✓	✓	✓	✓
20. Public involvement	✓	✓	✓	✓	✓	✓
21. Training or demonstration of MSWM	✓	✓				
22. Consistent support and promotion			✓	✓	✓	✓
23. Basic MSWM in household	✓	✓				
24. Risks and impacts	✓	✓	✓	✓	✓	✓
25. Service mindset of staff			✓	✓	✓	✓
26. Mindset of waste and the environment of residents	✓	✓				

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highlight that all staff should be trained to provide efficient service. An example case that happens in current MSWM in waste collection process is that people do waste sorting and put sorted waste into different bags. But once the waste is collected, staff mix all waste together and pick only materials that they consider valuable and put to big plastic bags. Those picked waste will later be sold to small recycle shops before mixed waste is dumped out at a transfer station. According to experts' insights, they suggest that waste management infrastructure be improved to be ready to support all types of waste. If all residents do waste sorting and waste collection trucks are fully equipped to support various types of waste collection, situation like the example case would not occur. Experts also comment that at each step of waste management, knowledge transfer and sharing are needed for effective KM.

Knowledge transfer can be done internally among service recipients or service providers, or externally between service recipients and providers or other indirect actors. All processes of waste management need knowledge transfer to lessen knowledge gaps. Some residents can transfer their knowledge on how to minimize waste generation by using reduce and reuse strategies. Staff in the same or different levels can train or suggest each other's knowledge to others in order to have the same knowledge leading to norm of waste management practice. Knowledge transfer can also be done when staff who are about to retire or move to another position. They should transfer their knowledge to new comers who are going to take their positions in the near future. Thus, knowledge transfer is a good and practical KM strategy that is beneficial to management of knowledge.

Knowledge sharing in waste management is practically done to give knowledge to a number of people (Piktialis & Greenes, 2007). It is a powerful way to prevent knowledge gap, as everyone receives the same information at the same time. Experts comment that knowledge sharing has been implemented in Bangkok MSWM but is not so successful. For example, demonstration of sorting waste had been done to encourage waste generators to sort their waste correctly. As time elapsed, this campaign was diminished. It can be easily seen in many places throughout Bangkok that waste is commonly discarded in all types of waste bins. Another knowledge sharing in MSWM is training, which applies to both service providers and recipients. Staff is trained to do correct waste collection and transportation procedures, whereas residents, mostly in community level, are trained to launch projects related to reduce waste generation amount and improve performance of waste management service. Community based waste management (CBM) is an example of the projects. Correct practices, procedures and important information are given by BMA. The same knowledge of creating a CBM project is shared to all residents. However, it is different when theories come into real practices. Staff still conducts same waste management practices. Only a number of CBM projects have successfully done.

Co-Created Values

A big concern for practically successful KM is ways to achieve an effective knowledge transfer and knowledge sharing. Avoiding hidden knowledge in waste management is a vital factor as it reveals out such knowledge. According to Polanyi's study, dialogues among individuals or groups lead to transferring and sharing of knowledge (Polanyi, 1964). When it comes to this question, residents respond that all processes should be transparent. They suggested that key waste management stakeholders be involved to create mutual waste management strategies which eventually provide mutual benefits.

Waste management infrastructure should be more ready to support increasing amount and types of waste. Laws should be more rigidly enforceable to ensure that everyone complies with laws. According to the interview, experts think that the most urgent problem is imperatively needed to find resolution for

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a sustainable MSWM with suitable infrastructure. Dwivedy (2010) stated that successful implementation of waste management, other than less generation of MSW, requires the establishment of appropriate infrastructure. The other two factors contributing to the success of MSWM are practical policies and strategies to manage the system. Having a smoothly run system, effective laws should be enforced. The study of Roomratanapun shows that law enforcement is the third rank solution to solve waste management problems (Roomratanapun, 2001).

Effective knowledge sharing and knowledge transfer lead to successful KM. In service provider side, if each MSWM process along waste management chain is transparently managed based on well-planned policies complying with all stakeholders requirements, provided MSWM service performance will be improved. On service recipients perspective, if residents who are the main waste generators and any other generators are informed, educated, or known how to correctly manage with waste, waste generation rate will be decreased. Furthermore, respondents and experts have agreed that if they know what or how to reduce waste, not only waste generation will reduce, but also consumption of natural resources will decrease. An example case of value that is co-created by BMA, manufacturers, and the residents in MSWM is that there should be a campaign created by BMA and manufacturers to promote consumption of products that have less packaging materials. With this campaign, end users can purchase the same products with less cost or at the same price but more quantity. Moreover, respondents have stated that it is better to be informed of what the results of using products with less packaging are. It is an emotional strategy to learn that they are part of many people who make a better environment and save the world.

Table 4. Residents' aspects on value co-creation when applying KM concept

MSWM Process	Required knowledge/practice	Co-created values
Generation	- Campaigns to promote 3Rs or less packaging products - Information of adverse impacts caused by MSW	- Less raw material consumption - Less waste generation
Storage	- Information on suitable and practical waste sorting method - Information on waste management at home	- More recyclable waste to be used as raw materials - Better household WM - Less concerns on odor
Collection	- Information on waste collection place, date and time - Equally trained staff - Appropriate use of technologies, machines, and trucks	- Effective waste collection service - Optimal utilization of machines and trucks - Collecting cost and time reduction - Less concerns on odors, uncollected waste, and leftover waste - Less health risks and impacts to staff and residents
Transfer	- Equally trained staff - Sufficient transfer stations - Appropriate use of technologies, machines, and trucks	- Effective waste transfer service - Optimal utilization of machines and trucks - Transportation cost and time saving - Less concerns on falling waste - Less risks to staff who expose directly to MSW
Processing	- Equally trained staff - Appropriate use of technologies, machines, and trucks - Clear and practical policies and standards	- Effective waste processing - Optimal utilization of machines and trucks - Risks to frontline staff or workers are minimized - Less environmental concerns (soil, water, air)
Disposal	- Equally trained staff - Appropriate use of technologies, machines, and trucks - Clear and practical policies and standards - Mitigation and monitoring impacts in short, medium, and long-term policies	- Effective waste disposal - MSW is correctly managed and meets management standards - Less social, economic, and environmental concerns and impacts to the society

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As shown in Table 4, values that are co-created by related stakeholders for each MSWM process are identified. Applying KM concept to MSWM service is aimed for sustainable MSWM service in Bangkok. If KM is successfully applied, respondents think that collaboration among key related actors is formed to create mutual benefits, which results in reduction of waste generation, better MSWM service, transparent and effective MSWM system as a whole, and less socioeconomic and environmental risks and impacts. In terms of value co-creation, there will be better understanding of how sustainable waste management should be among all sectors. Consequently, awareness of impacts caused by waste will be increased, so will awareness of the importance of ecosystem. Therefore, better waste management system and services eventually lead to better well-being of the society as a whole.

DISCUSSION

Based on the results of qualitative and quantitative analyses, this section provides essential factors that lead to practical implication of applying KM on sustainable waste management service in Bangkok. For waste management service providers, there are three factors that residents and experts concern on. Those three factors are readiness of waste management system, readiness of waste management strategies and legislation, and readiness of waste management human resource.

Readiness of waste management system means that the city needs to have all required infrastructures, qualified staff, and well MSWM informed residents which are important factors that support increasing amount of waste for all waste management processes including sufficient technologies of fleets and equipment, suitable number of waste transfer stations, and standardized waste disposal facilities. The city has to ensure that all infrastructures are in function and do not generate pollution to the environment. One of the BMA strategies is establishing networks to increase the efficiency of MSWM (Jungrungrueng, 2014). Knowledge sharing and transfer among MSWM staff and residents are imperative. For the staff, they have to correctly know what and how to effectively manage MSW as a whole system and especially specialize on their responsible tasks. For Bangkok residents, it is imperative to make them understand the importance of sustainable MSWM. One alternative is applying theory of planned behavior of Ajzen (1991) to MSWM plan. The theory links people's behaviors and beliefs under three concepts, including behavioral, normative, and control beliefs. If BMA informs the residents how importance of having sustainably effective MSWM system is; what roles they can have; or what roles the residents should do, the disseminated information makes residents perceive what consequences are. After a large number of residents have been informed with the same information, there happens perception of social pressures. These social pressures influence on decision of each resident whether they should be active actors who contribute to performance of MSWM system. When residents perform their roles in MSWM, they themselves perceive what changes or results that effect on performance of MSWM system. Therefore, the behaviors or roles of the residents are determined the residents themselves. Thus, it is essential for BMA to consistently and effectively share MSWM information to the residents.

All interviewed sectors agree that collaboration based on mutual agreement leads to better MSWM system. After having suitable infrastructures and appropriate technologies for waste management system, it is highly important that the city be provided with long-term strategic planning and policies on MSWM. In addition, enforceable laws should be in place. The analysis shows that public and private involvement of parties, for example, in waste management planning or policy setting creates mutual benefits. When all related parties agree with how management processes should be, problems on public appealing will

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no longer occur. This is a big challenge of knowledge sharing and it transfers to make all parties understand the same knowledge, create the same direction of mindset of having effective waste management strategies, and have the same perception of the importance of having sustainable waste management system with rigid punishment for those who deny following. This challenging issue of knowledge sharing among related parties can be solved by adapting the concept of social exchange theory based on the analysis of social behavior (Homans, 1958). Benefits that are socially exchanged such as information, knowledge, advice, assistance, or commitment have unique significance of their own depending on each individual's preferences. In case of Bangkok's MSWM system, to get people have the same direction of mindset, it is easier to exploit interpersonal relations among residents. People tend to believe or consult with ones whose have friendly relations or are trustable. Socially exchange of MSWM knowledge among those who have good relations may result in better quality of knowledge sharing.

The most important factor that drives MSWM system is human resource. The city needs to ensure that staff at all levels has correct knowledge and practices their work activities properly. KM plays a very important role here. According to the knowledge-based theory (Grant, 1996) that focuses on the efficiency of economizing on knowledge exchange, instead of that, this paper focuses on the efficiency of MSWM activities based on knowledge transfer and sharing perspectives. Knowledge is a key productive resource that contributes to value co-creation of all staff. Therefore, knowledge should be embedded at every process of waste management starting from waste generation to waste final disposal. This is also applicable to MSWM that KM is simply applied to a simple process to a very complicated activity, for example, using equipment correctly, sorting correct types of waste, or planning waste collection routes. In addition to that well-being of front line staff should be more focused. They are directly exposed to health risks. Many frontline staff do not wear gloves or masks to protect themselves from contacting or exposing to waste directly. For sustainable waste management and better provision of service, Bangkok is highly recommended to have KM in MSWM master plan to ensure that every staff conducts all activities correctly based on the same knowledge and norm.

When waste management system and staff are ready, readiness of waste generators to be part of MSWM system is also important. It is again a huge task to build up good mindset of waste generators on effective waste management. At the very start of waste generation chain, suggested by experts, manufacturers should produce goods with less amount of packaging in more environmentally friendly way. This business practice has started implementing in the past few years, manufacturers launched campaigns of using less raw materials to reduce amount of waste. Residents also have to minimize amount of waste. Reduction of waste at source is the most powerful way to reduce generation of waste. It can be done by 3Rs activities. Education and public relation to promote correct waste management practices should be consistently available. Knowledge on importance of having effective waste management should be given. The socio-economic and environmental impacts of having and not having sustainable MSWM system should be explained. People have been more environmental concern. As the residents, main waste generators would like to live in a clean city. They have willingness to join waste management collaboration for a better and more effective waste management system. Thus, it is a task of BMA, a main actor in waste management, to mutually work with the residents, encourage and draw participation of the public to join waste management schemes on the basis of consistently promote and provide knowledge on sustainable waste management.

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CONCLUSION

From the qualitative and quantitative analysis, the results show that KM is a potential factor that drives waste management to be more sustainable and better provision of service. According to the questionnaire surveys, respondents think that current waste management is acceptable but there are many concerns that the city needs improving. Odor is the most urgent problem that needs solving as it widely affects human well-being. Residents and experts suggest that knowledge is the most important factor to increase effectiveness of MSWM system in long-term. Thus, they would like proper knowledge to be consistently provided. According to the results, it is fortunately to see that people have more concerns on environmental impacts as they would like to join in waste management collaboration and have waste management system sustainable. They agree that knowledge is an important factor that makes the system effective. This leads to the importance of applying KM to waste management service.

KM cannot be effective unless successful knowledge sharing and knowledge transfer are not applied. Both residents and experts insist that all related stakeholders have the same mindset in implementing every waste management process. Thus, having an effective KM, it has to be ensured that knowledge gap is minimized, which can be done by applying knowledge sharing and knowledge transfer strategies. Moreover, it is essential to bring out personal hidden knowledge and utmost make use of this knowledge. From the results, every process from simple to complex inevitably needs KM. Thirteen needed types of knowledge are identified in this paper which the knowledge needs sharing and transferring to all related stakeholders. It is unnecessary that each person know all knowledge but at least every person needs to have the same mindset or organizational norm in business term.

We are living in service and knowledge economy, based on the analyzed results; it suffices to say that sustainable environmental service and KM concepts can perfectly blend together. This paper shows human aspects on current waste management service provided and the importance of KM. The results show that KM is an important factor for sustainable MSWM. Although thirteen needed knowledge for waste management system is identified, having an effective KM is a complicated task. This paper provides a concrete study of human aspects and requirements on having KM on an environmental service, MWSM. Further study on effective KM strategies especially on knowledge sharing and knowledge transfer is needed to identify practical implications for sustainable MSWM system which ultimately brings up the better step of well-being to the whole society in the very near future.

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APPENDIX

Bangkok Solid Waste Management: Sustainable Environmental Service and Knowledge Management

Figure 3.

Please check ✓on the box that you prefer or agree

Part 1: General information of respondents

1. Sex
   - ☐ Male ☐ Female
2. Age
   - ☐ 16 – 20 years old ☐ 21 – 25 years old ☐ 26 – 30 years old
   - ☐ 31 – 35 years old ☐ 36 – 40 years old ☐ 41 – 45 years old
   - ☐ 46 – 50 years old ☐ 51 – 60 years old ☐ > 60 years old
3. Education
4. ☐ Primary school ☐ Secondary school ☐ High school
   - ☐ Vocational school ☐ Bachelor's degree ☐ Master's degree
   - ☐ Doctoral degree
5. Occupation
6. ☐ Student ☐ Business owner ☐ Company officer
   - ☐ Housewife ☐ Government officer/state enterprise
   - ☐ Retired ☐ Unemployed ☐ Freelance
   - ☐ Others (please specify) _____
7. Monthly income
   - ☐ < 5,000 baht ☐ 5,001 – 10,000 baht ☐ 10,001 – 20,000 baht
   - ☐ 20,001 – 30,000 baht ☐ 30,001 – 50,000 baht ☐ > 50,000 baht
8. How many people live in your house? _____ persons
   Member(s) whose age less than 16 years old: _____ persons

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Figure 4.

Part 2: MSW sorting and disposal behavior of respondents

9. Do you sort waste into different types before disposing?
   ☐ Yes ☐ No
10. How do you dispose of waste at home?
   ☐ Put garbage bags in front of the house, to be collected
   ☐ Put garbage bags at a community dumpster, to be collected
   ☐ Burn
   ☐ Leave garbage bags along roadside
   ☐ Others (please specify)_____
11. How often do you dispose of waste per week?
   ☐ Everyday ☐ Twice a week ☐ Three times a week
   ☐ Four times a week ☐ Five times a week
   ☐ Others (please specify) _____
12. How much waste is generated each time of disposal? **Approximate volume**
   ☐ < 1 kilogram ☐ 1 – 3 kilogram ☐ 3 – 5 kilogram
   ☐ 5 – 10 kilogram ☐ > 10 kilogram
   ☐ Others (please specify)_____
13. Do you have to pay for waste collection service?
   ☐ Yes, _____ baht ☐ No

Figure 5.

Part 3: MSW situation and attitudes of respondents

14. How is current performance of provided MSWM service?
   ☐ Very good ☐ Good ☐ Okay
   ☐ Bad ☐ Very bad
15. What problems do you usually experience with MSWM service?
   ☐ Waste is not collected on time ☐ Waste is left over
   ☐ Falling waste during transportation ☐ Bad smell from leachate
   ☐ No waste collection service in your area
16. For an effective sustainable MSWM, who should responsible for managing waste?
   ☐ Everyone ☐ Residents ☐ Governments
   ☐ NGOs ☐ Private companies
17. Do you think collaboration among communities, NGOs, and government for sustainable MSWM is important?
   ☐ Yes ☐ No
18. If there is a reorganization of MSWM from current system to a new sustainable collaborative system, would you like to join?
   ☐ Yes ☐ No

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Figure 6.

Part 4: Needed knowledge and attitudes of respondents for sustainable management system

19. What MSWM knowledge should be provide to have a sustainable waste management system?

(1 = least important, 5 = most important)	1	2	3	4	5
- Waste sorting					
- Types of waste					
- Waste minimization					
- 3Rs (Reduce, Reuse, Recycle)					
- Education in schools					
- Laws and enforcement					
- Public involvement					
- Training or demonstration of waste management					
- Consistent support and promotion					
- Basic waste management in household					
- Risks and impacts of MSW					
- Service mindset of staff					
- Mindset of waste and the environment of residents					
- Others					

20. How should waste management system be when applying knowledge management concept? *(Please put a number according to what waste management process that will be impacted, 1=Generation, 2=Storage, 3=Collection, 4=Transfer, 5=Processing, 6=Disposal)*

- ☐ Less waste generation
- ☐ Less raw material consumption
- ☐ Less concerns on odor
- ☐ Less concerns on uncollected waste
- ☐ Less concerns on leftover waste
- ☐ Less concerns on falling waste
- ☐ Less social, economic, and environmental concerns and impacts to the society
- ☐ Less environmental concerns (soil, water, air)
- ☐ Less health risks and impacts to staff and residents
- ☐ Less risks to staff who expose directly to waste
- ☐ Save collecting cost and time
- ☐ Risks to frontline staff or workers are minimized
- ☐ Better waste management
- ☐ More recyclable waste to be used as raw materials
- ☐ Transportation cost and time reduction
- ☐ Effective waste collection service
- ☐ Effective waste transfer service
- ☐ Effective waste processing
- ☐ Effective waste disposal
- ☐ Optimal utilization of machines and trucks
- ☐ Waste is correctly managed and meets management standards
- ☐ Others _____

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Chapter 42
Leachate Generation, Transport, and Control

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ABSTRACT

This chapter will discuss in detail on the primary aspect influencing leachate generation, transport and control within the landfill area. The leachate generation will look into the various factors that contribute toward increment and reduction of water balance in the landfill cell cause by the physical, chemical and biological activities. The topic will include discuss on common methods and models for estimating water input and transformation into/inside the landfill layer. Meanwhile, leachate transport part would emphasis on the leachate movement and mobility due to the effect of waste percolation, moisture field capacity and the gravity pull. Dominant flow type and the effect upon solute transport as well as other landfill components would be emphasize within the discussion. Lastly, this chapter will elaborate on the conventional and advanced techniques that being utilized for the control of the leachate for further treatment system or as beneficial advantages in the landfill management system.

INTRODUCTION

In the past, the concern is primarily on the amount of leachate that would be generated from the landfill site as it would signify the environmental risk of the landfill area. Nowadays, leachate is being considered as multi-dimension pollutant that potentially can affect the land/soils, water and even air (either directly or indirectly). Because of that, the regulatory upon leachate was stringent for leachate treatment and the landfill gases are meant to be collected; that require the need to investigate into the waste layer

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moisture and leachate mobility within the landfill cell. Protection from leachate contamination has been imposed into various countries legislations such as "Regulation 15 of the Waste Management Licensing Regulations" (UK), "Groundwater Regulations"(UK), "Pollution Prevention and Control Act" (England and Wales), "Landfills Regulations" (England and Scotland), "EU Directive on IPCC", "EC Directive on EIA", "Water Framework Directive", "Strategic Environmental Assessment (SEA) Directive" and many mores (Butt, et al., 2014). These legal requirements push toward getting better understanding onto the reactions occurs inside the landfill layer especially on the generation and mobility of leachate. Such information open a more understanding onto the reactions occurs inside the landfill layer especially toward the waste anaerobic degradation and for optimal methane production. At the same time, it is also providing the essential knowledge to maintain and controlling the flow of leachate within the landfill containment and thus preventing leakage into the surrounding environment. In the long run, managing the leachate generation and flow would account into the reduction the treatment cost and maximize the biogas production if necessary.

LEACHATE GENERATION

Leachate generation is an important and necessary aspect to estimate for potential leachate leakage prevention especially into the groundwater system. Potentially leachate leakage could occur if the leachate head in the bottom liner happen to exceed 30 cm which could easily be measure by placing pressure transducer in the leachate collection well. Looking from this aspect, greater leachate generation rates would significantly increase the leachate accumulation at the bottom liners due to the downward, vertical movement of the leachate flow and mostly probably increasing the chances of leakage into the groundwater aquifer.

Leachate is produced mostly from the incoming or water input from outside primarily through rainwater infiltration apart from the water which is already present as moisture in the deposited waste stream and small fraction that could be produced from the multiple reactions inside the landfill. Usually sanitary landfills are well designed to prevent or at least minimize the water infiltration through various approaches and practices depending on the landfill owner or contractors. Therefore, overall leachate generation modeling would require information on all these aspects for overall estimation; which include the type of wastes being disposed, landfilling practice, landfill cover practices, leachate collection system and leachate recirculation (if being employed) as summarized in Table 1.

Leachate generation prediction would have to look into the conceptual model and the numerical model of each landfill aspects. Normally, estimation can be made by looking at water balance or water budget in the landfill cell, treating the cell as a spatial lump system and calculate the leachate volume from the water balance. Figure 1 shows water balance for a landfill site.

The water balance is influenced by the outside water entering into the landfill layer (rainfall, water infiltration, and surface runoff), the water presence in the deposited waste layer (moisture, field capacity) and the water addition or loss through physical process, chemical reaction and microbiological activities within the landfill layer. In a properly covered sanitary landfill, water infiltration by the rainfall will be minimized as it is shed away as surface runoff, evaporated or transpire away by the surface vegetation. Standard hydrological tools can be used to determine the amount of water rainfall infiltration into the landfill layer. The tools require hydrological data of the landfill site including climate and site condition. There are many other complex landfill water balance models are being developed that incorporate more

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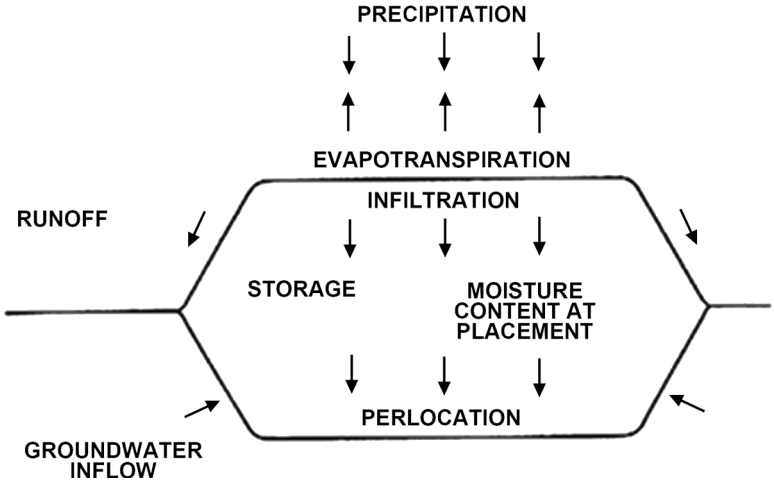
Table 1. Landfilling aspect and the significance on leachate generation

No	Landfill Aspect	Parameters	Significance
1	Waste	c) Volume of waste disposed d) Characteristic of waste	Amount of moisture being added into the landfill cell and decomposition type or rate which could either consume or generate moisture
2	Landfilling Practice	c) Landfill cell unit area d) Average high	Compaction ratio, vertical stress for the landfill layers and the influence on the moisture holding capacity
3	Landfill Cover Practice	e) Type of daily and interim cover f) Thickness of the covers g) Surface vegetation and slope h) Site precipitation data and surface runoff	Preventing water infiltration, possible erosion by surface runoff and also potential loss as water vapor or by plant uptake
4	Leachate Collection System	c) Piping layout d) Piping design parameter	Draining the excess water out of the landfill cell
5	Leachate Recirculation	c) Amount of leachate recirculation rate d) Type of recirculation system applied	The amount of water re-added into the landfill cell, the influence on waste solubilisation and possible water vapor loss from the system

advanced hydrologic techniques and climatological databases. The most commonly applied landfill water balance is the Hydrological Evaluation of Landfill Performance (HELP) which is a quasi-two-dimensional hydrological model of water mobility across, into, through and out of the landfill as well as leachate recirculation.

Any water that manages to infiltrate through the landfill cover will be either absorbed by the waste field capacity or migrate vertically due to gravity pull until it is collected at the bottom of the landfill. Many believe that the infiltrated water would be held by the waste field capacity first. Once the field capacity is reached, the amount of leachate produce would be equal to the amount of the infiltrating water. Probably about 1/8–3/8 of the water inputs would end up as leachate at the landfill bottom (Baumann & Schneider, 1998). As the rainfall infiltration is mostly retained by the surface tension (D. Bendz, Singh, & Ã…kesson, 1997), the collected leachate would came primarily from the waste material itself

Figure 1. Landfill water balance (Farquhar, 1989)



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that accountable for about 75% of the overall portion (Abichou, Barlaz, Green, & Hater, 2013) and it is estimated that only 1500 m^3 of water leaving the landfill cell through evaporation (U. S. EPA, 2006; Xuede, Koerner, & Gray, 2002).The bulk moisture content of the waste that represent the major portion of leachate input can be calculated as shown in Equation 1:

$$\text{Moisture Content } = M_i + \frac{\Delta S}{M_W} \times 100 \quad (1)$$

where

M_i = Initial Moisture Content (%)
ΔS = Change in storage (tons of water)
M_w = Wet weight of waste (tons)

WATER TRANSFORMATION AND LOSSES

Aerobic Phase

Generally, the first phase of aerobic degradation involving organic substances only occur within limited time duration due to the high oxygen demand of waste in relation to the limited and scarce quantity of oxygen presence inside the landfill cell after disposal (illustrated in Figure 2). Therefore, upper layer would be the only layer of within a landfill that would involve in aerobic metabolism since oxygen could only be found trapped in fresh waste or could potentially being supplied by diffusion process and rainwater infiltration. During this phase, it is observed that all the readily available proteins are to be degraded into amino acids before being further decomposed into multiple compound comprise of carbon dioxide, water, sulphates, nitrate and other typical catabolites or products from aerobic processes. In that sense, the carbohydrates content within the landfill layer or more precisely on the fresh/upper layer are converted to carbon dioxide and water. In the meanwhile, the fats content would be hydrolysed into forming fatty acids and glycerol until eventually it would be furtherly degraded into simpler catabolites through intermediate formation of volatile acids and alkalis. However cellulose, which constitutes the majority of organic fraction of wastes, is not so easily processed. The natural process would require it to be degraded by the means of extracellular enzymes, producing glucose as it monomer constituent which is used subsequently eaten away by bacteria into releasing carbon dioxide and water. Elevated temperature is assumed to occur during this stage due to the exothermal reactions of biological oxidation and if the waste is not compacted. With the scarce assess for the oxygen, the aerobic phase would be relatively short-term and no substantial leachate generation will take place. In comparison to the young landfill, very old landfills would comprise higher amount of refractory organic carbon remaining within the landfilled wastes, in which a second aerobic phase may appear in the upper layer of the landfill subjected to oxygen availability. Overall, the methane production rate would be very low during this aerobic phase and the air diffusion would promote formation of aerobic zones and redox-potentials zones that is too high for methane formation (Christensen &Kjeldsen, 1989).

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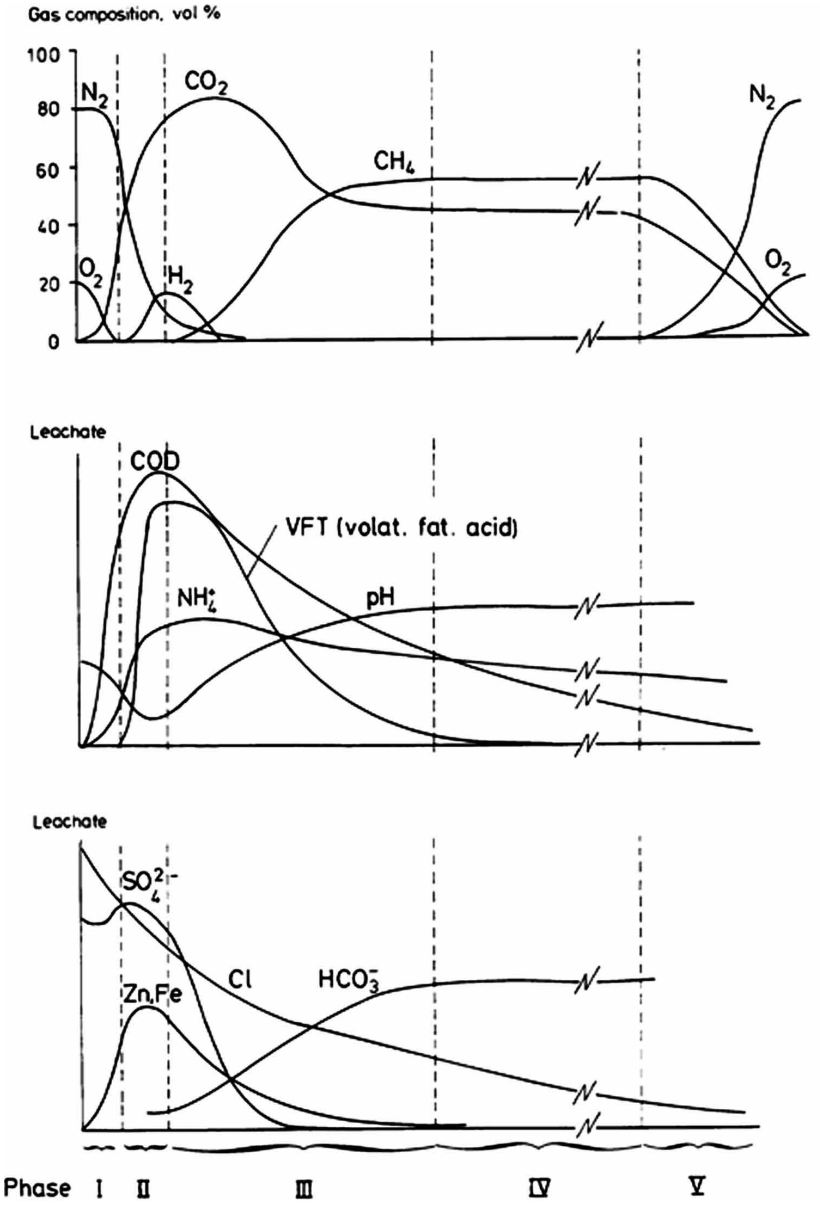
Figure 2. Illustration of developments in leachate and gas in a landfill cell (Christensen &Kjeldsen, 1989)



Anaerobic Phase

Anaerobic phase refers to the digestion processes of organic materials in the absence of oxygen, which will be degraded into biogas composed of mainly methane and carbon dioxide. The anaerobic digestion pathway of organic matter involves several biochemical reactions, performed by different microbial trophic groups, which sequentially degrade a variety of substrates and intermediate compounds (Figure 3). The microbial consortia that are involved ultimately mineralize the organic matter into methane (CH_4), carbon dioxide (CO_2), ammonium (NH_3), hydrogen sulphide (H_2S), phosphates (PO_4^{3-}) and water (H_2O).

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Anaerobic digestion can be divided into four phases, related to the characteristic microorganisms and main conversion processes taking place: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 3). Firstly, hydrolytic enzymes are excreted by fermentative bacteria, the so called 'exo-enzymes' and fermentative bacteria actively colonized the organic matter. The non-dissolved material is converted into less complex, dissolved compounds, which can be taken up by the fermentative bacteria. Secondly, during acidogenesis, the dissolved compounds present are converted by fermentative bacteria into a number of simple compounds, which are then excreted. The compounds produced during this phase include volatile fatty acids (VFA), alcohols, lactic acid, CO_2, H_2, NH_3, and H_2S. Thirdly, the acetogenic phase, or intermediary acid-production, converts the digestion products into acetate, hydrogen (H_2) and CO_2. Lastly, methanogenesis converts acetate, hydrogen plus CO_2, formate or methanol into methane.

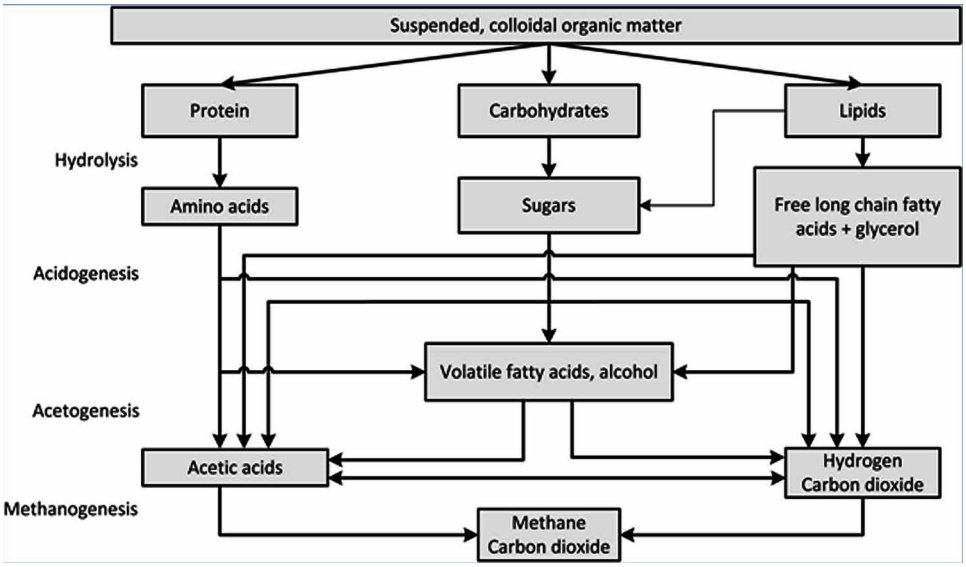
Methanogenic Phase

Methanogenic bacteria play in important role for converting organic compounds into methane and carbon dioxide during anaerobic degradation process (Figure 4). These microorganisms can be divided into two groups. First, acetate using microorganisms known as aceticlastic methanogen (producing methane from acetic acids or methanol). Second, hydrogen-using microorganisms known as hydrogenotrophic methanogen (producing methane from hydrogen and carbon dioxide).

Aceticlsastic Methanogen

This methanogenic species are prevailing in anaerobic digestion in which are capable to form methane from acetate even though at a few species number. Around 60 to 70% of all methane production being produced by this species, starting from the methyl group of the acetic acids. Two genera utilize acetate to produce methane known as Methanosarcina(prevails above 10-3 M acetate) and Methanosaeta(prevails

Figure 3. Simplified schematic representation of anaerobic degradation process



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below this acetate levels). Methanosarcina may have higher yields and be less pH sensitive, as compared toMethanosaeta. Methanosarcina has greater growth rate thanMethanosate. However, Methanosate needs a longer solid retention time, but can operate at lower acetate concentrations. The Methanosaeta genus is known to be exclusive used of acetate and has a higher affinity with it than the methanosarcinas.

Hydrogenotrophic Methanogen

Generally methanogenic species are capable of producing methane from hydrogen and carbo dioxide, unlike aceticlasticmicrooganisms. Methanobacterium, Methanospirllium and Methanobrevibactor are among the species that frequently find in anaerobic conditions.Aceticlasstic and hydrogenotrophic are two importantmicroorganisms in anaerobic digestion since they are responsible for the essential function of consuming the hydrogen produced in the previous phase.

Leachate Generation Modeling

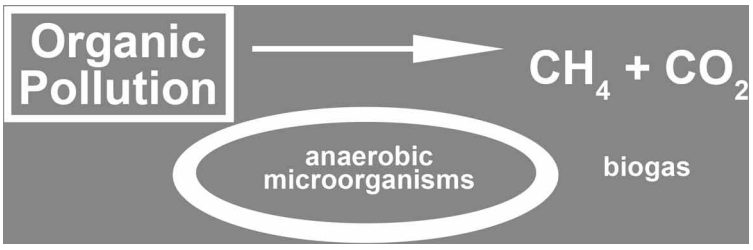
Among the modes that are commonly used to estimate the leachate generations are the water budget method and Hydrological Evaluation of Landfill Performance (HELP) method. However, water budget method tends to show too much uncertainty and a very large error since it assumes that the waste is at the field capacity and the water input produces similar amount of outflow. Simple water budget calculation is as shown in Equation 2:

$$I = P - ET - \frac{\partial S_s}{\partial t} \tag{2}$$

where

I = Net water input
P = Precipitation
ET = Evapotranspiration
dS_s/dt = Change in the water storage

Figure 4. Conversion of organic pollutants to biogas by anaerobic microorganisms



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Simple water balance could be developed by connecting data such as rainfall, infiltration, evapotranspiration and leachate drainage as being done by O'Reilly (2004) and Heimovaaraet. al. (2015). Usually, this method only considers the presence of three layers within the landfill which is the cover layer, the waste layer and drainage system. The top cover water balance would be influenced by the precipitation, surface runoff and in some case, consider the potential of evapotranspiration which are commonly only limit to the rooting depth of vegetation. From there, a small fraction of water is estimated to infiltrate into the waste layer, flowing through all the way to the drainage system. Heimovaaraet. al. (2015) assumed that the water flow is based on bimodal lognormal distribution and being model using a stochastic transfer function approach. An example of transfer-function-model is mentioned in the next sub-chapter for leachate transport. In his study, the storage volume of the top layer that would permit evapotranspiration is at about 4.1 mm/m^2 with reasonable travelling time between 8.5 (fast flow) to 64 days (slow flow). It is believed that the time taken for the water to residence in the waste layer would be an essential output for solute leaching model. As for the HELP method, the model takes into account the initial water accumulation up toward reaching the field capacity and the flow rate through the landfill (D. Bendz, et al., 1997). Moreover, the HELP can also be used to estimate infiltration, runoff and evapotranspiration (Abichou, et al., 2013; Schroeder & Ammon, 1994; Schroeder, et al., 1994). The model requires inputs such as type and thickness of cover material, slope of the surface and presence of surface vegetation. The usage of intermediate cover having high permeability material and the influence of runoff volume through relative adjacent cells could possibility increase the water infiltration volume (Abichou, et al., 2013). Table 2 below summarizes the hydrological aspects being considered by HELP method in predicting leachate generation and flow.

LEACHATE TRANSPORT

Investigation upon leachate transport is crucial because of the water content being the major constituent for landfill metabolisms. It would provide the fundamental understanding and enable prediction or simulation of landfill potential pollution and even for estimating landfill gas production. In terms of pollution prediction, leachate mobility is commonly associated with solute transport especially involving contaminants which are being solubilized from the waste media, brought along by the water content and eventually accumulates at the landfill bottom. For landfill reactions specifically involving gas collection system, those solutes would represent substrate and nutrients being redistributed by the leachate movement and thus facilitate anaerobic degradation process especially since the flow also spreads microorganism throughout the landfill layer.

Leachate generation mentioned before already emphasizes on the main factors that contribute towards the landfill water balance; present within the landfill layer either coming from the outside and inside sources. For the leachate transport, the influential factors are signified more by the space and time availability for the water storage inside the landfill layer apart from other factors which reflect on the volume of water. In that manner, one of the main aspects for leachate mobility is referred to the field capacity that define as the maximum volume of water per unit volume of landfill material held by capillary forces against gravity. Field capacity could be determined by drying a small portion of the waste (already saturated) and left to drain until the moisture cease to flow out. In actual landfill, the moisture retaining characteristic tends to be diversifying depending on the waste compositions and compaction factor imposed at each landfill site. Commonly, MSW landfill observation indicates that domestic waste

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Table 2. Summary of methods and estimation used in HELP model (Schroeder, P.R., Dozier, T. S., Zappi, P. A., McEnroe, B. M., Sjostrom, J.W., & Peyton, R. L., 1994)

SURFACE PROCESSES
Weather Generator
1) WGEN Model of the U.S. Department of Agriculture (USDA) Agricultural Research Services (ARS) based on the procedure by Richardson. 2) Use to generate daily precipitation, solar radiation and the mean temperature. 3) The daily precipitation is generated by Markov chain-two parameter gamma distribution model. 4) Infiltration is equal to the sum of rainfall in the absence of snow cover (precipitation at the temperature of more than 0°C) and in the presence of snow cover, equal to the sum of outflow from the snow. Ground melt less the sum of evaporation from surface moisture or outflow of snow cover and runoff.
Runoff Modelling
1) Estimated using USDA Soil Conservation Service (SCS) curve number method. 2) Required necessary soils data such as: • Field capacity o Volumetric water content at a soil water suctions of 0.33 bars. o Must be greater than wilting point and less than the porosity. • Porosity o Volumetric water content as in the volume of water per total volume or the volume of active pore space present. o Must be greater than the field capacity but less than 1. • Initial moisture storage o Volume of water per total soil volume (soil, water and air). o Relative moisture storage is estimated using the common practice in agronomy and soil physic (on volume basis) rather than the one used by engineer (on mass basis) • Wilting point o Volumetric water content at a suction of 15 bars. o Must be greater than zero but less than the field capacity. • Hydraulic conductivity o Function of the media properties which is the void ratio, particle size, fabric, composition, degree of saturation and the kinetic viscosity of the flowing fluid. • Soil Conservation Service (SCS) runoff curve number for antecedent moisture condition II 3) All this parameters is required for all layers except for the liners and the soil liners are assumed to be saturated at all times.
Evaporation
1) **From Soil (including plant transpiration and growth):** Ritchie method as used in Simulator for Water Resources in Rural Basins (SWRRB) and the Chemicals, Runoff and Erosion from Agricultural Management System (CREAMS) 2) **Potential Evapotranspiration:** Modified Penman method 3) **Interception:** Method proposed by Horton 4) **Snowmelt Modelling:** SNOW-17 routine of the National Weather Service River Forecast System (NWSRFS) Snow Accumulation and Ablation Model 5) Evaporation coefficient is related to the unsaturated hydraulic conductivity at 0.1 bar capillary pressure at which upper and lower limits is imposed. Set to equal to 3.30 for relative field capacity less than 0.20 (for typical sand) and saturated hydraulic conductivity is less than 5×10^{-6} cm/sec (for compacted clay) while the upper limit is set at 5.50. 6) Soil water evaporation or plant transpiration is assume not occurring when the soil is frozen. 7) Potential evapotranspiration refer to the maximum quantity of evaporation rate that the atmosphere may extract in a day, when the mean daily temperature is above 32°C and the soil is not frozen. Rate of evapotranspiration is influenced by the solar radiation, humidity, temperature, vegetation type and growth, soil water content, retained surface water and other soil characteristic.
SUBSURFACE PROCESSES
Drainage
1) **Vertical:** Darcy's Law using the Campbell equations for unsaturated hydraulic conductivity based on the Brooks-Corey relationship 2) **Saturated Lateral:** Boussinesq equation model by analytical approximation to the steady-state solution, employing the Dupuit-Forchheimer assumptions 3) **Leakage:** Modelled by a compilation by Giroud utilizing a series of equations. 4) Include four types of layer which is the lateral drainage layers, vertical percolation layers, barrier soil liner and geomembrane liners. 5) Significant lateral drainage occur when the saturated hydraulic conductivity is greater than 1×10^{-3} cm/sec. 6) Leakage percolation occur by the mean of manufacturing flaws (pinholes), installation defects (cracks, tears, punctures and bad seams) and vapor diffusion

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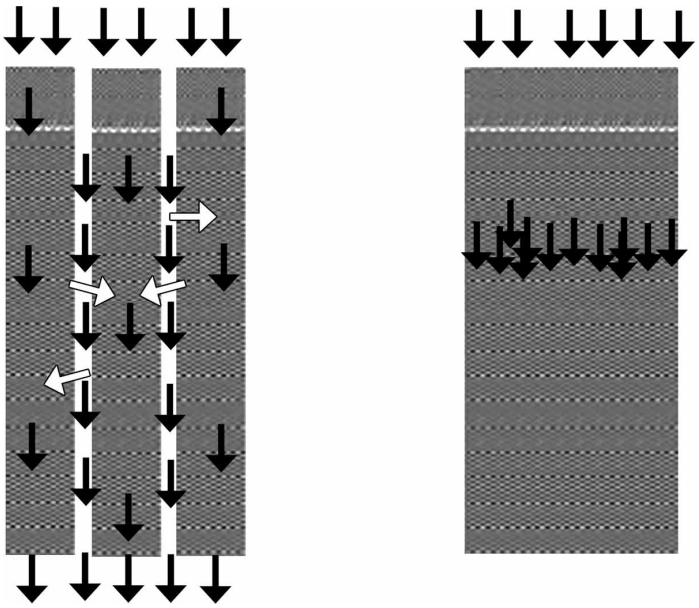
has high adsorptive capacity for further moisture uptake (Holmes, 1983) even for landfill operating after 10 years deposit (Bengtsson, Bendz, Hogland, Rosqvist, & Ã…kesson, 1994). However, those capabilities would soon to reach it limit as the field capacity is found to be decreasing with age primarily due to the degradation of the adsorbing material (Blight, Ball, & Blight, 1992; El-Fadel, Findikakis, &Leckie, 1997). Therefore, significant moisture accumulation by the waste media would have to consider the aspects of waste composition and age, initial moisture content and density.

Another aspect of the leachate transport is on the flow type as it determines the amount of water reaching certain volume of waste especially on the influence of non-uniform flow. Non-uniform water flow would create unmixed and water deficient inside the landfill layer which adversely affect the biodegradation process (Bogner&Spokas, 1993). In most studies, non-uniform flows are found to be predominant because of the highly heterogeneous physical structure of the landfill layer; plus the availability of channels and voids between solid waste media. Studies have exhibited the existence of flow pathway favored through the waste media; suggesting fast flow through selective pathways and bypass parts of the media called preferential flow. As the consequence of preferential flow occurrence, the flow of the remaining water in the bypassed parts of the solid media would be very slow or could even be stagnant. Other flow routes could also be developed caused by high infiltration rate (Jasper, Atwater, &Mavinic, 1985) that would influence on the amount of moisture from the top layer of the landfill cell. Figure 2 shows the differences between preferential flow and matrix flow for downward movement of leachate. Figure 5 shows the differences between preferential flow and matrix flow for downward movement of leachate.

For fresh landfill cell, it seems that preferential flow dominantly takes place because the waste deposits have coarser structure (D. Bendz, et al., 1997) and thus makes the leachate moving with less uniformity in an actual landfill system (Fellner, Döberl, Allgaier, & Brunner, 2009). The preferential flow occurs very fast due to introduction of waste deposit and compaction activities which would draw out moisture from the new deposited waste onto the old waste layer. Similar to waste field capacity characteristic, it

Figure 5. Comparison between preferential flow (left) and matrix flow (right)



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would also soon change depending on the waste structure, voidage volume and precipitation rate at the landfill site. As time goes by, the waste would start to settle and become more homogeneous, decreasing the voidage volume while increasing the dry density. Flow type can be determined through liquid to solid (L/S)-ratio or LRS which stands for the amount of water (in liters) passing through a given waste mass (in kg dry matter of waste) to relate on the laboratory result to actual landfill site (Fellner, et al., 2009) and use to determine the remaining pollution potential of MSW landfill (Allgaier&Stegmann, 2003).

Leachate Transport Modelling

Various methods have been utilized for stimulating the processes within MSW landfills either based on laboratory experiments (Fellner, et al., 2009; He, Liu, Zhang, &Shen, 2007; Prantl, Tesar, Huber-Humer, &Lechner, 2006), actual landfill observation (Fellner, et al., 2009) and even by using mathematical modeling (McCreanor& Reinhart, 2000; Noble & Arnold, 1991). The studies include various aspects to predict the emission such as the analysis of waste composition, batch tests, leaching tests and the operation of landfill simulation reactors either by using a made-up waste layer or the one dredged from an actual landfill site. The first three methods are mainly performed to determine the potentially mobile fraction in the overall or partial wastes deposited into the landfill whereas landfill simulation reactors test are primarily used to predict future emission from the landfills either in laboratory small scale or at the actually landfill site.

Existing approaches in predicting water flow come with their own underlying complexity and assumption ranging from relatively simplistic models to a more complex physically based model of either dual-porosity, dual-permeability or multi-region types (Šimůnek, Jarvis, Van Genuchten, &Gärdenäs, 2003). Both dual-porosity and dual-permeability models assume that the matrix or medium consist of two different regions in which water in the matrix is assume to be stagnant (does not move at all) for the dual-porosity models meanwhile dual-permeability even allow water flow in the matrix itself. These models are more fitted to determine leachate flow compared to single pore models, yet it also became the main disadvantages since more input ranging from 9 to 16 parameters depending on the existing models are required to characterize the different pore systems. The numbers of these parameters significantly increase for multi-porosity and multi-permeability models because of the need to determine the matrix hydraulic (retention and hydraulic conductivity) and mass transfers coefficient for each transport domain. For modelling leachate, hydraulic conductivity happens to be the most sensitive parameters for both preferential and matrix flow within the landfill (Fellner, J., & Brunner, P. H., 2010). Therefore, even though software had been developed and improved to ease upon the studies of these models for real time application but however, there also the need for new approaches in analyzing the complex parameter required for those models, such as through the practical use of disc or tension infiltrometers and simulation using inverse modelling techniques (Šimůnek, Jarvis, Van Genuchten, &Gärdenäs, 2003).

For practical leachate prediction, landfill investigation usually employs experimental column in the shape of cylinder, carefully driven into the waste after the top soil layer has been removed. It would alternately require excavating the waste material surrounding the column as pressure being applied to the top of the column until the bottom liner is reached. Then, a sheet could be placed flat on the bottom to cover the underneath of the column and enables the whole column assembly to be lifted out. The experimental column containing waste layer would react both as a sampling device for the tracer experiments and to reflect different condition that could occur in the landfill site such as ponding of water, water sprinkle and pulses of water inflow. Boundary effect could exist in the column that might

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affect the flow estimation but for small water velocities, it can be assumed to be negligible. For better result, slurry of very fine quartz sand could be firmly packed around the edge of the column to avoid the boundary effect and prevent the water from flowing preferentially along the wall of the column (H. k. Rosqvist&Destouni, 2000).

Using the experimental column, tests on the leachate mobility and solute transport within the landfill layer are determined by using tracers, dyes or/and morphology methods. Tracer experiments would involve using non-reactive tracer (e.g.: lithium bromide, Brilliant Blue FCF, fluorescence dye uranine, deuterium and etc.) as its concentration could later be measured using simple analysis including photometry and the data could be used to develop the breakthrough curve. Lithium has been a conservative tracer for solid waste material (Blakey, Bradshaw, Reynolds, & Knox, 1997) but study by Woodman et. al. (2015) suggested re-evaluation on the usage of lithium as a tracer for landfill waste since only 50% of lithium was retrieved back from the column outlet. It also question the experimental validation concerning sample degradation that could occur from batch tests which employed oven-drying that possibly destroy important bio-film media and emphasize on the need for exploratory modelling regarding scale of flushing from waste in column study. Apart from those suggestions, the study reveals a good conservative result for other type of tracers which is bromide and deuterium oxide. The same could be said for other tracer such as Brilliant Blue FCF that provides simplicity in the concentration analysis while assuming minor adsorption for test conducted in high water velocities (Flury&Flühler, 1995). Sometimes, common salt such as sodium chloride could also be used as tracer if it exhibits good correlation in influencing the leachate electrical conductivity value. The breakthrough curve can be built up from the tracer experiments data and indicates the flow types experienced by the tracer transport. Early peak observed in the breakthrough curves is indicator of rapid solute transport (preferential flow) and prolonged shape indicates slow water flow.

Most of field tests involve different experimental approaches such as to predict the leachate flow for either steady state or transient flow using either constant water head or sprinkling boundary conditions. Test performed under sprinkling conditions are used to predict solute travel time probability density functions (PDF). It would enable estimation on the expected solute travel times and the solute transport volume fractions that actively involve during the leachate transport. Simple leachate transport model which also involves solute mobility can be built from those experimental data and it is usually by assuming that the deposited waste stream are evenly spread creating homogenous, porous media within the landfill layer. It would involve the use of one-dimensional water balance model. However such approach is questionable since MSW is known to be highly heterogeneous which most probably cause the water content to move in non-uniform patterns throughout the waste media. This is believed to be the main reason for inconclusive, in-different results obtained between model assumptions and actual field observations. Even more as there is evidence in the existence of fast flow or preferential flow for actual landfill site. Predictability of the flow and solute transport would be significantly affected without consideration on those two factors of waste heterogeneous nature and preferential flow. Therefore, two-domain or multi-domain concept would provide a better prediction involve the presence of preferential flow in the structured media (Gerke&Genuchten, 1993) and dual-porosity (DP) model appear to be the most suitable for waste layer compared to advection-dispersion (AD) model and hybrid AD-DP model (Woodman, N., Rees-White, T. C., Stringfellow, A., Beaven, R., & Hudson, A., 2015). Table 3 listed some models and equations use to estimate leachate flow and solute transport inside the landfill.

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Table 3. Summary of models and equations used for estimating leachate flow and solute transport

Type	Equation	Description	References
Unsaturated moisture flow or Richards equation	$\frac{\partial\theta}{\partial t} = \nabla(K(\theta).\nabla H)$ or $\frac{\partial\theta}{\partial t} = -\frac{\partial K(\theta)}{\partial z} + \frac{\partial}{\partial z}\left[D(\theta)\frac{\partial\theta}{\partial z}\right] - r$ where; θ = volumetric moisture content (mm^{-1}) t = time (s) K = unsaturated moisture conductivity (ms^{-1}) H = hydraulic potential of water inside a porous media z = length (m), positive downward D = moisture diffusivity (m^2s^{-1}) r = moisture sink ($mm^{-1}s^{-1}$)	Leachate flow by assuming vertically distributed unsaturated flow; highly non-linear $D = K.\frac{d\psi}{d\theta}$ where Ψ_t = unsaturated tension head (m) (length)	(Di Bella, Di Trapani, Mannina, &Viviani, 2012; Fellner& Brunner, 2010; R. Kerry Rowe & Yu, 2012)
Macroscopic flux flow	$q=bw^a$ where; q = water flux density (ms^{-1}) a = dimensionless exponent; between 2 – 8 for macropores flow b = channel conductance (ms^{-1})	Leachate flow whereas capillary force is negligible a = 2 indicate laminar flow or saturated medium, a < 2 indicate tubular flow and a > 10 indicate complete dispersion	(David Bendz, Singh, Rosqvist, &Bengtsson, 1998; Seven &Germann, 1981)
Accumulated leachate flow rate	$L_{gen}=P+U_W-AET-RO\pm\Delta I$ where; L_{gen} = cumulative volume of leachate generated per unit area of the refuse tip monthly (mm or dm^3/m^3-month) P = inlet of water through rainfall U_w = incoming water as waste humidity AET = actual loss of water by evatranspiration RO = surface runoff ΔI = net exchange of water between the landfill and the surrounding area (lateral flow, infiltration or deep percolation)	Leachate generation assuming homogeneity by neglecting leachate storage because of low water permeability or preferential flow	(Camba, et al., 2014)
Transfer-function-model	$g(t) = \frac{1}{\sqrt{2}.\pi.\sigma.t}.e^{\frac{-(\ln(t)-\mu)^2}{2.\sigma^2}}$ where μ and σ are fitting parameter; represent the mean and the variance of ln(t), respectively and t is the time variable	Analyzing breakthrough curve of tracer experiments by assuming solutes are transported in an isolated channel tubes at different velocities without mixing	(Fellner, et al., 2009; H. Rosqvist&Bendz, 1999)
	$g(t) = \frac{q.C_{ex}(t)}{\rho_A}$ where; q = steady-state Darcian water flux $C_{ex}(t)$ = solute concentration in the output flow ρ_A = mass per unit area of the applied solute	Estimating the expected solute travel time by assuming steady water flow and non-reactive solute	(H. Rosqvist&Bendz, 1999)

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Effect of Leachate Flow within Landfill

The one most significant effect of leachate movement within the landfill is mainly on the landfill layer settlement (Abichou, et al., 2013) and the effect it bring to the waste degradation rate especially by accelerating physical, chemical and biochemical processes in the landfill layer (Kylefors, Andreas, & Lagerkvist, 2003). It is already revealed that water flux has a huge impact upon the waste degradation rate (Klink & Ham, 1982) since moisture is considered to be most important parameter for landfill biochemical process (Hans-JurgenEhrig, 1991).

It is believed that the movement of leachate brings about advective solute transport in which solutes or contaminants are carried along with the leachate flow. Fast advective solute transport could be accompanied by potential dominant diffusive mass transfer between different flow domains (H. k. Rosqvist&Destouni, 2000). Therefore, the contaminants movement would be dependent upon the rate and direction of the flow. However, a study conducted by Fellner et al. (2009) revealed only a small fraction about 0.2% for the actual landfill in comparison to 40% participation of pore water on the solutes transport. The differences in laboratory and actual landfill simulation were caused by faster decrease in leachate emissions and stock remaining from the landfill portions. The still on-going studies on these aspect since the hydrodynamic properties of fluid movement and solubilisation of waste portion are very much correlated and still not well define either separately and even more on the intercorrelation.

This is cause by the poor ability to fully understand and predict the fluid movement and contaminant mass removal from the waste body at different flushing. Typically there is the need for model that coupled those several processes together involving physical transport mechanisms (advection, dispersion and diffusion), biological, thermal, mechanical and multiphase flow effects. Woodman et. al (2015) had listed out the particular experimentation problems as: 1) difficulty in obtaining representative in-situ samples; 2) difficulty to reproduce the actual process in the laboratory due to the high compression stress and compaction and 3) difficulty in controlling liquid flow during gas production.

Leachate Movement Outside Landfill

The effects on leachate mobility outside the landfill are mostly concerning the contaminants movement that could pollute the groundwater aquifer and surrounding water bodies. The leachate movement could contribute toward the natural attenuation effect both upon the waste characteristic as well as the leachate quality within and outside of the landfill boundary. The process of natural attenuation is defined as any combination of physical, chemical or biological reactions that occur naturally and could effectively reduce contaminant mobility, concentrations or toxicity (A. EPA, 1999). Slow mobility of the pollutant could minimize the impact by which lowering or degradation of the contaminants; usually amplify in longer time period and differ depending on the natural attenuation properties of the landfill site.

The leachate that has penetrated and travelled outside of the landfill boundary would definitely change both in it physiochemical and biochemical compositions (Islam &Singhal, 2002). The degree of groundwater contamination is affected by physical, chemical and biological actions. The relative importance of each process may change, however if the leachate moves from the landfill to the sub-surface region (Ramachandra, 2006). Evidence of such changes has been observed by looking into the down gradient of the landfill site. Focusing and establishing the type of contaminants' presence including the reactions taken place in those layers has exhibited the differences of redox zones occurring at the down gradient of the landfill aquifer such as reduction zones for oxygen, nitrate, sulphates, ferric, manganic

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and methane production zone depending on the presence of electron receptors (Christensen, et al., 1994). As for the geological attenuation effect, Thornton et. al. (2000) found that leachate–rock interactions are signified by acid–base and redox reactions, ion-exchange processes and sorption/precipitation of metal species whereas attenuation of leachate NH_4 is dominated by cation exchange with aquifer sediments. Even been retarded by the ion exchange, heavy metals could still impose serious problem since the soil would reach breakthrough over time causing significant increase in metal concentration over soil depth (Sizirici&Tansel, 2015). Such attenuation effect could be studied using chemical mass balance approaches, aqueous equilibrium speciation modeling and simple transport modeling. These methods are used to evaluate the key processes and aquifer geochemical properties in the landfill site which could naturally help in preventing and controlling the contaminant fate.

Apart from chemical effect, physical impact such as clogging of soil could also be expected by the leachate permeation. Studies show that the hydraulic conductivity can be reduced up to three orders of magnitude due to microbial growth and metal precipitation (R. Rowe, et al., 1997) caused by the leachate infiltration including calcium carbonate precipitation that mostly regard as the 'clog-slime' in leachate drainage (Rittmann, Fleming, & Rowe, 1996). As such it would react in further control of the leachate mobility as well as expected to contribute further for the natural attenuation especially by the biological processes of the microbial growth.

LEACHATE CONTROL

Leachate control discussed in this chapter emphasizes on the concept of containment systems to prevent water input from entering the landfill body and controlling leachate infiltration from polluting the soil, groundwater and surface water bodies. The topic involves various approaches for an effective containment strategies including on the managerial aspects; all the way down to the technical and engineering scopes. It also addresses current issues on leachate usage within the landfill boundary such as leachate recirculation that has been adopted by various landfill contractors and common problem that need to be coped for a full working containment of the landfill leachate.

Landfill Management Practice

Main contributions on leachate generation come mostly from the deposited waste and the waste that will be disposed. Management practices that allow the settlement of deposited waste and incoming waste stream could very well be employed in regulating the flow and amount of generated leachate. From legal perspective, the strict leachate control measures are primarily focused to prevent the leakage of leachate from the landfill and thus to avoid groundwater contamination (Davis &Masten, 2004). Without proper controls, infiltration by the rainwater has a very high potential to transfer pollutants from the landfill site to nearby lakes and streams. Moreover, soluble and partially soluble substances can be easily leached out from the waste site by rainwater becoming the leachate that can contaminate underground aquifers (Weiner & Matthews, 2003). Apart from preventing rainfall infiltration, the influence of soil cover could also involve upon the hydraulic resistance, smoothing between the rainfall event, evapotranspiration and the storage capacity to hold the rainfall volume. For practical purposes, neuron probe can be used to measure the soil moisture content whereas water infiltration through the soil cover can be detected using lysimeter. However, only the top shallow layers of soil that consist of the upper 0.3 m (Booth & Price,

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1989) would have high fluctuation to seasonal change; making the soil moisture value having insignificant differences in the respect to time and rainfall events (D. Bendz, et al., 1997). Evapotranspiration can be assume to be similar as regional evaporation for a landfill with thick soil cover and good surface vegetation (H-J Ehrig, 1989); allowing taking the value of potential evaporation according to Penman's definition. Though it is generally difficult to predict the movement of escaped leachate accurately, however, the main controlling factors are the surrounding geology and hydrogeology. Escaping to the surface water may be relatively easy to control, but if it escapes to groundwater sources, it can be very difficult both to control and clean up.

Because of the possible potential risk involved in allowing leachate to percolate to the groundwater, its elimination or containment would be the best practice that needs to be employed. The best way to control leachate is through prevention that needs to be considered and systematically integrated into the site design. Under the Subtitle D rules (40 CFR 258) promulgated by EPA, new landfill must be lined in a specific manner or meet maximum contaminant levels for the groundwater at the landfill boundary (Davis &Masten, 2004). In most cases, it is necessary to control the potential liquid access, collection steps and required treatment using the following steps in implementing landfill liners as suggested by Ramachandra (2006).

1. **Natural Liners:** These refer to compacted clay or shale, bitumen or soil sealants, etc and are generally less permeable, resistant to chemical attack and have good sorption properties. They generally do not act as true containment barriers, because sometimes leachate migrates through them.
2. **Synthetic (Geo-Membrane) Liners:** These are typically made up of high or medium density polyethylene and are generally less permeable, easy to install, relatively strong and have good deformation characteristics. They sometimes expand or shrink according to temperature and age.
    - Natural and geo-membrane liners are often combined to enhance the overall efficiency of the containment system

Weiner and Matthews (2003) suggests adaptation of a contoured system for leachate collection at the landfill to secure leachate infiltration as shown in Figure 6. Such system is to promote leachate movement from the waste to the pumps for extraction with active drainage toward the surface and subsequent treatment. The arrangements are divided into three levels. In level 1, one or more pumps direct the collected leachate to the surface toward the readily available treatment technologies for the leachate, including:

1. **Sorbent Material:** Carbon and ash fly packed inside a column through which the leachate is allowed to pass through.
2. **Packaged Physical-Chemical Units:** Numerous units could very well includes chemical addition or pH adjustment before being induce for flash mixing controlled coagulation, flocculation, sedimentation, pressure filtration and reverse osmosis system.

Before a reliable leachate treatment system is established, tests must be carried out. All methods or treatment system that produces waste sludge must reach ultimate, end-point disposal.

Level 2 comprise of a secondary safeguard system made of another barrier contoured to provide a backup leachate collection system. This reacts as a fail-safe system in case of failure of the primary system. During breakdown of the level 1 system, the secondary collection system would take controls

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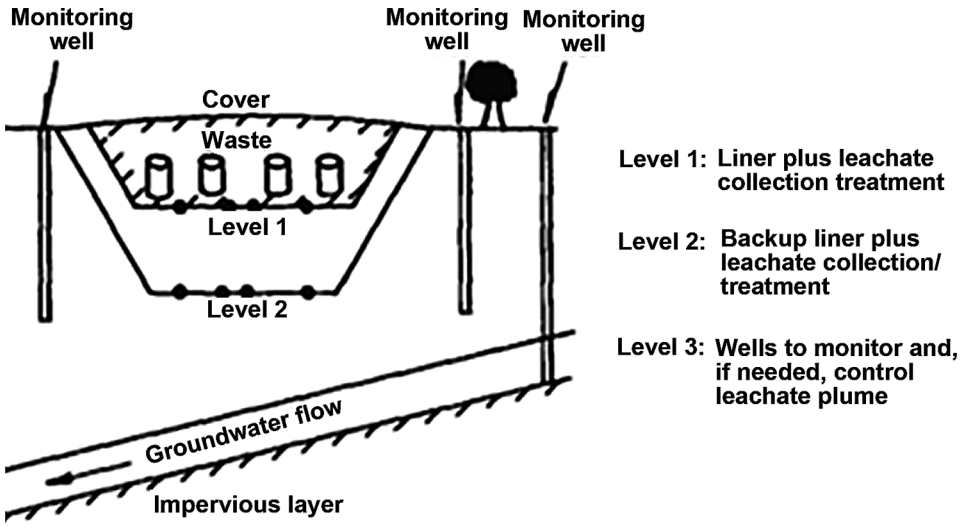
for directing and channeling the leachate to a pumping station, which in turn relates the leachate to the surface for treatment.

Finally, a secondary safeguard system (Level 3) is also advisable that would consists of a series of up gradient and down gradient discharge wells having the primary purpose for monitoring the groundwater quality in the area, and in worst case scenario, to control leachate plumes if the primary and secondary systems fail. For this purpose, the up-gradient wells will act to define the background levels of selected chemicals or recognized pollutants in the groundwater and to serve as a basis for comparing the concentrations of those chemicals/pollutants in the discharge from the down-gradient wells. Through this monitoring process, this system is able to function as an alarm mechanism if the primary and secondary systems fail.

Engineering Approaches

Commonly, landfill liners are used to limit or eliminate or restrict the movement of leachate and landfill gases from and out of the landfill site. The type of liner system selected will depend on a large extent on the local geology and environmental requirements of the landfill site. For example, in locations where there is no groundwater, a single compacted clay liner may be sufficient. In locations where both leachate and gas migration must be controlled, a combined liner comprising a clay liner and a geomembrane liner with appropriate drainage and soil protection layer will be necessary. Liners made of either impervious clay or synthetic materials such as plastics are used to try to prevent the movement of leachate into the groundwater. The seams have to be carefully sealed and a layer of soil is placed on the liner to prevent landfill vehicles and waste from puncturing it. Clay is favored for its ability to absorb and retain many of the chemical constituents found in leachate and for its resistance to the flow of the leachate (Tchobanoglous, Theisen, & Vigil, 1993). Synthetic landfill liners are useful in capturing most of the leachate but infiltration is still possible. No landfill is sufficiently tight that groundwater contamination by leachate is totally avoided. Wells have to be drilled around the landfill to check for groundwater contamination

Figure 6. Three levels of safeguard in hazardous waste landfills (Weiner & Matthews, 2003)



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from leaking liners, and if such contamination is found, remedial action is necessary (Vesilind, Morgan, & Heine, 2004). However, the use of combine composite geomembrane and clay liners is gaining in popularity, especially because of the resistance afforded by geomembranes to the movement of both leachate and landfill gases. The characteristics, advantages and disadvantages of the geomembrane liners (also known as flexible membrane liners, FMLs) that have been used for MSW landfills are summarized in Table 4 and Table 5.

The objective of designed landfill liners is to prevent or eliminate leachate infiltration into the subsurface soils below the landfill so as to minimize the contamination risk of the groundwater. A number of liner designs have been designed and developed for that purposes and one of the proposed types of liner designs is as illustrated in Figure 7 for double layer system and Figure 8 for monofill layer system.

In the multilayer landfill liner design, each of the multiple layers has its own specific function in which the two composite liners react as a barrier to the flow motion of both the leachate and landfill gas. Meanwhile, the drainage layer is specifically design for the collecting all the leachate that were generated within the landfill. The final soil layer performs as the protective layer for the drainage and barrier layers. A geomembrane and clay layer employed into the composite liner designs will provide more protection and function more effectively in term of hydraulic compare to either type of liner alone. However, several options might be considered if leachate migration may occur at an old or existing landfill. These options include putting a cap on the surface on the landfill. The cap usually comprise of clay or a liner coated with topsoil seeded to grass to effectively provide some shade from precipitation; some sort of cutoff walls or dams keyed into an impermeable stratum to isolate the fill, pressure treatment, sealing of the bottom and sides of the fill; provide up gradient surface-water drains that goes through and around the landfill area; installed curtain drains or wells to counter and drain away the contributing groundwater flow, collection and recirculation of leachate with treatment of any excess, or in special cases, the ma-

Table 4. Landfill sealants for the control of gas and leachate movement (Tchobanoglous, et al., 1993)

Sealant		Remarks
Classification	**Representative types**	
Compacted soil	-	Should contain some clay or fine silt
Compacted clay	Bentonites, illites, kaolinites	The most commonly used sealant for landfills; these type of sealant would have a layer thickness varies from 6 to 48 in and the layer must be continuous to prevent any disfiguration of the protective layer and are not allowed to dry out or it would eventually cracked
Inorganic chemicals	Sodium carbonate, silicate or pyrophosphate	Use depends on local soil characteristics
Synthetic chemicals	Polymers, rubber latex	Experimental; use in field not well established
Synthetic membrane liners	Polyvinyl chloride, butyl rubber, hypalon, poluethylene, nylon-reinforced liners	Commonly used for leachate control; increased usage for control of landfill gas
Asphalt	Modified asphalt, rubber-impregnated asphalt, asphalt-covered polyethylene fabric, asphalt concrete	The layer must be sufficiently thick enough to maintain continuity under differential settling conditions as could be impose by the landfilling proces and leachate accumulation.
Others	Gunite concrete, soil cement, plastic soil cement	Not commonly used for control of leachate and gas movement because of shrinkage cracks after construction

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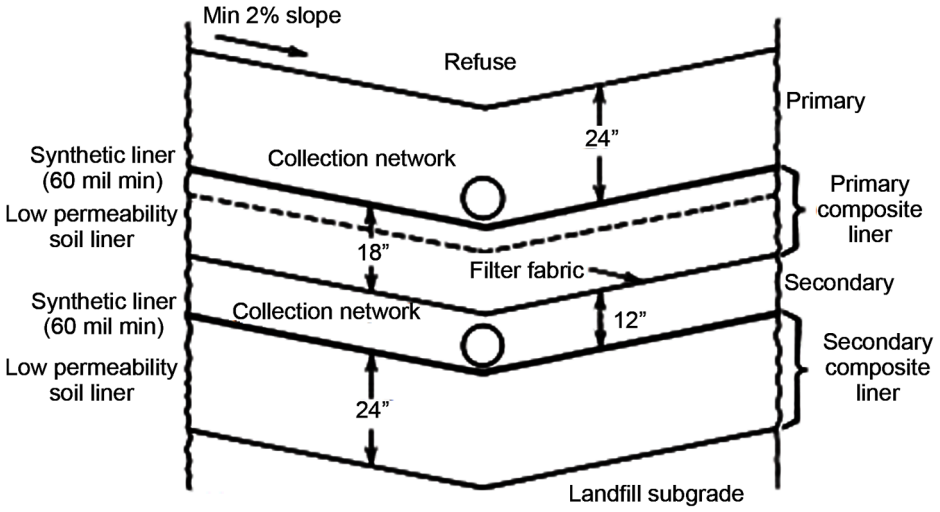
Table 5. Guidelines for leachate control facilities (Tchobanoglous, et al., 1993)

Item	Comments
Synthetic flexible membrane liners (FMLs)	Liners must be designed and constructed to contain fluids, which include wastes and leachates. For MSW waste management units, synthetic liners are not required. However, if this alternative is selected, synthetic liners must have a minimum thickness of 40 mils. These liners must be installed to cover all natural geologic materials that are likely to be in contact with waste or leachate at a waste management unit.
Bottom seals	No specific regulations exist governing the application of bottom seals at MSW waste management units. Design, construction and installation of bottom seals are subjected to the approval of the local enforcement agencies.
Artificial earthen liners	Clay liners are optional for MSW landfills. If required by site conditions, clay liners for MSW waste management units must be a minimum of 1 ft thick and must be installed at a relative compaction of at least 90 percent. A clay liner must exhibit a maximum permeability of 1 x 10^{-6} cm/s. Clay liners, if installed must cover all natural geologic materials that are likely to be in contact with waste or leachate at a waste management unit.
Subsurface barriers	A subsurface barrier is intended to be used in conjunction with the readily available, natural geologic materials of the landfill site to assure that lateral permeability standards are satisfied. Barriers may be required by regional agencies at MSW waste management units where there is high probability for lateral movement of fluid, including waste and leachate and by looking at the permeability aspect of the naturally obtained geologic materials that are used for waste containment in lieu of a liner. Barriers must be a minimum of 2 ft thick for clay material or a minimum of 40 mils for synthetic materials. These structures are required to be keyed a minimum of 5ft into the naturally obtained geologic materials that already tested and known to satisfy the permeability requirements being in the range of 1 x 10^{-6} to 1 x 10^{-7} cm/s. If a cutoff walls are to be used, excavations of the waste management units must also be keyed into the natural geologic materials that exhibiting permeability properties lower than 1 x 10^{-6} cm/s. These barriers are required to have fluid collection systems in the up gradient position to the structure. Buildup of hydraulic head against the structure need to be prevented through properly designed, constructed, operated and maintained systems. For continuous maintenance, the collection system itself must be inspected regularly and required that the accumulated fluid is constantly removed.

Figure 7. Double-bottom composite liner systems



Composite liner = Synthetic liner + Low permeability soil

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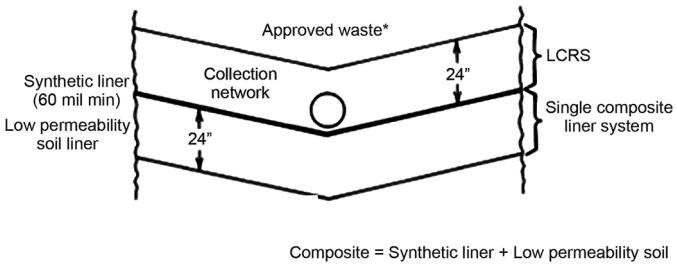
Figure 8. Monofill waste landfill liner configuration



terial in the landfill can be excavated, treated, recycled, and/or disposed of at a controlled landfill site. However, excavating of an existing landfill might pose some other problems if hazardous wastes are involved and hence must be carefully conducted from the very beginning (Nemerow&Agardy, 2009).

Apart of the designed and installed liner system, a continuous groundwater-monitoring program is essentially important for confirming the integrity of the liner system. At an early stage of site preparation, therefore a number of monitoring boreholes that needs to be provided around the site, inside and at the boundary of the landfill area. However the location, design and number of boreholes depend on the size of the landfill which need to look at the background of the area geological aspect such as the proximity to an aquifer and on the operation of the landfilling, for example on the types of waste deposited. Installation of a double liner system can make the monitoring exercise more accurate and easier to perform but it does not necessarily required excessive data analysis. Study by Sizirici and Tansel (2015) revealed that by proper adjustments in the sampling strategy could reduce the amount of collected data up to 97.7% through the mean of concentrating the monitoring point for aligned wells and suitable monitoring depth for selected contaminants in interest. However, for better maintenance and efficiency, the water should be regularly flushed through the secondary leachate collection system in order to maintain the stability of the system. In the case of the flushed water found to be polluted, the primary leachate carrier will be damaged and the collected leachate must be transported to the leachate treatment facility if the repair is unattainable (Ramachandra, 2006).

Leachate Collection System

Properly designed and managed leachate collection system should provide a good drainage of water balance in the landfill cell, both for controlling the leachate flow through the waste layer and more importantly preventing leakage into the surrounding environment. The basic elements of the leachate collection system consists of a drainage layer, leachate trench, collection pipes, leachate line clean-out ports, a leachate collection pump and lift station and a leachate storage tank (Bagchi, 2004; Ramachandra, 2006). All those components must be installed readily above the liner, prior before any waste is deposited. However leachate storage tank may not be necessary for a site in which the leachate is discharged directly to a sewer (Bagchi, 2004). In any case, particular care must be taken to prevent and maintain the drain and collection pipes from settling. During the landfill operations, waste cells are covered with soil to avoid additional contact between the waste layer and surrounding the environment but that soil layers have to be sufficiently permeable to allow downward leachate transport (Ramachandra, 2006) for the collection purposes. The leachate is discard out from the sump through piping that extending to the

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ground surface of the active landfill area, prior for treatment and being disposed of in an environmentally acceptable manner. A leachate collection system must be designed and constructed accordingly because it could pose specific construction problem which would indefinitely result in the failure of the collection system. The sort of requirements that need to be considered including:

1. Using other specification of material than the ones in the approved design;
2. Neglecting to properly installed material specifically to the designated positioned and to follow the correct procedures specified in the design
3. Improperly clear out all the foreign objects (e.g. clumps of soil, rocks, construction debris) which would be left in drainage system piping and resulted in plugging or restrict leachate flow. It may not be able to be removed by using the designed maintenance procedures;
4. Improper usage of the construction equipment and improper placement of materials which cause damage to system components. Example: to be doing crushing or misalignment of pipes due to vertical loading of heavy equipment or dumping soil and siltation of filter or drainage layers causing unwanted up gradient drainage during construction and/or careless construction techniques; and
5. Non-conforming layout of the leachate collection system such as insufficient slope or the misalignment of piping joints or and over-elevations of piping/drainage.

The structural performance of the pipes depends on: a) the earth's pressure acting on the pipe (which is influenced by burial depth, overburden density and lateral confinement) b) the backfill configuration (i.e. whether the pipe is placed within a trench, mound or blanket) c) backfill material d) properties of the pipe and e) service conditions (e.g. temperature and chemical exposure). The functions of collection system according to Rowe et al.,(2004) are listed below:

A. For lowering the height of leachate mounding and seeps which then consequent minimized contamination of surface waters.
B. Maintaining the hydraulic gradient through the underlying barrier by reducing leachate head acting on the base of the landfill and by doing so, the Darcy velocity out of the landfill can be lowered down to an acceptable levels in many cases
C. Keeping the mass of contaminant presence within the leachate during the transport for removing contaminant from the landfill.

A leachate collection system is required above a liner in order to avoid build-up of the leachate head above the 1-ft (30.5 cm) level stipulated in the regulations. Leachate collection pipe is sized to handle the anticipated flow. A collection pipe is usually 6 inch (15 cm) in diameter, although some designers prefer an 8 inch (20 cm) diameter as a minimum (Oweis&Khera, 1990). The structural design of the leachate collection pipe depends on the vertical load on the pipe and bedding conditions. The types of pipes and their functions are as shown in Table 6.

A leachate collection and removal (LCR) system is designed for collecting leachate and to discard the leachate by flowing it out of the landfill for treatment process. The LCR system is need to be constructed by making sure that less than 30 cm of leachate accumulates above the composite liner as it is the allowable amount of leachate that the liner is designed to maintain according to Subtitle D. Therefore, the designing of a LCR system need to consider the following components:

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Table 6. Type of collection pipes (Oweis&Khera, 1990)

Pipes	Functions
Flexible pipes	Usually used in a leachate collection system. The load carrying capacity of such pipes is derived mostly from interaction with the surrounding bedding. Examples are plastic, steel and ductile iron pipes. Steel and ductile iron are susceptible to corrosion by leachate and perforations cannot be easily made
Plastic pipes	More common and may include polyvinyl chlorine (PVC), polyethylene (PE), acrylonitrile-butadiene-styrene (ABS) and others
Rigid pipes	Such as a concrete pipe (CP) derive mist of their strength from their inherent structure but are subject to chemical attack and perforations are hard to make. Corrosion-resistant rigid pipes such as vitrified clay also lack adequate bending strength. Because of all these limitation, rigid pipes are not normally used in a leachate collection system

1. **Area Collector:** The piping drain that covers the liner and collects the leachate. The area collector are also known as the blanket drain are designed to covers the entire surface of the geomembrane liner and collects the leachate accumulate over the liner. Typically, the area collector system is constructed with at least a 30 cm (12 in.) and the system is overlay with a layer of sand having hydraulic conductivity above 10^2 cm/sec. Alternatively, the blanket drain could also be constructed using geosynthetic drainage nets comprise of porous synthetic materials being applied over the geomembrane liner
2. **Lateral Collection Pipes:** The pipe network that collect and drains the landfill area. According to the U.S. EPA (1994), the regulatory limit of a 30 cm maximum liquid head above the liner cannot be achieved using an area collector alone which would require the need for collection laterals. The collection laterals are consisting of perforated pipes that direct collected leachate toward the sumps for removal purpose. During landfill operation, leachate are being directed to passes through the area collector, flow into the collection laterals before it would be finally drains to a sump and removed from the landfill. Polymeric pipes are by far the most common material for collection lateral but however, there are a number of appropriate materials that could be choose for the leachate collection systems. For that matter, HDPE and PVC are the kind of materials that were used exclusively and are available as either profiled or smooth wall construction.

Basically, the design of perforated leachate collection pipes must take into account on the stated issues:

A. The estimated leachate flow
B. Selected pipe sizes
C. The maximum allocation for pipes spacing
D. The physical and structural strength of the pipe
E. Allowable maximum range for drainage slopes

Spacing of the collection pipe being laid laterally would depend on the permeability of the collection pipes, the assumed entry rate of rainfall and the slope of the liner beneath the landfill area. The pipes need to be allocate closer if the permeability is lower. However, the slope of collection laterals should be greater than 2% as it would need to react as cleansing mechanism by achieving adequate flow velocity to clear the flow path the pipes and also prevent any kind of reverse flow within the pipelines.

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3. **Sump:** The low point where the leachate exits the landfill. In the composite liner system, sumps are usually located in the engineered low points and are constructed for the purpose of collecting leachate. Sumps are also often designed with an additional layer of geomembrane to cater for the seam-testing sumps difficulty. The leachate collection and removal standpipe must be extended through the entire landfill from lowest liner to the cover to capture leachate from the each landfill cell, and then through the cover itself. It must be maintained for the whole post closure care period whether it going to be for the next 30 years or longer.
4. Storm water and leachate separation system.

As polluted leachates appears shortly after disposal of the waste that may cause groundwater pollution and pollution of streams through sub-surface migration; liners, drainage collection, treatment of leachate and groundwater and downstream water quality monitoring are necessary to control this problem (Ramachandra, 2006). Other than the design aspect, leachate collection system would have to consider the possibility of clogging experienced within the drainage system especially for long usage duration throughout the landfill life and even after the landfill is closed. The leachate collection and removal system should be designed to be accessible for routine and constant maintenance and for the purpose of cleaning especially due to the potential for biological film clogging. It is shown that landfill producing leachate with high concentrations of organic matter (referred as COD), calcium and pH value of 7 would be highly exposed to clogging due to the anaerobic bacteria activities (Brune, Ramke, Collins, &Hanert, 1994). It was proposed that clogging is a result of mobilization processes which involve fermentative, iron and manganese-reducing bacteria followed by precipitation processes involving sulphates-reducing and methanogenic bacteria. The clogging could underlay the stone drainage blanket with significant amount of soft black slime and occupy most of the void space after 1 to 5 year exposure to the leachate (R. Rowe, et al., 1997). Field studies also had shown the increase in clogging rate caused by leachate recirculation because the system promote deposition of suspended particles, biomass growth and mineral precipitation (Feng, Cao, Zhang, &Xie, 2015a).

Leachate Recirculation

Leachate recirculation is one of the simplest forms of leachate control through the process of reintroducing collected leachate back into the landfill. It is useful in controlling the leachate volume whilst accelerating waste decomposition through addition of supplemental liquids. Recirculation of leachate also seems to facilitate in reducing the hazardous nature of leachate (Ramachandra, 2006). Leachate recirculation is known to be effective in enhancing biodegradation because the process is capable in increasing the moisture and movement of moisture (which carries nutrients). But observation by Barman et. al (2015) reveal that nutrients (sodium, calcium and potassium) leaching might be more dominant compared to nutrient trapping for higher ponding depths and higher inflow recirculation rate. Increasing the moisture content and flux in landfill waste layer would create a suitable environment for the organic waste degradation by microbes because initial moisture is not sufficient (Benbelkacem, Bayard, Abdelhay, Zhang, &Gourdon, 2010). Furthermore, the leachate percolation by the recirculation process would have a significant effect on the mobilization that accelerates solid-mass transfer, improves substrate accessibility and enhances degradation of the waste soluble organic matter (Benbelkacem, et al., 2010; Chugh, Clarke, Pullammanappallil, & Rudolph, 1998). It is assumed that the leachate addition would also react by softening the porous waste material, increase unit weight of the waste, lubricating the waste contact

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and promote biological degradation. Bae et al. (1998) also found agreement data which reported that leachate recirculation is capable for increasing the moisture content in a controlled bioreactor system and provided overall distribution of nutrients and even valuable enzymes between methanogens and solid/liquids. In physical sense, it promotes the loss of leachate as water vapor and through consumption by the organic waste degradation process.

Various methods existed for leachate recirculation purposes that would include surface or spray irrigation, vertical injection wells, horizontal trenches and infiltration ponds (Feng, S.-J., Cao, B.-Y., Zhang, X., & Jiao, Y., 2015b). However, all those leachate recirculation procedure has to be carefully designed in preventing unnecessary consequences and to induce optimum benefit from the process since waste stabilization and biodegradation of the organic matter can be accelerated by leachate recirculation. Establishment of early gradual recirculation would promote the presence of active anaerobic biomass which are important for biological processes in each landfill cell. In legal term, RCRA Subtitle D allows leachate management by recirculation for modern landfills with a regulated composite liner and a leachate collection system (Oweis&Khera, 1990).Controlled leachate recirculation would include nutrient addition to maintain optimum moisture and pH, breakdown organics that could be exhibited through reduction of the total organic carbon (TOC) and chemical oxygen demand (COD), can enhance anaerobic microbial activity for converting solid waste organics to methane and carbon dioxide as well as encourage precipitation of heavy metals. With the aid of the process, rapid and complete biological stabilization could even be achieved within four to five years. For a landfill being design for leachate recirculation should, as a minimum requirement, would need to install a conservatively designed liner system and proper system to effectively maintained leachate collection, removal, and recirculation distribution system. Apart from that, it would at least required a venting system or in addition to a gas collection system. A double liner system with leak detection monitoring wells is suggested that would enable the landfill owners or the regulatory agencies to closely monitor the liner system performance since the leachate recirculation would accelerate fill stabilization and also increase the strength of the already concentrated leachate composition. A final site closure would definitely require the need for implementation of a relatively impermeable crowned cap and surface-water drainage system.

Improper leachate recirculation would impose problems indicating by the lab test using high recirculation rate (Sponza&Ağdağ, 2004) such as flooding, pooling or clogging especially at high precipitation area (Šan&Onay, 2001). Therefore, the optimal recirculation should be designed properly to be close but not exceeding the waste field capacity. For unsorted domestic waste, it is suggested that 50% w/w of moisture content maybe the optimal value (Gurijala&Suflita, 1993) and it might not be suitable for fresh waste or for methane production purposes since accumulation of volatile fatty acid or ammonia nitrogen could inhibit the methanogenesis process (Price, Barlaz, & Hater, 2003). As for the recirculation volume concern, a study on the leachate recirculation reveals that high volume leachate addition does not have significant effect on the leachate accumulation at the bottom liner (Abichou, et al., 2013) and high volume is required for the periodical injection to ensure uniform distribution of humidity in waste layer (Benbelkacem, et al., 2010). In term of temperature value, heating of recirculated leachate to 30°C has been found to accelerate the stabilization process (Nemerow&Agardy, 2009).

The most common methods being used for simulating the effect of recirculation upon bioreactor landfills are vertical wells and horizontal trenches (Jain, Townsend, &Tolaymat, 2010). In most cases, horizontal trenches are more common in modern landfill liners except for when vertical well are installed dues to the cost inefficiency or the difficulty in installing the horizontal trenches. Feng et. al (2015a) had simulated the effect of recirculated leachate volume and the influence upon waste layers using vertical

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wells. The study found that leachate recirculation had significant effect by gradually decreasing the void ratio and hydraulic conductivity of the waste being measured through the pore water pressure as one of the most important factor related to landfill slope stabilities. The study concluded that the influence width of leachate recirculation is a function of waste settlement, leachate injection pressure head, initial void ratio, unit weight, and compression coefficient and biodegradation rate. Khire and Mukherjee (2007) recommended that the maximum influence width will be reach in 25 - 45 days and center-to-center spacing between wells should obtained above 90% for the degree in saturation, to eliminate dry zones between adjacent wells. Apart from that, such studies also needs to consider the difficulties in representative measurement of water content and hydraulic properties of municipal solid waste (McCreanor& Reinhart, 1999) because of the anisotropic and heterogeneous material with complex biochemical properties.

CONCLUSION

It can be conclude that the hydrological phenomena occurring from outside, into and through the landfill layers dominate the processes inside the landfill in so many ways. The leachate generation alone comprise of multiple factors coming from physical (precipitation, infiltration, transpiration and etc.) as well as being influenced by the biological and chemical interactions. Consecutively, those generated leachate would latter play an important role forthe organic portions degradability and stability of the waste layer affected through the different forms of flows movements, either horizontal or vertical channelling. The most prominent type of flow channels that need to be highly regard are the preferential flow paths apart from other flow paths and all those flow channels need to be correctly model or estimate depending on the physical characteristics of the heterogeneous waste stream, which are totally different that soil properties. The leachate movement in the multichannel flows brought not only the moisture down to the landfill base but also transporting along the contaminant constituents. In the end, effective prevention and control measure were required to completely contain the leachate for prior treatment process. Plus, those systems had to be well maintain and sufficiently controlled for a long run even after the landfill closure; especially for inducing leachate recirculation system which in part function well for minimizing the leachate quantity whilst simultaneously making good use of the leachate organic constituent to speed up the degradation of the waste layer.

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Chapter 43
Bioremediation of Agricultural, Municipal, and Industrial Wastes

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ABSTRACT

Growth of agriculture and manufacturing industries has resulted in increased a wide range of complex and hazardous compounds to the environment. Excess growth of hazardous waste has led to reduce availability of clean water and disturbances of soil thus limiting crop production. Waste generated from different sources like Industrial, domestic and agricultural etc. having different kinds of chemical compound i.e. organic or inorganic. Traditional methods are not able to deal with some of these chemical compounds. Bioremediation process is good option in such environmental problems. Bioremediation provides a technique for cleaning up pollution by enhancing the natural biodegradation processes. It treats such waste with the help of microorganism. Number of microbes including aerobes, anaerobic and fungi are involved in bioremediation process. Specific types of microbes are used to treat specific type of chemical contaminant. The chapter include all the techniques of bioremediation used to treat different kinds of contaminant.

INTRODUCTION

Ecosystems are threatened with natural environmental changes and disturbances that remove biomass from a community, such as fire, flood, drought, or predation over time and geographic space. (Levin, 1992) These disturbances needs new techniques emerge out of the patchwork of natural experimentation and opportunity implying a good measure of ecological resilience are a cornerstone theory in an ecosystem (Folke et al., 2004). The most common types of waste can be categorized into four types: agricultural, industrial, municipal and nuclear (Alloway, 1995). Agricultural waste, have both natural and non-natural wastes, is a general term used to describe waste produced from the fields through various activities. Agricultural wastes are the by-products of various agricultural activities such as crop production, harvesting of crops, saw milling, agro-industrial processing, and others. In India sugar industry alone produces about 90 MT of bagasse per year and being used in the manufacturing of insulation boards, wall panels,

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printing paper and corrugating medium (Sengupta, 2002). Generally, agricultural waste is produced in two forms- solid and liquid waste. The food harvesting and production industry generate crop residuals, as well as pre- and post- consumer food wastes. Some of the farmer burn agro- wastes after harvesting time; this causes a huge amount of air and land pollution. Municipal waste (MSW) composition can vary considerably with places and time depending on many factors, including socio-economic, climatic conditions, living standards, waste collection, and disposal methods, sampling and sorting procedures. MSW is heterogeneous in nature and have a number of different materials derived from various types of activities. Municipal waste generated from residential and domestic sources. This type of waste is commonly called trash or garbage and includes everyday items, spoiled food, broken things, or simply any item a person no longer needs or wants. The most commonly disposed of items as municipal solid waste are paper, yard trimmings, food, plastics, metals, rubbers, and textiles. In recent years, the amount of electronic waste, also known as e-waste, has increased drastically as people become more dependent on electronics, such as cell phones and computers that are replaced and disposed of frequently. Based on the definition of municipal solid waste, the waste that you dispose of everyday would fall into this category. Municipal solid waste categorized into two types: garbage and rubbish. Garbage or food waste is the animal and vegetable residue resulting from the preparation, cooking and serving of food. These wastes contain organic matter and moisture. Kitchens, restaurants, and markets are sources of garbage. Rubbish consists of old tin cans, newspaper, tires, packaging materials, bottles, plastics etc. Both combustible and non-combustible solid wastes are included in this category but do not include garbage. Trash is the combustible portion of rubbish. The rise in the number of industries producing glass, textile, leather, plastic and metal products food, and electronics, has significantly contributed to waste production. Rapid industrialization has resulted in the generation of a huge quantity of wastes, both solid and liquid, in industrial sectors such as fruit and food processing, pulp and paper, sugar, sago / starch, distilleries, dairies, tanneries, poultries, etc. These wastes are generally dumped on land or discharged into water bodies, without adequate treatment, so pollute environment and cause health hazard. In a broad sense, industrial wastes could be classified into two types i.e. Hazardous wastes and non- hazardous wastes (Table 1). Hazardous industrial wastes in India can be categorized broadly into two categories: Hazardous wastes generated from various industries in India and Hazardous industrial wastes imported into India from Western Countries for re-processing and recycling. Hazardous waste, in particular, includes products that are explosive, flammable, irritant, harmful, toxic, carcinogenic, corrosive, infectious, or toxic to reproduction. The other one is Non-hazardous or ordinary industrial waste that generated by industrial or commercial activities but is similar to household waste by its nature and composition. It is not toxic, hazardous and requires no special treatment. In particular, it includes ordinary waste produced by companies, shopkeepers and tradespeople (paper, cardboard, wood, textiles, pack, etc.). Due to its non-hazardous nature, this waste is often sorted and treated in the same facilities as household waste.

Bioremediation involves use of microbes to detoxify and degrade environmental pollutants. Recently, research is being focused in the development of genetically modified microbes or consortia for the detoxification of environmental pollutants. Microbes degrade the complex substances to simpler one that can be reuse or recycle in environmental processes. Microbes involved in the degradation naturally are aerobic or anaerobic bacteria, fungi or algae. Most of the techniques in bioremediation are aerobic in nature, but anaerobic processes are also being developed to help degrade pollutants in oxygen deficit areas (Franchi et al., 2016). In bioremediation processes, microorganisms use the contaminants as nutrient or energy sources (Hess *et al.*1997; Agarwal, 1998; Tang et al., 2007). Bioremediation is a process by which microorganisms are stimulated to rapidly degrade hazardous organic pollutants to environmentally safe

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Table 1. Different types of industrial waste classified on the basis of their composition

	Hazardous Waste Component	Sources
Heavy Metals	Arsenic	Mining, non-anthropogenic geo-chemical formation
	Cadmium	Mining, fertilizer industry, battery waste
	Chromium	Mining areas, Tanneries
	Lead	Lead acid battery smelters
	Manganese	Mining areas
	Mercury	Chloro-alkali industries, healthcare institutes
	Nickel	Mining, metal refining
Hydrocarbons	Benzene	Petrochemical industries, solvents
	Vinyl chloride	Plastics
Pesticides		Insecticides
Organic chemicals	Dioxins	Waste incineration, herbicides
	PCBs	Fluorescent lights, e-waste, Hydraulic fluid

levels in soils, sediments, substances, materials and ground water. Environmental parameters should be favourable for microorganisms to grow and remediate the pollutants at a rapid rate (de la Cueva et al., 2016). Bioremediation is currently being used to reduce the organic chemical waste content of ground water, soils, effluent from food industry and chemical plants, sludge from petroleum refineries and oil spills in the ocean. Bioremediation techniques fall into two categories — in situ and ex situ bioremediation. Using bioremediation technology TERI, India, has treated 48,914 tons of waste oily sludge in batches at various oil refineries in India (Mandal et al., 2012). Bioremediation is concerned with the biological restoration and rehabilitation of historically contaminated sites and with the clean-up of areas contaminated in more recent times, either accidentally or incidentally, as a result of the production, storage, transport, and use of organic and inorganic chemicals. The uses of plants can improve bioremediation rates as plants provide habitats to microbes; improve soil porosity and help in cycling of micro nutrients with their microbial metabolism. In return, microorganisms improve plant growth by reducing soil toxicity, producing plant growth promoting metabolites, provide plant nutrients by sequestration from soil etc. (Gkorezis et al., 2016)Some examples of bioremediation technologies are phytoremediation, bioleaching, bioventing, bioreactor, land farming, composting, bio augmentation, rhizofiltration, and biostimulation. The biological approach of remediating the environment with the help of bioremediation, defined as *'the process that use biological agents to reclaim waters and soils contaminated by hazardous substances to human health and the environment'* (Atlas and Pramer, 1990). Bioremediation is an option that offers the possibility to destroy or render harmless various contaminants using natural biological activity. Industrial waste contains much kind of organic and inorganic components. Wastes produced from different sources may be in solid, liquid or gaseous form. Treatment of different types of wastes is done with the help of processes listed in Figure 1. All the techniques require specific type of conditions such as, microbial profile, energy source and electron acceptor, moisture and pH, nutrients and temperature, absence of toxicity, removal of metabolites, absence of competitive microorganisms, etc. for digestion and degradation. Some of the processes are explained below which are used for the treatment of agricultural, municipal or industrial waste. The main objective of this chapter to study and

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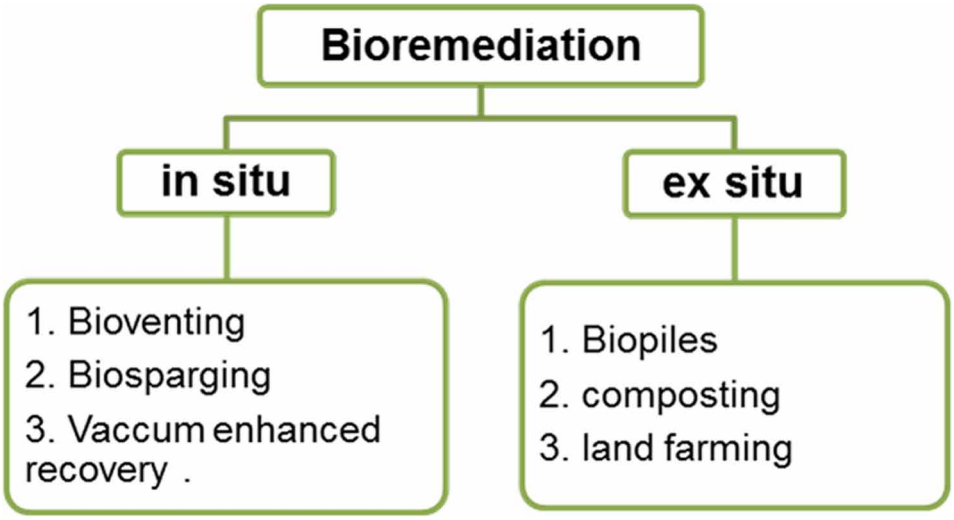
Figure 1. Different strategies used for management of wastes with bioremediation



find out the different bioremediation processes which is effective in dealing with agricultural, municipal and industrial waste disposed or present in the environment and cannot be degraded by conventional processes or naturally without harming the environment.

BIOREMEDIATION OF AGRICULTURAL WASTE

There are two main methods of bio remediating agricultural waste. The first method is anaerobic digestion. The other method is composting, an aerobic process where microorganisms break down the organic material in the waste when air and water are added to the waste product. Following processes are involved in the management of agricultural waste with the help of bioremediation process which are commonly used:

- Anaerobic digestion,
- Composting,
- Vermicomposting,
- Biogas production,
- Biopile,
- Land farming, etc.

Digester systems consist of a vessel in which the waste is heated to a certain temperature, to allow the microorganisms to consume at an efficient rate. The method in which this is done varies widely, from using simple composting piles to composting vessels. Yet another option is to combine one or more composting methods to produce the desired composition of compost. All the techniques are used for bio remediating agricultural waste explained in detail below.

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Anaerobic Digestion

In this process about 95% of biodegradable carbon is decomposed into biogas and the rest 5% into biomass. Three main steps are involved in the breakdown of organic waste under anaerobic conditions. These steps essentially hydrolysis of biopolymers to monomers, fermentation of monomers to volatile acids and Methanogenesis. The microbial species responsible for anaerobic degradation are *Actinomyces, Arthrobacter, Citrobacter, Escherichia, Lactobacillus, Micrococcus* etc. Anaerobic treatment is a biological process carried out in the absence oxygen for the stabilization of organic materials by conversion into methane and inorganic end-products such as CO_2 and NH_3. Anaerobic process is of two types: anaerobic fermentation and anaerobic respiration. In anaerobic fermentation, the product obtained by accepting the electrons released during breakdown of organic matter and ethanol is also produced along with energy. Anaerobic respiration is used mainly by prokaryotes that live in environments devoid of oxygen. In this process, energy is used by the reaction for degradation of organic material. General process of anaerobic digestion of organic agricultural waste is as follows

There are four different types of anaerobic wastewater treatment bioreactors which are anaerobic filter reactor, anaerobic contact process reactor, fluidized bed reactor and up flow anaerobic sludge blanket (UASB). Most commonly used bioreactor is up flow anaerobic sludge blanket (UASB).

Up Flow Anaerobic Sludge Blanket Reactor (UASB)

UASB reactors can treat all type of high-strength wastewater. It can be used at large-scale (e.g. agro-industrial wastes) or as decentralised treatment systems for domestic wastewaters; yet domestic treatment is still relatively new and not always successful as domestic wastewater generally lower strength. Anaerobic treatment systems such as UASB do not require an energy consuming aeration system and can be built simply than aerobic process. This process converts the organic matter into biogas, which can be recovered. The nutrient-rich effluent can be used for agricultural irrigation. Sludge, even is partly stabilised (mineralised) and can be used as an organic soil fertiliser after composting or drying. The UASB reactor is a methanogens (methane-producing) digester that evolved from the clarifier. UASB uses an anaerobic process whilst forming a blanket of granular sludge which suspends in the tank. Wastewater flows upwards through the blanket and is processed (degraded) by microorganisms. The upward flow combined with the settling action of gravity suspends the blanket with the aid of flocculants. The blanket begins to reach maturity at around 3 months. In the absence of any support matrix, the flow conditions create a selective environment in which only those microorganisms, capable of attaching to each other, survive and proliferate (Figure 2).

Figure 2. Process of anaerobic digestion of organic agricultural waste

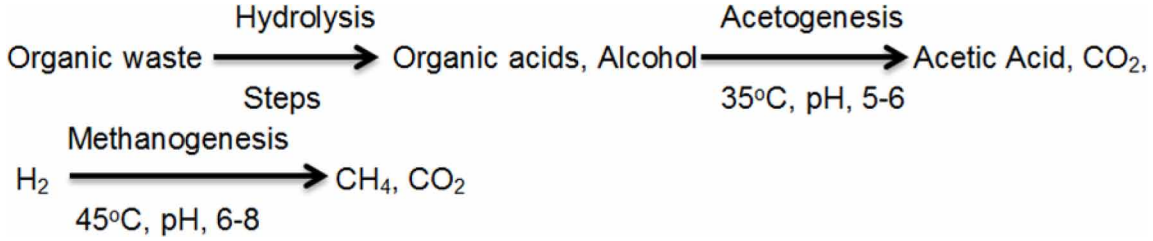

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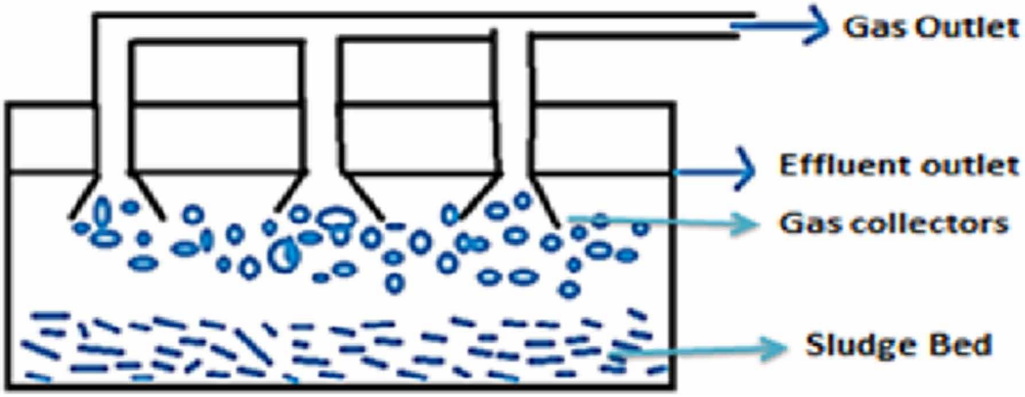
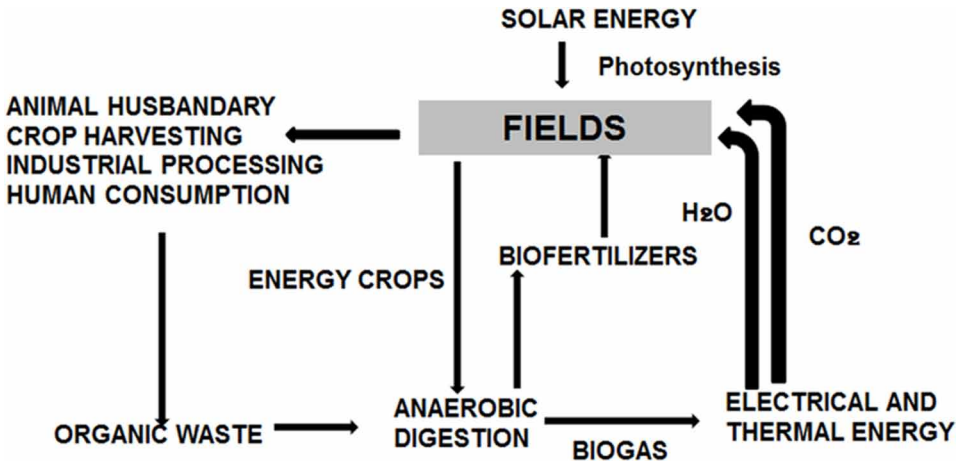
Figure 3. General model of up flow anaerobic sludge bioreactor for treatment of wastewater



Eventually the aggregates form into dense compact biofilms referred to as "granules". The government of India has made a major commitment to anaerobic treatment technology in its national river basin improvement program. As of 1996, 13 new anaerobic treatment plants, with an aggregate treatment capacity of over 306 MLD are under construction in India. Anaerobic waste water treatment is the most popular method, cheaper for treatment of high strength waste water; produce energy is in the form of biogas and required very small space for installation than aerobic treatment. Biogas produced form this technique can be used for domestic or commercial purposes in household industries. This technique usually used for the treatment of liquid waste i.e. wastewater generated from agricultural land or domestic area dependent on agriculture for their occupation, sewage waste and industrial effluent. It could be recognised by some newly developed European waste treatment systems that some microbial degradation or transformation occur only in the absence of oxygen. Under anaerobic conditions, microorganisms growing on wastes can produce valuable fuels. The dry anaerobic composting process converts the organic fraction of biodegradable organic waste and refuse into energy in the form of biogas (methane and carbon dioxide) and humus- like material (Figure 3).

Figure 4. Natural method of Biogas production and uses of biogas in electricity production



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Composting

Composting of manure is a valuable management tool that increases the flexibility for land application and storage, while significantly reducing the potential for contamination to soils and water that might occur if raw manure were to be improperly stored or land spread. Composting of carcasses should be restricted to poultry and small animals. Composting systems should be located at least 90 metres from a water course or a water body. Proper management of the composting system is required to ensure optimum conditions are maintained for decomposition. It is a self-heating, substrate-dense, managed microbial system and one solid phase biological treatment technology which are suitable to treatment of large amount of contaminated solid materials. It is a biological process where fresh organic wastes are allowed to be decomposed into humus like substance. The process is conducted by a complete automatic system which consists of several steps: dumping of refuse into a container, metallic particles removed by magnetic separator or mechanically, and then material is transferred to wet condition to a rotatory cylinder, analogous to a rotatory drier. The cylinder rotates slowly on large tyres and the wastes move from one end to the other. They are thoroughly mixed and pulverized by abrasion. Air is introduced at low pressure throughout the length of the cylinder. The hazardous compound reported to disappear through composting include aliphatic and aromatic hydrocarbons and certain halogenated compound. Composting can be done in- open system i.e. land treatment and closed system. The open land system is inexpensive treatment method but the temperature fluctuates from summer to winter. Therefore, rate of biodegradation of waste material declines. Secondly, land treatment system may become oxygen limited, depending on amount of substrates, depth of waste application etc. However efficiency of open treatment system can be increased by passing air. This approach is referred to as engineered soil piles and forced aeration treatment. Closed treatment system is preferred over the open land treatment system because controlled air is supplied to maintain the microbial activity. As a result of microbial growth and volatilization of hazardous compounds, increase internal temperature gradually. Therefore, use of blower for air circulation and exhaust for removal of toxic volatile are set up in closed treatment system. Ventilators supply O_2 and remove heat through evaporation of water. The main products of the biogas plants are fuel gas and organic manure (Figure 4). Biogas is a flammable gas. Composition of biogas is methane, carbon dioxide, hydrogen, nitrogen and hydrogen sulphide.

In several parts of India, compost plants are in operation for example, in Ahmedabad, Kolkata, Mumbai, Chennai, Delhi, Pune and Hyderabad. Compost has been used by Indian Agricultural Research Institute (IARI) to produce blue green algae- coated granulated compost.

Vermicomposting

Vermiculture or use of earthworm in biotechnology, where the earthworm feed on and degrade a variety of organic waste, eliminate toxic elements and convert the waste into vermicompost which is high- grade, nutrient- rich compost and a very significant bio fertilizer and soil conditioners. Vermicomposting enhances soil productivity and increases crop yield. Over 3000 species of earthworm have been identified from different parts of the world out of which 385 species have been found in India. The useful species found in India are *Lampito mauritii, Dichogaster boloui, Drawida willsi I etc.* The most important effect of earthworms in agro-ecosystems is the increase in nutrient cycling, particularly nitrogen. Lorimor et al. (2001) concluded that, in comparison with conventional composting system (as commonly used

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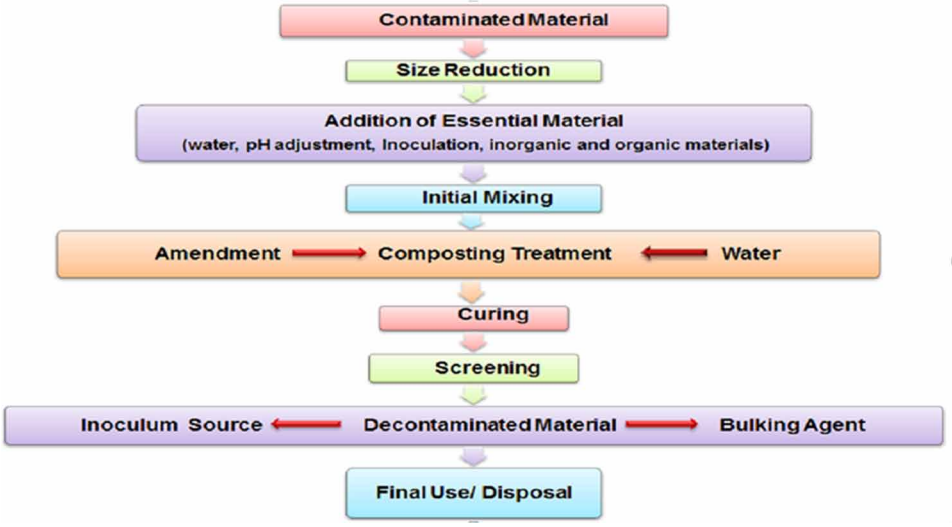
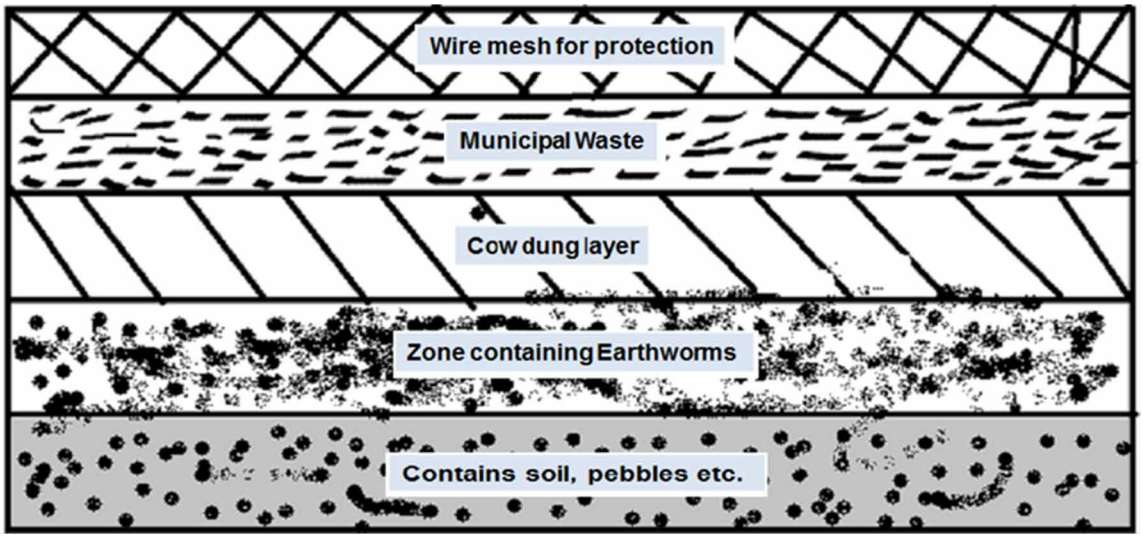
Figure 5. Flowchart of composting treatment sequence
Hogan,1998.



in India to manage crop residues and other related wastes), the vermicomposting often results in mass reduction, in shorter time for processing, and produce more humus with reduced phytotoxicity in ready material, i.e., vermicompost (Figure 5).

The crop residues amended with cattle dung in different ratios in order to produce three feed mixtures. The mixed substrate material served as bedding as well as feed for the earthworms. Earthworms alter the chemical properties of the substrates and indirectly promote microbial propagation and colonization, resulting in higher mineralization rates in vermicomposting beds than general composting (Suthar, 2008). It was concluded that the vermicomposting process accelerates the mineralization rate and subsequently

Figure 6. General model of vermicomposting pit for treatment of municipal waste



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enriches the end product with more available forms of plant nutrients. Earthworms keep on turning the material through different layers and decompose the organic material. It takes about 45 days to make vermicompost, which is a black granular material.

Biopiling

It is a hybrid form of composting and land farming. Bio pile treatment is also known as bio cells/ bio heaps/ bio mounds/ compost piles which are used to reduce the concentration of petroleum hydrocarbon constituents in soil through the use of biodegradation. This technology involves heaping the contaminants soil into piles and stimulates the aerobic microbial activity within soil through aeration and addition of mineral nutrients and moisture. Soil bio piles are a process where piles of soil are placed over top of a bug vacuum pump. The vacuum pump pulls air through the pile of soil to allow oxygen to get though the soil to the microorganisms. Contaminants turn into gas forms is easily recovered. The basic bio pile system includes a treatment bed, an aeration system, an irrigation/nutrient system and a leach ate collection system. For proper treatment, there should be control of moisture, heat, nutrients, oxygen, and pH. The irrigation system is buried under the soil and provides air high temperature. It is mainly used for the removal of gasoline, oil, petroleum etc. The rate removal of these substances is varied from one site to another site. Bio pile treatment is a full-scale technology in which excavated soils are mixed with soil amendments, placed on a treatment area, and bio remediated using forced aeration. The contaminants are reduced to carbon dioxide and water. Soil piles can be up to 20 feet high and may be covered with plastic to control runoff, evaporation and volatilization, and to promote solar heating. If volatile organic compounds (VOCs) in the soil volatilize into the air stream, the air leaving the soil may be treated before they are discharged into the atmosphere. Treatment time is typically 3 to 6 months.

Landfarming

Land farming is a bioremediation treatment process that is performed in the upper soil zone or in bio treatment cells. In this technique the waste is carefully mixed with surface soil on a suitable tract of land. Microbes that can metabolize the waste may be added, along with nutrients. The soil is spread out over a pad which has a system that is used to collect any of the residual liquids from the soil which may be toxic. The soil is mixed regularly to allow aeration of excavated soil. So that the micro-organisms present in the soil are more able to break down the contaminants in the soil. Contaminated soils, sediments, or sludge are incorporated into the soil surface and periodically turned over or tilled to aerate the mixture. In land forming make a sandwich layer of excavated soil between a clean soil and a clay and concrete. Firstly, the clean soil at bottom and uppermost layers should be concrete layer. After this allow it for natural degradation. Proper maintenance of oxygen, nutrition and moisture and pH should also require with near the pH 7 by using lime. Land forming is useful mainly for pesticides. Biological treatment of certain organic wastes, such as those from the petroleum industry, is also an option (Figure 6).

BIOREMEDIATION OF MUNICIPAL WASTE

According to Ministry of Urban Development (MoUD, 2000), Government of India 1 lakh MT of Municipal Solid Waste was generated daily in the country (Figure 7, Table 2). During the year 2004-05,

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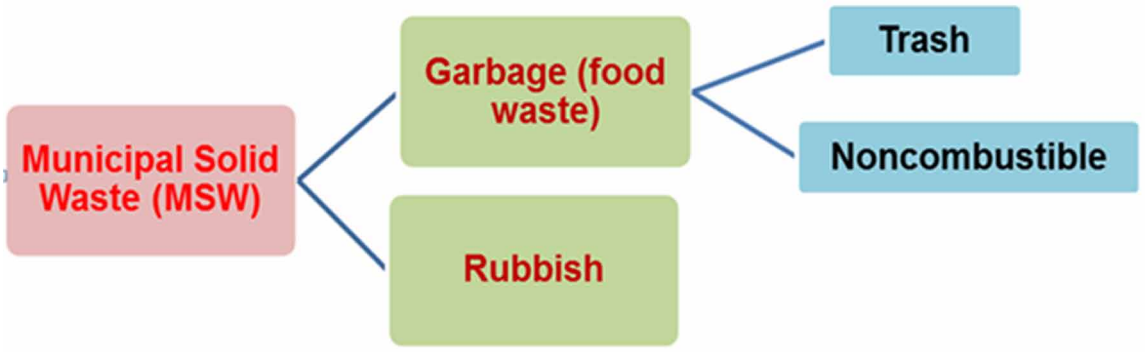
Figure 7. On the basis of nature, different types of municipal solid waste



Central Pollution Control Board (CPCB) through National Environmental Engineering Research Institute (NEERI), Nagpur, A survey conducted in 59 cities and estimated that 39,031 Tons per day MSW generated in these cities. The survey conducted by the central institute of Plastics Engineering and technology (CIPET) at the instance of CPCB has reported generation of 50,592 tonnes of MSW per day in the year 2010-11 in same 59 cities (Keisham and Paul, 2015). Annually, Asia alone generates 4.4 billion tonnes of solid wastes and MSW comprise 790 million tonnes (MT) of which about 48 (6%) MT is generated in India (Yoshizawa, Tanaka, Shekdar, 2004). Despite the best efforts to reduce, reuse and recycle, there will always be residual waste requiring disposal. The alternative treatment and disposal technologies are:

1. Composting,
2. Anaerobic digestion,
3. Pelletisation / Refuse Derived Fuel (RDF),
4. Landfills - Sanitary Landfill / Bioreactor landfill / Secured landfill (for inert waste),
5. Incineration include gasification and pyrolysis.

Among the various treatment and disposal processes as mentioned above, MoEF (Ministry of Environment and Forest) has notified composting (windrow composting, vermicomposting), anaerobic digestion, incineration, pelletization and landfill technologies and has given relevant standards for compost quality, leachate disposal, incineration operations and emissions and landfill specifications.

Bioremediation process is a natural process so MSW management include composting, anaerobic digestion, and landfill and palletisation process. These all the techniques are explained in above part as bioremediation of agricultural wastes excluding palletisation and incineration but these both the process are chemical based process not natural and bioremediation process is a natural phenomenon.

BIOREMEDIATION OF INDUSTRIAL WASTE

The degradation and bioremediation of industrial wastes are a challenging task because there is no reliable technology till date which is effective in complete removal/reduction of these pollutants. Ultimately, diverse groups of microorganism that are already present in the nature may provide solution for the degradation and bioremediation of toxic industrial wastes. Microorganisms that are being used

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Table 2. Physical characteristics of municipal solid waste in Indian cities

Population Range (in Millions)	No. of Cities Surveyed	Paper	Rubber, Leather, Synthetics	Glass	Metal	Total Compostable Matter	Inert Material
0.1- 0.5	12	2.91	0.78	0.56	0.33	44.57	43.59
0.5- 1.0	15	2.95	0.73	0.56	0.32	40.04	48.38
1.0-2.0	09	4.71	0.71	0.48	0.49	38.95	44.73
2.0-5.0	03	3.78	0.48	0.48	0.59	56.67	40.07
>5.0	04	6.43	0.28	0.94	0.80	30.84	53.90

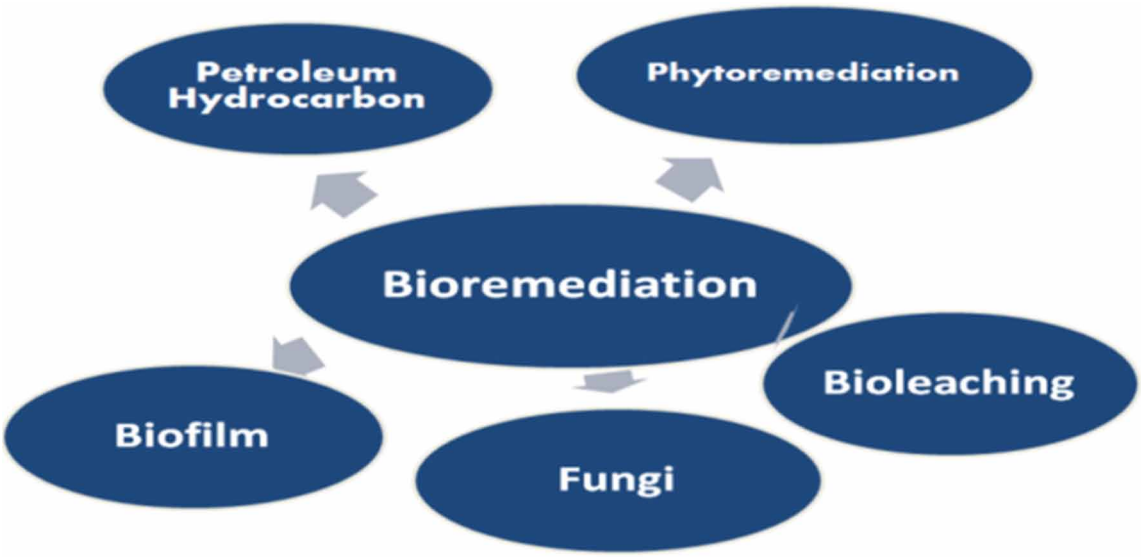
Source: Sharholy et al., 2008.

for the bioremediation and transformation of pollutants from long times (Okpokwasili, 2007). For the management of industrial waste, bioremediation processes are classified according to composition of waste to be managed.

Bioremediation of Hydrocarbons or Toxic Organic Pollutant

Petroleum and its products are hydrocarbons. Oil constitutes a variety of hydrocarbons like xylenes, naphthalene, octane's, camphor etc. The pollutants can be degraded by a consortium of microorganisms, e.g. *Corynebacterium, Pseudomoas, Mycobacterium, Arthrobacter,* and *Nocardia*. Genetically engineered bacterial strains are used to enhance bioremediation.In 1990, the USA government allowed him to use this superbug for cleaning up of an oil spill in water of State of Texas (Figure 8). It was produced on a large scale in laboratory, mixed with straw and dried.

Figure 8. Process involved in bioremediation of hydrocarbons



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Bioremediation of Pesticides

Effluent discharge from pesticide manufacturing or formulating industry and agricultural runoff are major sources of pesticides in the environment and the wastewater discharged from these industries cause a high hazard for waterbodies (Rajeswari and Kanmani, 2009). Excess fertilizer, herbicides and pesticides when washed by rain into rivers causes serious danger to life. However, improper handling and disposal may cause pollution. The immediate consequence is drop in dissolved oxygen and the Biological Oxygen Demand (BOD). Water pollution is also caused by hot water discharge from cooling engines in the industries. This increases water temperature and lowers the metabolic rate of organisms. The constituents of gases that are produced in wastewater are carbon dioxide (CO_2), carbon monoxide (CO), nitrogen dioxide (NO_2) and sulphur dioxide (SO_2). There are numerous example of bioaccumulation of different organosynthetic insecticides and pesticides due to their uncontrolled use in the past decades. Bioremediation of pesticides from wastewater can be enhanced by the use of lignolytic enzymes such as Laccases. Removal of phenolic or xenobiotic pollutants from wastewater using Laccase can be occured in several ways: 1) using purified immobilised enzyme; 2) using purified free enzyme; 3) using enzyme obtained directly from culture broths; and 4) bioremediation in reactors with immobilized or free cells (Majeau, Satinder and Tyagi, 2010). Advanced oxidation processes (AOPs) in which hydroxyl radical ($OH-$) is produced by different reactions like chemical, photochemical, photocatalytic or electrochemical reactions, are very effective for treatment of wastewaters containing highly recalcitrant organic pollutants (Gogate and Pandit, 2004). Rajeswari and Kanmani (2009) used TiO_2 for photocatalytic oxidation of pesticide wastewater. The degradation revealed 99% removal of active ingredient of pesticide and 76% mineralization. Complete mineralization could be achieved by further increasing the reaction time or by adding some additives, which would speed up reaction.

Microbial Degradation of Pesticides

It has been observed that a significant portion of pesticides residues in the environment is degraded in the soil and aquatic environment by microbes. The majority of pesticides can be degraded by fungi and bacteria. The transportation of parent pesticide molecules to less complex products is often achieved by concerted efforts of microbial communities. It is estimated that 1 g of soil contains more than 5000–7000 different species of bacteria and more than ten thousand fungal colonies (Dindal 1990; Melling 1993). The use of microbial metabolic potential for eliminating soil pollutants offers a safe and inexpensive substitute to other commonly used physico-chemical strategies (Vidali, 2001). Indigenous microorganisms (natural attenuation) can be used for detoxification of contaminants in the environment (Siddique, Okeke, Arshad and Frankenberger 2003; Kumar and Philip 2006). Soil conditions include warm temperatures, favourable pH levels, adequate soil moisture, aeration (oxygen) and fertility favours microbial growth. The amount of adsorption also influences microbial degradation. The soil fungi for e.g., *Fusarium, Penicillium* are now known to degrade pesticides with greater efficacy (Twigg and Socha, 2001). The branching, filamentous mode of fungus allows more efficient colonization and exploration of contaminated soil (Aust, Swaner and Stahl, 2004). White-rot fungi are filamentous organisms offer advantages over bacteria able to oxidise many compounds (Pointing, 2001). In addition, they are robust organisms and are generally more tolerant to high concentrations of chemical pollutants than bacteria (Evans and Hedger, 2001) and are a powerful prospective tool in soil bioremediation and some species have already been patented.

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Phytoremediation of Pesticides

Phytoremediation technology comprises growing plants on contaminated sites so that polluting components percolate through the radical system of the plants and accumulate in various parts (roots, stems, leaves, etc.). There are other constraints to the use of plants alone in remediation; plant growth is dependent on a number of environmental factors like nutrients and water availability, soil texture and pH, etc. The maximum benefits of phytoremediation may therefore, be achieved in long-term applications, or when used in conjunction with other immediate remedial actions. Excluding these limitations, plants are identified to absorb a wide range of air-borne chemicals through the foliage surface. The in situ (on-site treatment) phytoremediation has widely used in Europe and the United States (Meharg and Cairney, 2000; Gaur and Adholeya 2004). This technology is beneficial when the roots of the plant are in contact with the pollutants. It could also be necessary to proceed through several cycles of culture and harvest to restore a site completely. And harvested plants must be disposed carefully (Mulligan, Yong and Gibbs, 2001).

Some Other Bioremediation Processes for Degradation of Pesticides

Bio-Stimulation

This refers to addition of specialized nutrients and suitable physiological conditions for the growth of the indigenous microbial populations. This promotes increased metabolic activity, which then degrades the contaminants (Trindade, Sobral, Rizzo, Leite and Soriano, 2005). Bio stimulation has been used to remove pesticides contamination in the environment. In this process, the activity of the indigenous microorganisms is stimulated by adding the organic and/or inorganic additives such as N or P, etc. The modifications added would be used by the indigenous microorganisms for cell growth to increase cell number as well as their activities to degrade the pesticides. In addition, the amendments could be necessary as the enzyme-inducers and/or the co-metabolic substrates in the pesticide degradation pathways (Robles-Gonzalez, Fava, Poggi- Varaldo, 2008).

Bio-Augmentations

Bio-augmentation is the introduction of exogenous microorganisms with specific catabolic abilities into the contaminated environment or into a bioreactor to initiate the bioremediation process. This can be an in situ or ex situ treatment process in which naturally occurring microbes are added to contaminated sites to eliminate toxic contaminants (Head and Oleszkiewicz, 2004; Perelo, 2010). The technique is reported to be an effective bioremediation approach for improving pesticide degradation in contaminated soils and water that lack indigenous microbial activity (Dams et al. 2007; Plangklang and Reungsang, 2010). It has been employed to degrade a wide range of chemical contaminants such as ammonia, hydrogen sulphide, insecticides, petroleum compounds, and a growing number of toxic organic chemicals present in soil and water (Hwang and Cutright, 2002; Jianlong, Xiangchun, Libo, Yi and Hegemann, 2002; Quan, Shi, Liu, Wang and Qian,2004).

Both bio-stimulation and bio-augmentation possess the ultimate goal of decontamination through biotransformation. The toxic substance is generally converted into other nontoxic forms (transformed) by a chemical reaction using microbes, aerobically or anaerobically. Anaerobic biotransformation is essentially used for degradation of organic compounds such as chlorinated hydrocarbons, polychlori-

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nated phenols, and nitro aromatics which are recalcitrant to aerobic treatment processes (Ferguson and Pietari 2000; Marschner, Yang, Lieberei and Crowley, 2001; Somsamak, Cowan and Haggblom, 2001; Bhushan et al. 2003).

Bioremediation of Metal Contaminated Site

Accumulation of heavy metals by emissions from industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, spillage of petrochemicals, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, land application of fertilizers, animal manures, and atmospheric deposition contaminated soil extremely and rapidly. Soils are the major sink for heavy metals released into the environment and also their total concentration in soils persists for a long time after their introduction. To overcome the problem of soil or land pollution and restore the fertility of the soil, it is necessary to remediate it. Bacteria, algae, fungi, actinomycetes and higher plants accumulate high amount of heavy metals in their cells and bio remediate the contaminate site.

Algae

The species of *Chlorella*, *Anabaena inaequalis*, *Westiellopsisprolifica, Stigeocloniumtenue, Synechococcus sp.* tolerate heavy metals. However, several species of *Chlorella, Anabaena,* marine algae have been used for the removal of heavy metals. But the operational condition limits the practical application of these organisms. The naturally occurring cells showed higher efficiency for Cd^{++} and Ni^{++} as compared to laboratory cells.

Fungi

Fungi also are capable of accumulating heavy metals in their cells. However, several mechanisms operate in them for removal of heavy metals from the solution; a few of these have been discussed below:

Metabolism-Independent Accumulation

The positively charged ions in the solution are attracted to negatively charged ligands in cell materials. Biosorption of metal ion occurs on microbial cell surface but composition of biomass and other factors affect biosorption. For example, in Rhizopusarrhizus adsorption depends on ionic radius of Li^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Hg^{2+} and Pb^{2+}. However, binding of Hg^{2+}, Ag^{2+}, Cd^{2+}, Al^{3+}, Ni^{2+}, Cu^{2+} and Pb^{2+}strongly depends on concentration of yeast cells.

Metabolism-Dependent Accumulation

In fungi and yeast, heavy metal ions are transported into the cells through cell membrane. However, as a result of metabolic processes ions are precipitated around the cells, and synthesized intracellularly as metal-binding proteins. Energy-dependent uptake of Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, $Zn^{2+}$by fungi has been demonstrated. Moreover, intracellular uptake is influenced by certain external factors such as pH, anions, cations and organic materials, growth phase, etc. Microbes like algae, bacteria and fungi as well as higher plants have capabilities to uptake these pollutants. After uptake, these either accumulates or is assimilated by them. Accumulated heavy metals are recovered by recycling or disposal.

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The following bioremediation processes are used for metal contaminated sites:

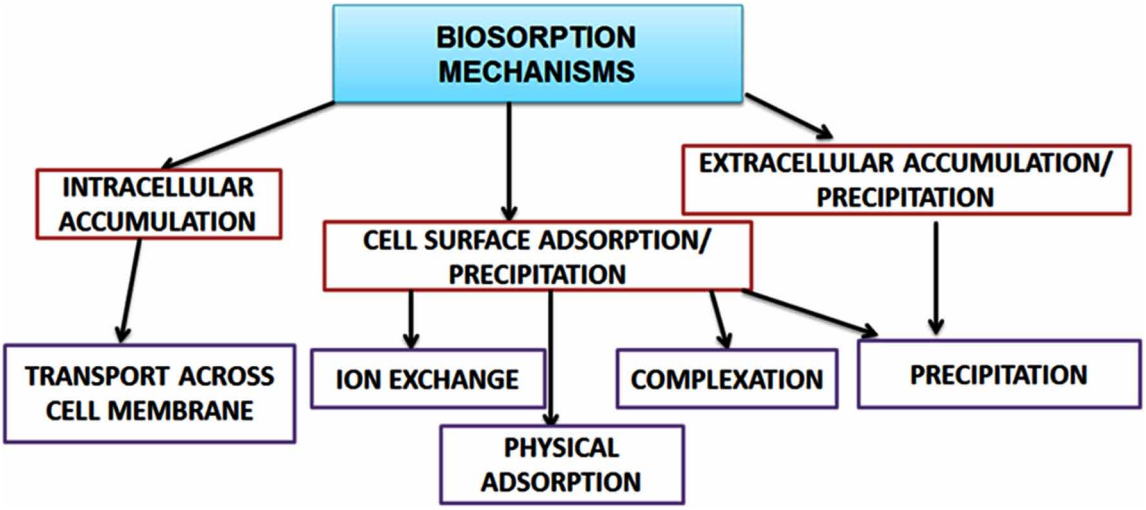
- Biosorption,
- Bioprecipitation/ Biomineralization,
- Biomining:
  - Biooxidation,
  - Bioleaching.

Biosorption

It is the physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind the contaminant on its cellular structure. Microorganisms responsible for this process are called biosorbents. It involves the microbial immobilization of free metal ions and their changed species and is also used for the remediation of mine waste soil. Biosorbents which are used for biosorption of metals from solutions could be classified into three broad categories i.e. exo-polysaccharides, living cultures and non- living biomass and preparations. Living and non- living microbial both cells are active in metal sorption. Non- living microbial biomass is usually preferable for biosorption technology as those precludes the necessity of adding nutrients required for microbial development, maintaining sterility of the process and adjusting parameters to values favourable for microbial growth. The biosorption process involves a solid phase and liquid phase containing a dissolved species to be sorbed. Due to the higher affinity of the absorbent for the absorbate species, the latter is attracted and bound there by different mechanisms.

The process continues till equilibrium is established between the amount of solid- bound absorbate species and its portion remaining in the solution. The degree of absorbent affinity for the absorbate determines its distribution between the solid and liquid phases. The metallic species could be deposited in the solid biosorbent through various sorption processes such as transport across membrane, physical adsorption, precipitation and chemisorption by ion exchange, coordination, chelation, and complexion.

Figure 9. Processes of bio sorption mechanism



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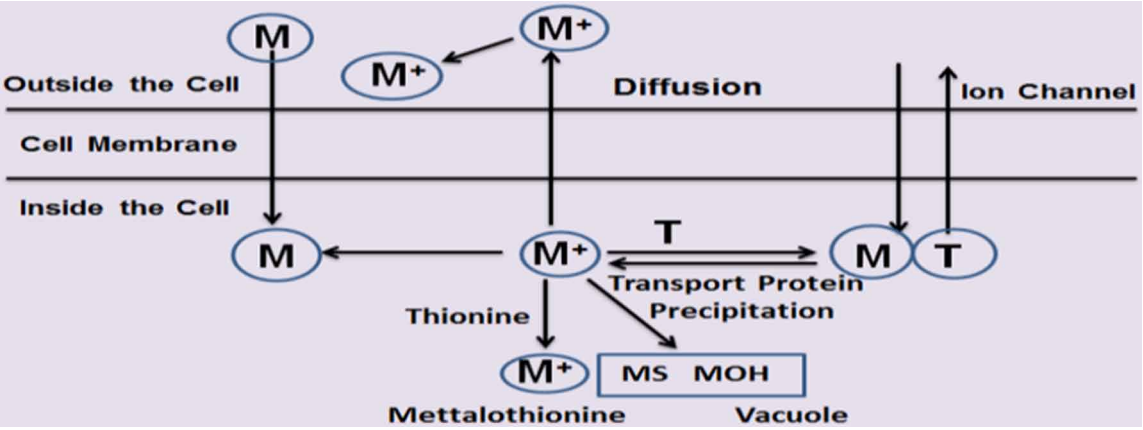
1. **Transport Across Membrane:** Heavy metal transport across microbial cell membranes may be mediated by the same mechanism used to convey metabolically important ions such potassium, magnesium and sodium. The metal transport system may become difficult by the presence of heavy metals ions of the same charge and ionic radius associated with metabolic activity.
2. **Physical Adsorption:** it includes the Vander Waal's forces, Electrostatic interactions between the metal ions in the solution and cell wall of microbial cells (Figure 9 & 10).
3. **Ion Exchange:** it is reversible chemical reaction wherein an ion in the solution is exchanged for a similarly charged ion attached to an immobile solid particles. Cell walls of microorganisms contain polysaccharides and bivalent metal ions exchange with the counter ions of polysaccharides.
4. **Complexion and Precipitation:** The metal removal from solution may also take place by complex formation on the cell surface after the interaction between the metal and the active groups. Complexion found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and mercury accumulation by *Pseudomonas suringae*. Fungi produce several extracellular products which can complex or precipitate heavy metals. For example, many fungi and yeast release high affinity Fe-binding compounds that chelate iron. It is called siderophores. The Fe^{3+}chelates which are formed outside the cell wall are taken up into the cell. In *Saccharomyces cerevisiae* removal of metals is done by their precipitation as sulphides e.g. Cu^{2+} is precipitated as CuS (Beveridges, 1989).

Bioprecipitation

It is the concept of rainmaking bacteria in which metal contaminants get precipitated by microorganisms in liquid medium. It is also called biomineralization. It removes metals by forming insoluble precipitates that either move into deeper layer osf soil or remain in soil without imposing any harmful effect on crops or vegetation.

Figure 10. Mechanism of bio sorption across the cell membrane of microorganisms



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Biomining

It is the extraction of desired minerals from their ores through the use of living microorganisms. It is used to aid the recovery of metal form low grade ores. It is economically sound hydrometallurgical process with lesser environmental problems than conventional commercial application. It has tremendous practical application. It consists of two processes:

Bio Oxidation

It is the process which is applied to enhance the extraction of gold and silver. An oxidation process caused by microbes where the valuable metal remains (but becomes enriched) in the solid phase. Bio-oxidation leaves the metal values in the solid phase and the solution may be discarded. This contrasts with bioleaching where the valuable metal is solubilized. (Both bioleaching and biooxidation are oxidation processes. If the valuable metal in the ore is hosted by, but not bound to, a surrounding undesired mineral matrix which is blocking the valuable metal from further chemical treatment the matrix can be degraded by selective dissolution of the undesired mineral matrix. Here the microbes causing the selective dissolution may enrich the valuable metal and facilitate metal extraction by selective dissolution of the undesired mineral matrix.

Bioleaching

Bioleaching is the process by which metals are dissolved from ore bearing rocks using microorganisms. For the last 10 centuries, microorganisms have assisted in the recovery of copper dissolved in drainage from water. Microbial technology renders helps in case of recovery of ores which cannot be economically processed with chemical methods, because they contain low grade metals. The low grade ores are discarded in waste heaps which enter in the environment. The low grade ores contain significant amount of nickel, lead, and zinc ores which could be processed by microbial leaching. Bioleaching of uranium and copper has been widely commercialized. But large scale leaching process may cause environmental problems when dump is not managed properly. These results in seepage of leach fluids containing large quantity of metals and low pH into nearby natural water supplies and ground water. Thus, bio mining is economically sound hydrometallurgical process with lesser environmental problem than conventional commercial application. However, it is an inter-disciplinary field involving metallurgy, chemical engineering, microbiology and molecular biology. It has tremendous practical application. In a country like India bio mining has great national significance where there is vast unexploited mineral potential (Mogal and Desai, 1992). The most commonly used microorganisms for bioleaching are *Thiobacillus thiooxidans* and *T.ferrooxidans*. The other microorganisms may also be used in bioleaching, *Bacillus licheniformis, B. luteus, B. megaterium, B. polymyxa, Leptospirillum ferrooxidans, Pseudomonas fluorescens, Sulfolobusacido caldarius, Thermothrix thioparus, Thiobacillus thermophilica, etc*.

Bioremediation of Dyes

Synthetic dyes are widely used in a number of industries, such as textile dyeing or printing, paper printing, cosmetics, pharmaceuticals and leather industries. These industries uses large amounts of energy and water, and they release a substantial amount of waste water with many contaminants. With the increased

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demand for textile products, the waste waters generated from this industry have also increased proportionally and polluting the receiving water worldwide. In India, mill discharges is an average about 1.5 million litres of effluent per day, which causes chronic and acute toxicity (Sandhya et al., 2005 and Arami et al., 2006). The organic dye stuffs, chrome dyes and other chemicals during various operations and produce a large quantity of solid and liquid waste containing hexavalent chromium [chromium (VI)], salts of zinc, sulphates, copper, sodium and potassium etc., which causes severe toxicity to aquatic organisms. There is limited study on microbial degradation of azo and reactive dyes. Maximum number of dyes undergoes degradation through reduction. Kulla (1981) discussed azo- reductase of Pseudomonas strains in the chemostat culture. These enzyme catalyses azo-linkage of the dye. During degradation process of azo, NAD(P) acts as electron donor. Srivastava et al. (1995) observed degradation of black liquor pulp mill effluents by the strains of *Pseudomonas putida.* Some anaerobic bacteria, Streptomyces and fungi (e.g. *Phaenerochaete chrysosporium*) have been characterized for decoloration of chromogenic dyes. The enzymes involved in dye degradation are lignases (lignin peroxidase), Mn (II) dependent peroxidase and glyoxal oxidase. These enzymes are well associated with lignin degrading system.

Bioremediation of Xenobiotic Compounds

Man-made chemicals present in the nature at high concentrations polluting the environment are known as Xenobiotic compounds. Some microbes are capable in breaking down of xenobiotic compounds to some extent. But most of the xenobiotic compounds are non-degradable in nature and remain in the environment for many years leading to bioaccumulation or bio-magnification. Such compounds are known to be recalcitrant in nature. The recalcitrant xenobiotic compounds can be divided into different groups depending on their chemical composition like halocarbons, synthetic polymers, alkyl benzyl sulphonates, oil mixture etc. These compounds are highly toxic in nature and can affect survival of lower as well as higher eukaryotes. It also poses health hazards to humans like various skin problems, reproductively and even known as a trigger for causing cancer. They also find a way into the food chains.

For breaking down xenobiotics compounds, the enzymes act on certain groups present in the compound. For e.g. in the halocarbons, the halogen group is targeted. Enzymes like oxygenases play a major role. The bonds like ester-, amide-, or ether bonds present in the compounds are first attacked leading to breaking down of compounds. In some cases the aliphatic chains and in aromatic compounds the aromatic components may be targeted. Often it is seen that the xenobiotic do not act as a source of energy to microbes and as a result they are not degraded. The presence of a suitable substrate induces its breakdown. This substrate is known as co–metabolite and the process of degradation are known as co-metabolism. In another process, the xenobiotic serve as substrates and are acted upon to release energy. This is called gratuitous metabolism. Certain microbes on continuous exposure to xenobiotic develop the ability to degrade the same as a result of mutations. Certain mutations also resulted in developing new enzymatic pathway for xenobiotic degradation. Use of mixed population of microbes is usually recommended as it has been seen to yield faster results as the two different microbes attack different parts through different mechanisms resulting in effective break down. It also creates a condition of co metabolism. The modification of certain genes of microbes to break down xenobiotic is also recommended and is seen to produce high level of accuracy.

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CONCLUSION AND FUTURE PROSPECTS OF BIOREMEDIATION

The compounds or chemical which are produced from different sources are needed to be reused or recycle if possible so that their direct impact can be reduced on environment. It is dynamic to increase understanding of microbial communities and their activities to the environment and pollutants, expanding the knowledge of the genetics of the microbes to increase capabilities to degrade pollutants, conducting field studies of new bioremediation techniques which are cost effective, and dedicating sites which are set aside for long term research purpose. These opportunities offer potential for significant advances. *Trichoderma viridie, Beauveria bassiana, Verticillium lecanii, Metarhizium anisopliae* are tested for remediation of waste materials like temple waste, vegetable waste, fruit waste and saw dust waste. Despite its short-comings, its importance to the world is unquestionable considering present day environmental hazards. There is no doubt that bioremediation is in the process of paving a way to greener pastures and national safety in general. Bioremediation technology has also some limitations like several microorganisms cannot break toxic metals into harmless metabolites and have inhibitory effects on microbial activity. Modification in the outer membrane proteins of bacteria with potential bioremediation properties for improving metal binding abilities is to enhance their capacity for biotransformation of toxic metals. Future studies should focus on the factors involved in improved by using genetically engineered microorganisms (GEM) in situ bioremediation strategies and also the applicability and adaptability of these GEMs in all the possible adverse conditions and multiple heavy metal polluted conditions. Bioremediation and phytoremediation can be good treatment strategies for PHC pollutants but more research information and techniques is required to prepare methods for treatment.

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KEY TERMS AND DEFINITIONS

Agricultural Waste: Waste in the form of the crop residues in the farm, manure from livestock operations, including dairy and piggery effluent, and poultry litter.

Anaerobic Digestion: The conversion of biodegradable waste matter into compost in the absence of oxygen.

Biogas: Biogas is the gaseous emissions from anaerobic degradation of organic matter (from plants or animals) by a consortium of bacteria. Biogas is principally a mixture of methane (CH_4) and carbon dioxide (CO_2) along with other trace gases.

Bioremediation: Bioremediation is a waste management technique that involves the microorganisms to remove or neutralize pollutants from a contaminated site.

Industrial Waste: Industrial waste is the waste produced by industrial activity which includes any material that is rendered useless during a manufacturing process such as that of factories, industries, mills, and mining operations.

Municipal Waste: Commonly known as trash or garbage—consists of everyday items we use and then throw away, such as product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances, paint, and batteries. This comes from our homes, schools, hospitals, and businesses.

Pesticides: A pesticide is any substance or mixture of substances used to destroy, suppress or alter the life cycle of any pest. Pesticides include bactericides, baits, fungicides, herbicides, insecticides, lures, rodenticides and repellents.

Vermicomposting: The processing of organic wastes through earthworms. It is a natural, odourless, aerobic process, much different from traditional composting.

Xenobiotic Compounds: Man-made chemicals present in the nature at high concentrations polluting the environment are known as Xenobiotic compounds. These compounds are not commonly produced by nature.

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Chapter 44
Polymer Consumption, Environmental Concerns, Possible Disposal Options, and Recycling for Water Treatment

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ABSTRACT

The increasing awareness of the environment has raised so much concerns in the way we live and the manner to which we dispose our waste. The rapid growth in polymer production has resulted in increasing concerns about the consumption of nonrenewable resources and the environmental impacts associated with its production and disposal. Polymer waste is one of the major components in municipal solid waste and is increasingly becoming a huge burden in industrialized nations. The rise in the use of plastic, coupled with increasing concerns about its disposal, has led to a renewed interest in its recycling and recovery. The technologies involved in the recovery and recycling of polymers are rapidly growing, however, there is no specific pattern of treating polymer waste. The technology depends on the type of material used in the production and consumption pattern. This chapter, therefore, discusses the patterns of polymer consumption, the environmental concerns, and different modes of recycling polymer waste.

1. INTRODUCTION

Plastics are lightweight durable and inexpensive materials, which can be converted into a wide array of products that can be used in a wide range of applications. The production of plastics has dramatically increased in the last 60 years due to their wide applications and ease of molding (Jefferson *e*t *a*l., 2009). The amount of polymers used in the industry far exceeds that of metals and is rapidly growing due the

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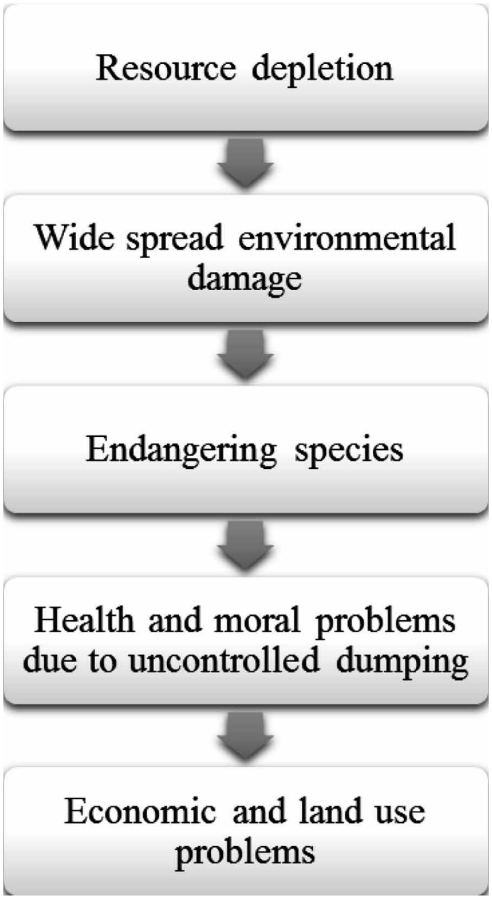
Figure 1. The impacts of polymer production



industrialization of some developing nations (2003). Polymers are inevitable products in our lives today; they are widely used in place of alternate materials because they are inexpensive and they possess better environmental disposal options due to their light weight, minimal pressure on agricultural resources, and superior insulation abilities. Despite all the advantages, the current level of their usage and disposal pose serious danger to the environment and the health of the populace. In addition, around 4 percent of annual oil and gas production (non-renewable resource) is used as the parent material (precursor for synthesis) and the sole provider of energy for plastic production (British Plastics Federation 2008). Secondly, most of the plastic produced is directed for the production of disposable items that always end up in the landfills and in delicate habitats within short period of time. The impacts of polymer production have been sum up and depicted in Figure 1.

There are so many approaches in use to reduce the impacts of polymer disposal which include: source reduction, composting, degradation, incineration, recycling and landfilling (Richard 1992). Source reduction aim at reducing the volume or toxicity of waste generated and it is the most preferred management option, composting utilized biochemical means with the aid of microorganisms to reduce the volume of plastic waste generated, degradation uses factors such as heat, chemical or light to alter the properties of the polymers and lower its molecular weight for efficient recycling. Incineration which converts combustible waste to inert residue is a viable option because energy is generated but combus-

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tion of plastics generates significant amount of pollution. Incineration requires well-designed systems, adequate control and efficient maintenance. Disposal of plastics by landfilling is not a problem so long as space is available, however, most plastics are not biodegradable.

Recycling represents one of the most effective areas in polymer industry; it has significant advantages compared to other means of reducing polymer impacts because it reduces the consumption oil and gas, lowers emissions associated with polymer production, reduces the amount of waste generated and has ecological advantages, but its application is dependent upon the feasibility of elements of waste management i.e. handling, storage, processing, collection, sorting, and transport. Recycling of plastic materials has received rapid growth in the past few decades however, the quantities been recycled vary with locations according plastic type and application. Developments in the field of recycling are generating wide array of opportunities to people, legislators and government agencies and with proper investments, most plastic wastes been disposed to the landfills will be siphoned and directed for efficient recycling.

The recovery and recycling rate of plastics compared to other materials such as glass, paper, and metals is generally very slow. Plastic recycling even in developed nations with well-developed waste management systems in place is generally slow as compared to other materials because of the huge varieties of plastics, composites and additives used in their production. This complex nature of plastics confer added advantages when compared to other materials but it is generally problematic to recycling.

2. POLYMER CONSUMPTION

The major producers of plastics in the world are China (23.9%), Europe (20.4%), North America (20%) and the rest of Asia excluding China (15.8%) (PlasticsEurope 2013) In the Europe, (39.4%) of the whole plastic production is directed for packaging materials, followed by construction (20.3%), automotive accounts for 8.2%, electrical and electronics accounts for 5.5% the plastic demand, agricultural applications account for 4.2% while other applications such as: medical, furniture, household and consumer products and appliances accounts for 22.4% . The world plastic production from 1950-2012 is shown in Figure 2.

There are different types of plastics and they are subdivided into thermoplasts and thermosets. Thermosets are liquids or malleable products that undergo curing with the aid of heat by irradiation or irreversible chemical reaction to produce a hardened thermoset resin that cannot be reformed or tainted. Once a thermosets solidifies they stay solid which makes it difficult to be recycled. Thermosets can only be recycled through a chemical process. Types of thermosets include: epoxy resin, polyester resin, and urea and melamine formaldehydes. Thermoplasts polymer on the other hand do not undergo chemical changes when heated and can be molded again upon cooling. The classes of thermoplastic include: nylon (polyamide), Acrylic (polymethyl methacrylate), Teflon, polyurethane (PU) polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polyethene (PE) which is subdivided based on the distribution of polymers into: low density polyethene (LDPE), medium-density polyethylene (MDPE), high density polyethene (HDPE), ultra-high molecular weight polyethylene (UHMWPE) and cross-linked polyethylene. The types and classes of these polymers are given in Table 1 and their main applications in EU member states are depicted in Figure 2. The key plastic types used in the EU is depicted in Figure 2. The overall distribution and uses of plastics varies depending on specific conditions. This is evident as many countries have reduced the utilization of PVC in packaging however the same material when combined with PUR and PS serves as the main plastic used in building and construction. Polyolefin dominates the packaging industry.

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Figure 2. World Plastic Production 1950-2012 (including thermosets, thermoplastics, elastomers, polyurethanes, coatings and sealants, adhesives, and PP-fibers)

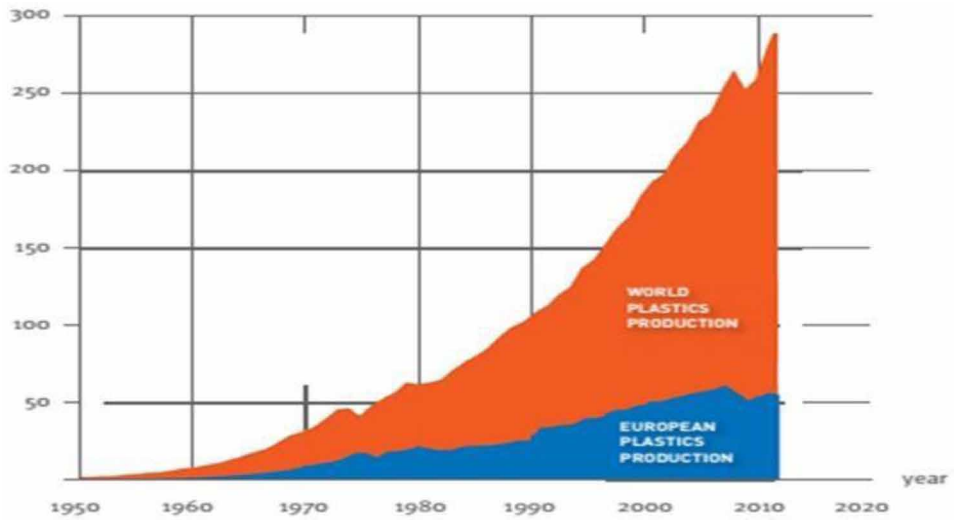
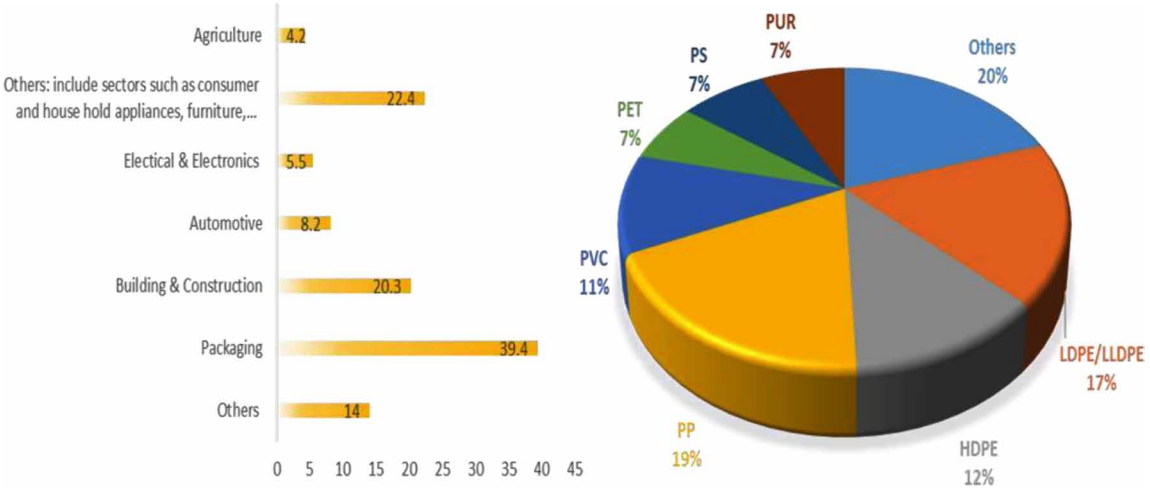


Figure 3: A) European plastic demand by segment 2012 and B) European plastic demand by resin type 2012



288 million metric tons of polymer was produced in the year 2012 for all types of polymers including thermoset plastics, thermoplastics, and adhesives and coatings. A 2.8% increase compared to 2011. This shows a growth rate of about 9%/annum. However in Europe, despite the growth in plastic consumption across the globe the production rate decreases by 3% from 2011 to 2012. Thermoplastic resins constitute around 2/3 of this production and their usage is growing at about 5%/annum globally (PlasticsEurope 2013).

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Table 1. The most common types of plastics used, their applications and the symbol which is used in their identification

Polymer Types	Examples of applications	Symbol
Polyethylene Terephthalate	Fizzy drink and water bottles. Salad trays.	
High Density Polyethylene	Milk bottles, bleach, cleaners and most shampoo bottles.	
Polyvinyl Chloride	Pipes, fittings, window and door frames (rigid PVC). Thermal insulation (PVC foam) and automotive parts.	
Low Density Polyethylene	Carrier bags, bin liners and packaging films.	
Polypropylene	Margarine tubs, microwaveable meal trays, also produced as fibers and filaments for carpets, wall coverings and vehicle upholstery.	
Polystyrene	Yoghurt pots, foam hamburger boxes and egg cartons, plastic cutlery, protective packaging for electronic goods and toys. Insulating material in the building and construction industry.	
Unallocated References	Any other plastics that do not fall into any of the above categories - for example polycarbonate which is often used in glazing for the aircraft industry	

The UK plastic industry contributes significantly to the economic strength and development of the geographical location. It accounts for 7% all the manufacturing activity in UK, a percentage much higher than pharmaceutical and automotive industries combined. In 2011, the industry's sales turnover was £19 billion and £6.7bn value of exports a 13% increase from 2010 was recorded. Approximately 8000 firms are engaged in the plastic industry in UK, more than 3000 of this firms are termed primary processors because they are engaged in the processing of plastics raw materials for goods production. 2.5 million tons of plastics raw materials are approximately produced annually in the UK. The distribution of polymer companies in UK is depicted in Figure and the plastic consumption in the UK by application is given in Figure 4.(BPF 2012)

It is estimated that the UK produces approximately 2·5 million tonnes of plastics raw materials annually. The companies known for manufacturing different forms of polymers and polymer products in UK are: DuPont, lyondellbasell, Sabic and Ineos. UK is among the top five plastic processors in the EU consuming approximately 4.8 million tonnes of materials. A lot of capital and personnel are required in plastic processing to satisfy the individual tasks due inert and assembly work. The number of people currently employed in the UK plastic industry is approximately 180,000.

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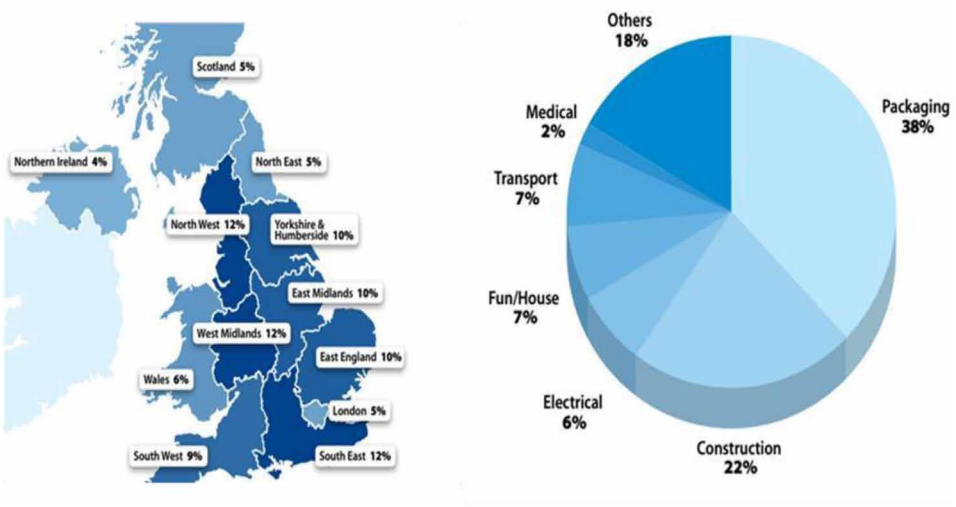
Figure 4. A) Location of polymer companies in UK and B) Plastic consumption in UK by application



3. LIFECYCLE ASSESSMENT (LCA)

Lifecycle assessment is an analytical tool developed by government for complete evaluation of environmental aspects in a particular process or system and it allows scientist to keep record of a product from the time the raw materials are harnessed to the manufacturing till its final disposal. Public opinion and environmental directives within the last two decades have played a cardinal role in the development of methods to evaluate the environmental impacts of an industrial process. It is believed that LCA is a tool that helps in the development of public policy and design decisions (Subramanian 2000). All aspects of environment are evaluated in a process through all stages of its life cycle. LCA has the ability of creating a tentative inventory elucidating all inputs and outputs including energy sources and environmental emissions of an industrial process. LCA helps in making decisions with regard to tradeoffs in a process and the level of capital to invest in a process. LCA of plastic production measures environmental impacts associated with materials manufacturing, to their packaging and distribution, their final use and disposal.

Life cycle assessment of plastics in Europe from converter demand to disposal and recovery showed that 25.2 Mtonne of plastics in 2012 ended up in the post-consumer waste streams of which 15.6 M tonne were recovered while 9.6 Mtonne were disposed of. Figure 5 gives an elucidation of the LCA of plastic in Europe.

3.1 Polymer Waste

The consumption and generation of plastic solid waste has increased remarkably over decades since industrial revolution. It was estimated that each individual in the world in 1990 produced an average of 250 kg of MSW generating in total 13 Mtons (Al-Salem *et al*., 2009). Plastic waste currently represents significant amount in MSW in 2012. 32 Mtons and 25.2 Mtons of plastics reached the post-consumer waste stream in America and Europe respectively. Environmental regulations and increasing awareness coupled with inadequate space and cost of disposal to the landfills are forcing for considerations of other environmentally and economically viable alternatives such as recycling and recovery to plastic disposal (Zia et al., 2007; Howard, 2002). Recycling has received much attention in the past few decades.

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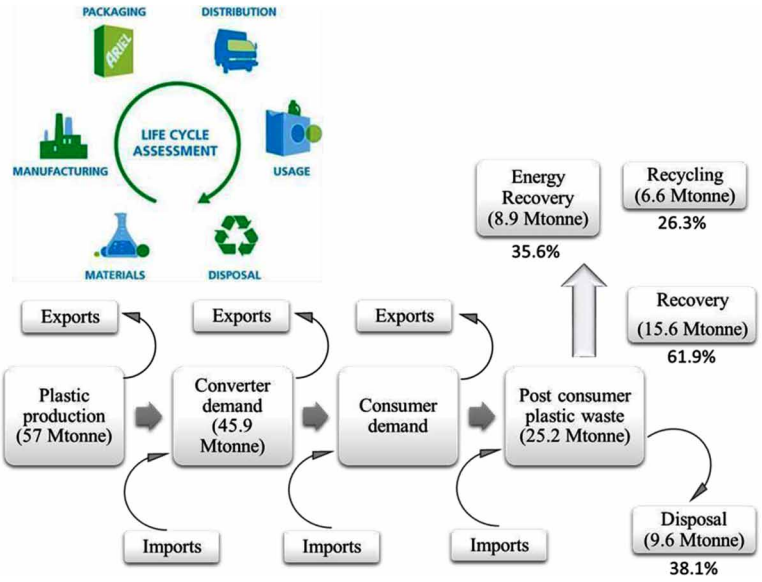
Figure 5. Life cycle assessment of plastic in Europe in 2012



Plastics make up 32 Mtons almost 13 percent of the total municipal solid waste (MSW) generated in America. Nearly 14 Mtons of plastics were used in packaging and containers production, 11 million tons and 7 million tons as durable goods (appliances) and non-durable goods (cups) respectively. Depending on the parent material, various forms of plastics have different recycling rates. The overall plastics recycling rate in 2012 was 9 percent (28 Mtons) but the recycling rate for some categories of plastic products was higher in the same year e.g. 31 percent of PET bottles and 28 percent of white translucent bottles (HPDE) were recycled (USEPA 2012). Total MSW generated in 2012 by material is shown in Figure 2 while the total MSW recovered by material is showed in Figure 6.

In 2012, plastics recycling and energy recovery reached 15.6 Mtonne approximately 61.9% of the post-consumer waste generated in Europe. The recycling and recovery of total plastic waste in Europe from 2006 to 2012 has showed increasing trend with an annual growth rate of 4% while the disposal

Figure 6. A) Total MSW generation (by material) in 2012 251 million tons before recycling and B) Total MSW recovery (by material)

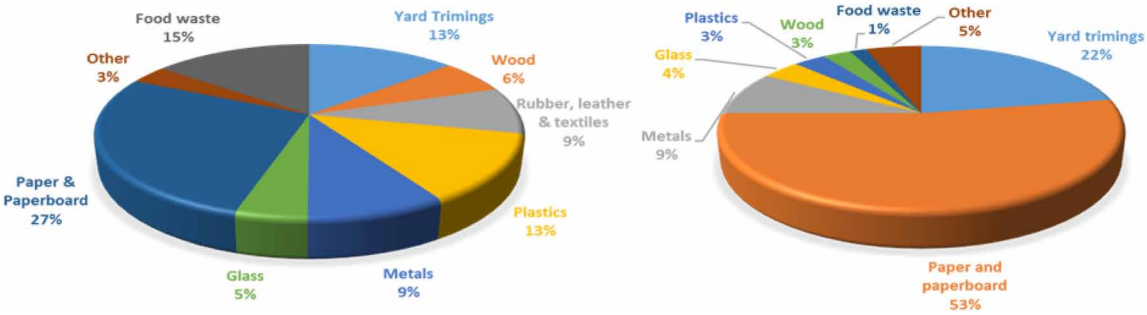


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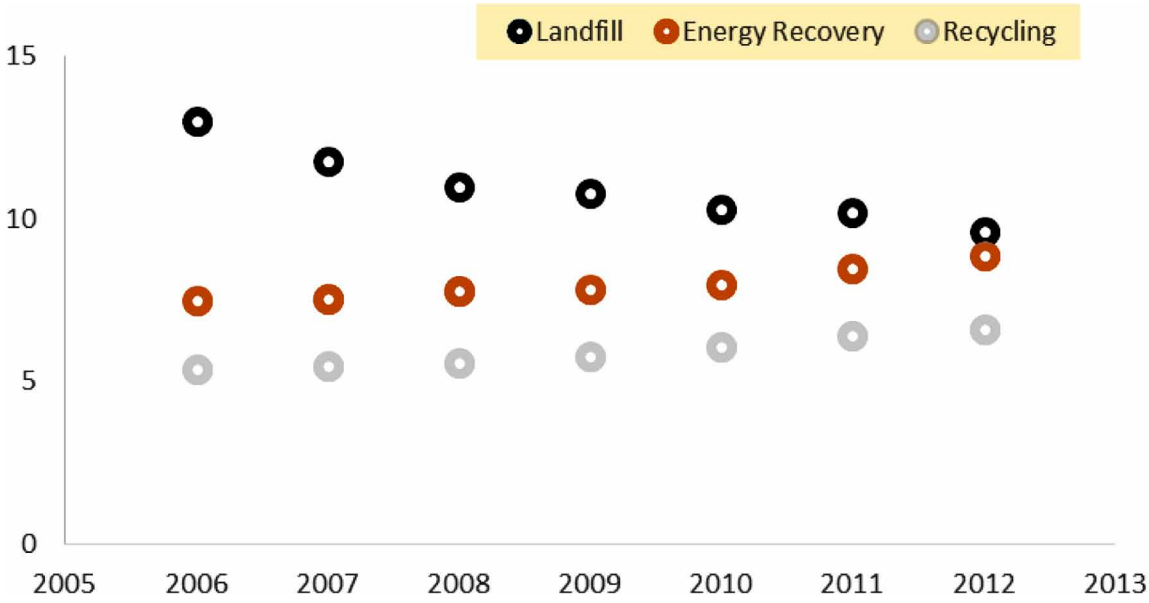
Figure 7. Total plastic waste recycling and recovery 2006-2012



through landfilling continues to diminish at an annual reduction rate of 5.5% which shows a considerable positive development. Europe is one the road towards zero plastic to landfills. Total plastic waste recycling and recovery 2006-2012 is shown in Figure 7.

4. ENVIRONMENTAL CONCERNS AND TOXICITY

The consumption and disposal of polymers have enormous effect to the environment and public health. There are evidences that the chemical building blocks of plastics contains substances that affect the environment and human health. This section will discuss the major environmental effects associated with polymer production. These effects include: excessive consumption of nonrenewable resources, emission of toxic substances such as heavy metals from uncontrolled incineration, and pollution of groundwater and surface water by landfill leachates.

There is increasing concern about the consumption of nonrenewable resources generally petroleum for the production of polymers. About 330 Mbarrels of oil (5% of total U.S. oil production) is consumed in plastic manufacturing. Petroleum products such as natural gas, liquid petroleum gas (LPG) and natural gas liquids (NGL) are used as feedstock and fuel for the production of plastics in the United States. About 190 Mbarrels of LPG and NGL equivalent to 2.7% of total U.S. petroleum consumption were used as feedstock and an equivalent of 1 Mbarrels were consumed as fuel in resin and plastic industry in 2010. About 412 billion cubic feet (Bcf) of natural gas in 2010 an equivalent of 1.7% of total U.S. natural gas consumption were utilized in plastic and resin production. In addition to petroleum product consumption, plastic manufacturing consumes a lot of electricity. It was estimated that 65 billion kW of electricity (1.7% of U.S. consumption) were consumed plastic manufacturing (EIA 2014)

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Plastic bags presents a significant danger to animal life because they are considered by the sea animals as food. Plastic bags floating in the sea when brightly colored or containing residues of food tend to attract the living species within the water bodies. Marine and land animals choke to death when strangled by plastics, causing so much distress and pain. The animals die of slow death from infection and starvation when they consume plastic bags. Plasticizers such as: Bisphenol A (BPA) and the phthalates are produced in a large quantity and they are regularly detected in aquatic environment due to their continuous release into the environment. Plasticizers used as additives in PVC and other plastics production are known to contain substances that pose adverse health effects to non-mammalian and mammalian species. They impede animal development by disrupting hormones production, interfere with normal reproduction by reducing the normal mitochondrial transport and induce cellular stress by increasing fatty acid oxidation (Justine *e*t *a*l., 2014; Jorg *e*t *a*l., 2008). Some countries still use banned plasticizers as clouding agents in food and beverages which attracts serious international attention (Tzung-Hai *e*t *a*l., 2011).

The growth of the plastic industry has a significant impact on the management of municipal solid waste by incineration and landfilling. Synthetic polymers are regarded as major SW environmental pollutants because they are resistant to physical and chemical degradation. Lack of available space and cost of disposal through the landfills have made incineration a viable alternative in plastic management, however, incineration causes the emission of toxic bottom and fly ash which contain trace levels of heavy metals such as cadmium and lead (Curlee *e*t *a*l., 1991). The presence of these substances brings about surface and groundwater pollution problems. Landfilling is the most common route for disposing of polymer waste. Brominated flame retardants (BFR) used as synthetic additives in plastic production are persistent and pose adverse effects on health. They are released in landfills leachates to the environment and they bio-accumulate (Natsuko *e*t *a*l., 2014; Ying *e*t *a*l., 2014)

5. PLASTIC WASTE MANAGEMENT

These are processes generally taken to minimize the effects of plastics on health, the environment and aesthetics. It is the systematic administration of activities that provide for the collection, source separation, storage, transportation, transfer, processing, treatment and disposal of plastic wastes. Plastic waste management is a distinct practice from resource recovery and it focuses on reducing the rate of consumption of natural resource and disposal of waste by landfilling. Figure 9 gives a graphical illustration of waste management hierarchy.

Philosophies of Waste Disposal and Management

- **Out of site out of mind**: It causes widespread environmental damage. The philosophy persists and continue to pose serious problem to the environment.
- **Dilute and Disperse**: The philosophy believes that the solution to pollution is dilution, it is no longer suitable for waste disposal and it causes widespread marine pollution issues.
- **Concentrate and Contain**: This philosophy is currently the most popular in waste management, however it is very energy intensive and expensive.
- **Resource Recovery**: The philosophy requires large volume of waste and technology to convert wastes into useful materials.

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- **Integrated Waste Management Facility (IWMF):** It is a complex set of alternatives that combines source reduction, recycling, composting, incineration and landfilling for efficient waste management.

Functional Elements in Solid Waste Management

There are six functional elements in the activities associated with the management of plastic waste from the point of generation to final disposal sites. These activities are depicted in figure and they include:

Figure 8. Plastic waste management hierarchy

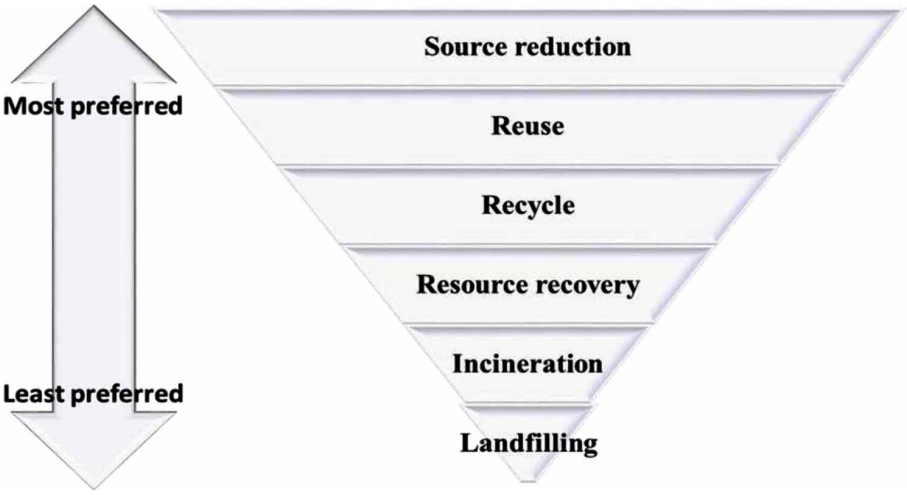

Figure 9. Functional elements of solid waste management

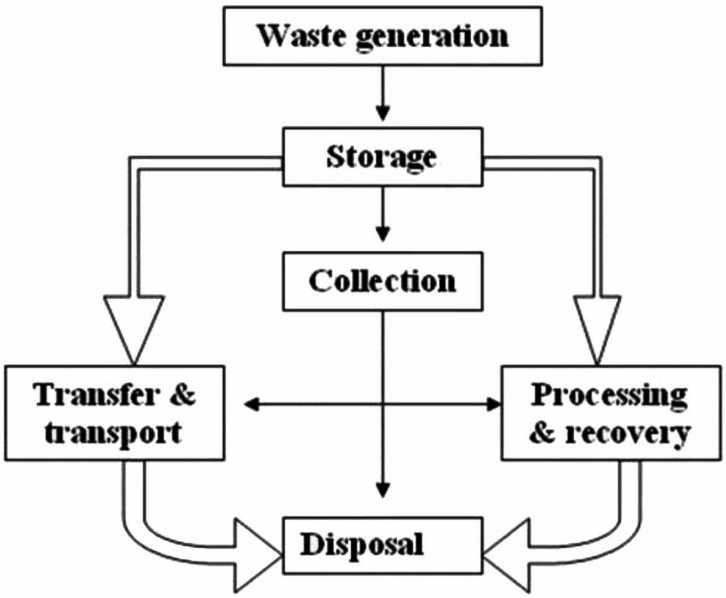

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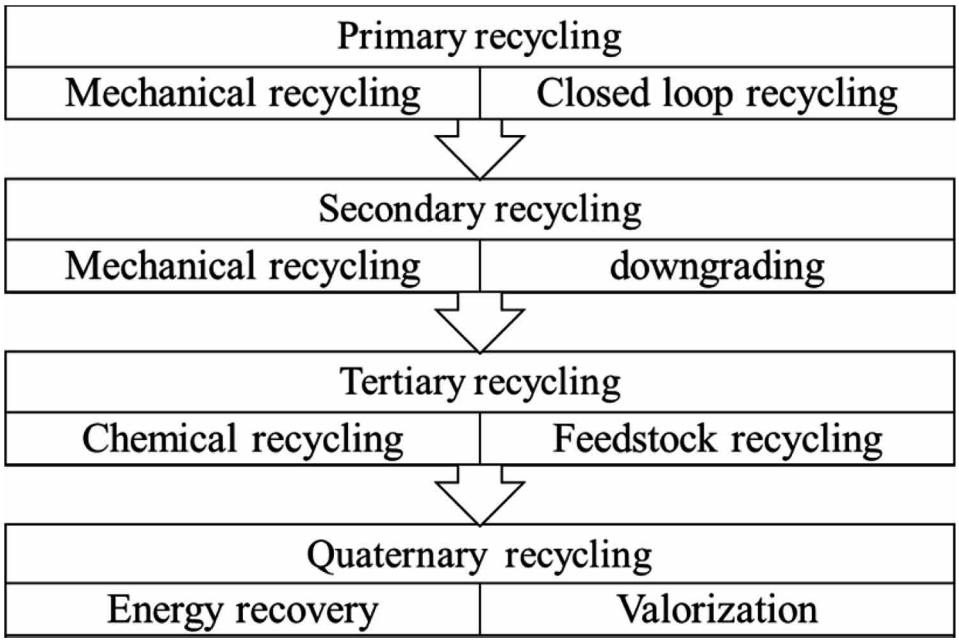
Figure 10. Categories of plastic recycling



- **Plastic Generation:** They are related to those activities in which materials are identified as no longer being of value and are either thrown away or gathered together for disposal.
- **Collection:** Concerned with those activities associated with the gathering of plastic wastes and the hauling of wastes to the location where the collection vehicle is emptied. Waste collection methods vary widely among different countries and regions. Residential, commercial and industrial locations have different collection procedures. Plastic wastes are collected through bring-schemes or kerbside procedures. Bring-schemes collection methods are very slow compared to the kerbside methods because they require the willingness and commitment of the public through economic incentives. Kerbside collection methods combine most recyclables together e.g. papers, glass, plastic containers etc. but the recovery rate of plastic using this method is around 30-40% (Jefferson *et al*., 2009).
- **On-Site Handling (Sorting, Storage & Processing):** Related to those activities associated with the handling, storage, and processing of plastic wastes at or near the point of generation. Sorting is carried out through manual or automated methods to separate plastics from other recyclables. Manual methods of separation depend on the use of color and physical properties to distinguish between different forms of plastics. Material recovery and recycling facilities use automated methods such as Fourier transform near infrared spectroscopy (FT-NIR) and optical recognition camera techniques to easily separate HDPE and PET bottles out of the stream. X-ray detection methods, ballistic separators, trommels, hydrocyclones, and density based air classification systems are also used for the separation of PVC containers and flexible packaging (Arvanitoyannis 2001; Fisher 2003). Sink/float separation can be used in the separation of polyolefin i.e. PP and all classes of PE from PET, PVC and PS. Air elutriation has been used in separation of labels (low density films) from denser plastics (Chandra 2007). Raman emission spectroscopy, froth flotation, thermal kilns

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and FT-NIR techniques have been used in reducing the PVC contaminants in PET flake (Marques *e*t *a*l., 2000). Laser-sorting is a new approach that uses emission spectroscopy in the removal of polymers by type and impurities such as nylon and silicones from other forms polymers.

- **Transfer and Transport:** Those activities associated with the transfer of wastes from the smaller collection vehicle to the larger transport equipment and the subsequent transport of the wastes, usually over long distance, to the disposal site.
- **Processing and Recovery:** These are techniques, equipment and facilities used both to improve the efficiency of the other functional elements and to recover useable materials, conversion products, or energy from plastic wastes.
- **Disposal**: They are activities associated with ultimate disposal of plastic wastes.

6. PLASTIC WASTE MANAGEMENT OPTIONS

There are several methods in use to curtail the impacts of plastic waste to our health, species, environment and aesthetics. This section will discuss some of the alternatives for plastic waste management.

Source Reduction

Source reduction means decreasing the amount and toxicity of the waste we dispose. It promotes the use of products that are environmentally benign. Plastic waste is an important target for source reduction because of their rapid growth in MSW. Plastic waste end up as litter that affects aesthetics, health, environment and the economy. Source reduction involves such measures of eliminating unnecessary packaging of products and reducing the amount of item used in packaging will reduce waste volume. The use of alternate materials that will have less ecological effects in place of polymers tend to be a viable economic and environment-friendly approach. Some notable examples are the replacements of paper for plastics in supermarkets and that of synthetic fibers (nylon) for natural degradable fibers (cotton) respectively.

Reuse

The reuse of post-consumer packaging materials is known for a long time. It has been applied for remanufacturing of vehicles and electronic equipment and in industrial scale for the reuse of pallets and containers in haulage (Thompson *e*t *a*l., 2009) Triple layer plastic bags are reused for cowpea storage in thousands of villages along West and Central African countries (Dieudonne *e*t *a*l., 2014). PET bottles are utilized as building units in some parts of Africa replacing the traditional concrete blocks. They are known for their thermal and structural stability (Ashraf *e*t *a*l., 2015). Other countries are known for reusing plastics to store medicine (Muluneh *e*t *a*l., 2014).

Recycling

This is the process of recovering and reprocessing of waste plastic into useful products that maybe entirely different from their original form. Example is evident in the production of tables and chairs by melting down plastic bottles. There are four categories in plastic recycling, these include: primary, secondary, tertiary and quaternary. Figure 11 outlines the categories in plastic recycling

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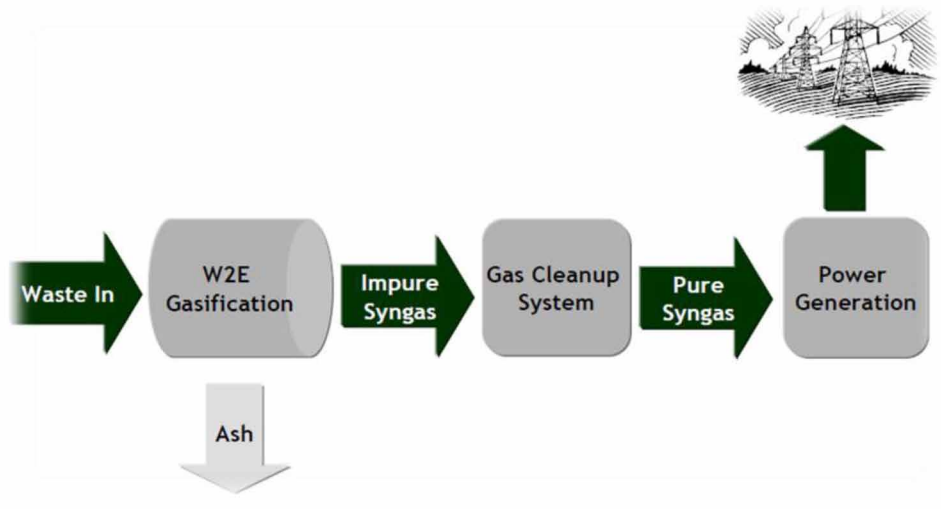
Figure 11. The waste to energy process



Incineration

Incineration is a waste treatment process that involves the combustion of organic substances contained in waste material. It converts combustible waste into ash, flue gas and heat at a temperature of around 1000°C. Incineration reduces the amount of plastic waste sent to the landfills however, it is associated with the environmental release of halogenated additives such as dioxins, furans and other polychlorinated biphenyls released upon the combustion of PVC (Gilpin *e*t *a*l., 2003). Incineration of plastic waste as a management option is less prevalent in so many countries due to the adverse pollution problems however it is widely used in Asia due to the limited space for landfills. Incineration with energy recovery is one of the several waste to energy technologies such as: gasification, pyrolysis and anaerobic digestion. The waste to energy process is given in Figure 12.

Composting

Composting is a biochemical process of converting organic waste to humus-like material and it helps in the reduction of garbage. Composting can significantly reduce the amount of garbage on a household or municipal scale, and is less expensive. Composting is a natural process of rotting material down to make a soil like product which can be used on the garden. Composting provide fertilizers helps in reduction of waste, save water, and reduces the carbon footprint. Landfill degradation rate is a relatively slow process compared to degradation in compost piles. Biodegradable polymers are decomposed effectively using composting mixtures but it requires controlled conditions in centralized facilities.

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Biodegradation

Landfilling

Plastics are difficult to recycle because both the manufacturers and consumers discard different forms of plastics. Private and public agencies are reluctant to investing in plastic recycling because it is mostly non-biodegradable plus the cost of collection, transport, sorting and degreasing. Landfills are the most common methods of waste disposal however disposal of plastic through landfills consumes a lot of space and is associated with long-term risks of contaminating groundwater and soils by persistent organic pollutants released through leachates of additives and degradation by product (Teuten et al. 2009). A major disadvantage of plastic disposal to the landfill is that none of the material used in the manufacturing process can be recovered. Some countries impose taxes on disposal of plastic to the landfill with the ultimate goal of increasing investments in energy recovery, recycling and attaining zero landfill disposal.

7. RECYCLING WASTE RUBBER POLYMERS FOR PRODUCTION OF ADSORBENTS FOR WATER TREATMENT

There are many methods to recycle waste rubber tires which are sub-divided into two categories. The first category involves physical methods of grinding the waste mechanically into smaller pieces to produce fine particles without altering chemical composition while the second category uses mechanochemical means to breakdown the three-dimensional network with the aid of different forms of energy. Thermal, mechanical, biological, chemical, ultrasonic and microwave treatments are used to convert the waste insoluble thermoset into a reprocessable elastomer (De *e*t *a*l., 2005). The best method suitable for tire recycling is pyrolysis (Kaminsky *e*t *a*l., 1995), pyrolysis is the thermal decomposition of rubbers in a closed system for the production of oil, gasses for reuse in petrochemical industries and solid remains such as carbon black for use as filler materials. There is a significant progress in the pyrolysis technology of waste rubber tire, however, despite the progress, pyrolysis is done on a limited scale due to the absence of market for the derived products (Saleh 2013; Saleh et al. 2016; Saleh and Danmaliki, 2016; Alansi et al. 2015; Saleh et al. 2014).

Researchers in recent years have focused more in the recycling and reuse of waste rubber tires among the initiative is the derivation of activated carbon after pyrolysis for various adsorption studies. Activated carbon from waste rubber tire have the ability of adsorbing different compounds however its adsorption capacity is relatively low compared with other adsorbent materials in use. There are various methods of improving the adsorption capacity of the fine powdered particles. Activated carbon from waste rubber tire was synthesized by pyrolysis at 500°C-700°C and later treated with activating agents such as zinc chloride and potassium hydroxide in a study conducted by (Nunes *e*t *a*l., 2011). The adsorbent showed a mesoporous structure containing sulfur and zinc and it showed the possibility of waste water treatment.

The work conducted by (Zabaniotou et al., 2014) derived activated carbon from waste rubber tires by pyrolysis at 800°C in a fixed bed reactor and physical method of activation using CO2 for the removal of pesticide(bromopropylate) by adsorption from aqueous solution. The surface area of the activated carbon was found to reach 432 m2 g−1 and nearly 100% of the pesticide was removed in just 60mins of the experiment. The study of (Edward et al., 2010) derived activated carbon from ELTs by carbonization for the effective removal of dyes from effluents. It was observed that temperatures above 770K resulted in lower yield adsorbent.

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Waste rubber tires were pyrolyzed in carbon dioxide and nitrogen atmospheres at various temperatures for char production (Manchon-Vizuete et al., 2005). The char was activated by oxygenation at different temperatures and were used for the removal of lead and copper from aqueous solutions. The study concluded that the optimum temperature for pyrolysis in carbon dioxide and nitrogen atmospheres is 550∘C. The study of (Sani et al. 2016; Danmaliki et al. 2017; Alswat et al. 2016) used spectroscopic and computational studies to examine the chemistry of cadmium adsorption by activated from waste rubber tires in aqueous solutions. The adsorption process was found to be fast and equilibrium was achieved after 60mins of interaction. Finally, binding energy of cadmium to carbonyl groups was found to be higher than other functional groups present.

The study conducted by AlSaadi et al., 2013 synthesized activated carbon from ELT by physical activation and used it as an adsorbent for the removal of nickel and lead ions from aqueous solutions. The adsorbent was found to have more affinity to the lead ions (96% removal) and the adsorption process was believed to start from initial surface adsorption followed by intra-particle diffusion. The regeneration ability of the adsorbent was also tested and they believed it may be a substitute to the expensive commercial activated carbon currently in use for pollution clean-up. Danmaliki and Saleh 2017 synthesized different brands of activated carbon from waste rubber tires by microwave assisted chemical treatment and physical heating for the adsorption of phenolic compounds.

Granular particles of tire were carbonized and pyrolyzed by heating at 773K and 1223K respectively in nitrogen atmosphere for the production of active carbon in a study conducted by (Mui *e*t *a*l., 2010). The product produced was activated by carbon di oxide in nitrogen atmosphere and later subjected to acid treatment. The synthesized adsorbent was used in the removal of dyes from waste water and it had a higher surface area and better yield. A study conducted by (Quek et al., 2009) synthesized activated carbon possessing high surface area (414 m2/g) without pyrolysis in a one-step cost effective approach. The study used thermochemical degradation of granular tires in a carbon di oxide environment.

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Chapter 45
Utilization of SVM, LSSVM and GP for Predicting the Medical Waste Generation

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ABSTRACT

The prediction of wastes generated in the hospital will help their management for several activities like storage, transport and disposing. This chapter adopts Support Vector Machine (SVM), Least Square Support Vector Machine (LSSVM) and Genetic Programming (GP) in order to estimate the rate of medical waste generation. In the event of predicting the rate, type of hospital, capacity and bed occupancy has been used as inputs of SVM, LSSVM and GP. SVM is based on statistical learning theory, which provides an elegant tool for nonlinear system modeling. LSSVM is the re-formulation to the general SVM. GP, a best part of evolutionary algorithm and also the specification of Genetic Algorithm (GA). These SVM, LSSVM and GP have been used as the regression techniques. The results show the performance of the developed SVM, LSSVM and GP models were elegant and outstanding.

INTRODUCTION

The development of industries, urban growth together with population and population densities will automatically increase the production of wastes. World Health Organization (WHO) has advocated that the hospital wastes should be treated as the particular wastes (Rushbrook et al., 2000). These hospital wastes are more hazardous and are rapidly increasing in the society. Inadequate hospital waste manage-

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ment will cause environmental pollution, generation of germs and insects, foul smell, etc, will lead to the contagious diseases like typhoid, cholera and AIDS through the wound from syringes and needles contaminated with the human blood (Henry & Heinke, 1996). This research has the better scope in the smart cities with more industries and population. Potentially dangerous hospital wastes can be predicted for the prevention of some hazardous diseases.

Through inventory, questionnaire survey and formal and informal interviews, data has been collected for empirical field observation in Dhaka city, Bangladesh (Hassan et al., 2008). Very deep interviews were carried out to obtain the knowledge of earlier and current management of medical wastes. Their examination provides the outcome of average waste generation 1.9 kg/bed/day. Hassan et al., (2008) delivers the reasons for improper management of medical wastes like, lack of awareness, appropriate policy and laws, and willingness. Omar et al., (2012) has considered the medical waste generation in Malaysia and determined the factors affecting management of medical wastes. They detected and detailed specifically flaw in segregation process of medical waste. Omar et al., (2012) has adopted Microsoft Excel and its pertinent statistical gadget like ANOVA for evaluating the management of medical waste. Maha et al., (2015) had thrown their limelight work distinctly on dental clinics at Lebanon. They considered 242 dental clinics arbitrarily and made survey with 32 framed questions. According to their scrutiny, the process of isolating the waste was vanished and it is mingled with the municipality wastes. Their audit provides the necessity of adopting efficient and responsible medical waste management, in order to prevent disaster in public health and pollution at Lebanon. Hence the adequate management of hospital waste is required to reduce the health and environmental risks. Unfortunately, collection, transport and disposal of waste have no proper strategy or planning behind its implementation. It urgently needs to that needs to be regulated by definitive rules (Askariana et al., 2004).

In order to determine the rate of waste generation, the data like (i) number of bed/patient available at the hospital; (ii) type of specialization (type and range of care); and (iii) number, kind, and size of departments have been utilized (Award et al., 2004). The goal of this chapter is to predict the rate of waste generation based on the mentioned criteria's. Artificial Neural Network (ANN) and Multiple Linear Regression (MLR) have been adopted for this determination (Jahandideh et al., 2009). Since ANN & MLR have some disadvantages such as the low accuracy of MLR and the black box approach, over fitting issues, lack of generalization capability and slow convergence rate of ANN (Park & Rilett, 1999; Kecman, 2001), various effective methods have been utilized.

The methodology of pursuing the medical waste generation includes the upcoming procedures. A total of 50 hospitals private, governmental, educational and non-educational, but university-related hospitals in Fars province, Sharz city, Iran have been considered for the collection of dataset (Jahandideh et al., 2009). The dataset contains information about type of hospital, Capacity(C), Bed Occupancy (B_0) and Waste generation rates (kg/day) (w_t). This chapter accommodates the machine learning techniques like Support Vector Machine (SVM), Least Square Support Vector Machine (LSSVM) and Genetic Programming (GP) for determination of rate of medical waste generation.

SUPPORT VECTOR MACHINE (SVM)

The SVM have been formulated by Vapnik (1998, 1999) based on statistical learning theory. Initially, SVM was utilized for two class classifications, later it was developed to multi-classification, regression, estimation and other similar works. Support Vector machines can be defined as systems which use hy-

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pothesis space of a linear functions in a high dimensional feature space, trained with a learning algorithm from optimization theory that implements a learning bias derived from statistical learning theory. The formulation uses the Structural Risk Minimization (SRM) principle, which has been shown to be superior, (Burges, 1998) to traditional Empirical Risk Minimization (ERM) principle. SRM reduces an upper bound on the expected risk, whereas ERM minimizes the error on the training data. This differentiation equips SVM with a greater ability to generalize, which is the goal in statistical learning. Since SVM follows the Structural Risk Minimization (SRM) principle, it reduces the occurrence of risk during the training phase as well as enhances its generalization capability. Due to its high performance and detecting the global optimums in real applications, it is most widely used technique in many fields ranging.

Details of SVM

Let us consider the typical regression formulation for predictive learning (Cherkassky & Mulier, 1998; Hastie, Tibshirani, & Friedman, 2001; Vapnik, 1999). The intention is to assess unknown real-valued function in the relationship

$$y = r(x) + \delta \tag{1}$$

where x is a multivariate input, y is the output and δ is the noise data which is uniformly distributed zero mean random error. The estimation is based on a finite number of samples i.e. training data (x_i,y_i), $(i=1,\ldots n)$. The uniformly distributed training data samples are engendered according to the probability density function.

$$p(x,y = p(x)p(y|x) \tag{2}$$

The unknown function in equation (1) is the mean of the output regression function

$$r(x) = \int yp(y|x)dy \tag{3}$$

An estimation procedure identifies the best model $f(x,\varpi_0)$ from the set of approximating functions $f(x,\varpi)$. It is then parameterized by a set of parameters $\varpi\in\Omega$. The eminence of the approximation can be determined by the inconsistency measure $L(y,f(x,\varpi))$. The ultimate aim of learning this is to pick the best model reducing estimation risk.

$$R(\varpi) = \int L(y,f(\varpi))p(x,y)dxdyf(x,\varpi) \tag{4}$$

The regression function is equation (3) is the one minimizing estimation risk (4) with the squared loss function

$$L(y,f(x,\varpi)) = (y\text{-}f(x,\varpi))^2 \tag{5}$$

It should be noted that, carried by the learning technique may or may not have the regression function (3). Hence we have to determine the regressor function $f(x,\varpi_0)$ that reduces the prediction risk function using only the training data.

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$$R(\varpi) = \int (y\text{-}f(x,\varpi))^2 p(x,y)dxdy \tag{6}$$

The risk functional ascertains the accuracy of the unknown target function $r(x)$. SVM maps the input x to the n dimensional space using some non-linear mapping and then the linear mapping will be developed in the feature space (Cherkassky & Mulier, 1998; Smola & Scholkopf, 1998; Vapnik, 1998, 1999).

$$f\left(x,\varpi\right) = \sum_{i=1}^{n} \varpi_i g_i\left(x\right) + b \tag{7}$$

where $g_i(x)$, i=1,…..,n indicates the non-linear transformations and b is the bias.

Regression forecasts can be procured by the reduction of the empirical risk on the training data. Typical loss functions used for minimization of empirical risk include squared error and absolute value error. SVM regression uses a type of loss function called ε-insensitive loss proposed by Vapnik (1998, 1999).

$$L_\varepsilon\left(y, f\left(x,\varpi\right)\right) = \begin{cases} 0 & \text{if } \left|y - f\left(x,\varpi\right) \le \varepsilon\right| \\ \left|y - f\left(x,\varpi\right) \le \ \varepsilon\right| & \text{otherwise} \end{cases} \tag{8}$$

The empirical risk is defined in the following equation (9)

$$R_{emp}\left(\varpi\right) = \frac{1}{n}\sum_{i=1}^{n} L_\varepsilon\left(y_i, f\left(x_i,\varpi\right)\right) \tag{9}$$

SVM performs linear regression in a high dimensional feature space by utilizing the ε insensitive loss. Also simultaneously it engages to deduce the complexity of the model by minimizing $\|\varpi\|^2$. This can be illustrated by setting up a non-negative slack variable $\xi_i, \xi_i^* \ \ i = 1,\ldots,n$ in order to determine the divergence training samples away from ε insensitive region. Thus SVM regression is formulated as minimization of the following function:

Minimize: $\frac{1}{2}\left\|\varpi\right\|^2 + C\sum_{i=1}^{n}(\xi_i + \xi_i^*)$

Subjected to: $\begin{cases} y_i - f\left(x_i,\varpi\right) - b \le \varepsilon + \xi_i^* \\ f\left(x_i,\varpi\right) + b \le \varepsilon + \xi_i^* \\ \xi_i, \xi_i^* \ge 0 \end{cases}$ (10)

where C is the regularization parameter which is a positive constant. This optimization formulation can be transformed into the dual problem (Vapnik, 1998, 1999).

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$$f\left(x\right) = \sum_{i=1}^{n} (\alpha_i - \alpha_i^*) K(x_i, x) + b \tag{11}$$

The dual variables are subjected to constraint $0 \leq \alpha_i, \alpha_i^* \leq C$ and $K(x_i,x)$ is the kernel function. The points that come into view with non-zero coefficients are called support vectors. SVM generalization performance depends on the better setting of hyper parameters and the kernel parameters. The problem of determining depends upon the above mentioned hyper and kernel parameters.

The parameter C measures the tradeoff whereas the degrees of deviation are determined by ε. For example, when C is too large i.e. infinity, then the empirical risk alone can be minimized without regards to model complexity. Parameter ε controls the width of the ε -insensitive zone, used to fit the training data (Cherkassky & Mulier, 1998; Vapnik, 1998, 1999). The value of ε can affect the number of support vectors used to construct the regression function. Larger ε - value result in fewer support vectors selected, and results in more 'flat' (fewer complexes) regression estimates. Hence, both C and ε -values affect model complexity (but in a different way).

Radial basis function has been adopted for this study.

$$K\left(x_i, x\right) = \exp\left\{-\frac{\left(x_i - x\right)^T \left(x_i - x\right)}{2\sigma^2}\right\} \tag{12}$$

x_i and x are the training and test patterns, T is the transpose and σ is a the global basis function width.

The total datasets have been divided into the following two groups:

- **Training Dataset:** This is used to construct the SVM model. In this article, 35 datasets out of 50 have been adopted as training dataset.
- **Testing Dataset:** This is used to evaluate the developed SVM. This article uses the remaining 15 datasets as testing dataset.

The datasets are scaled between 0 and 1. The programming of SVM has been done by using MATLAB.

LEAST SQUARE SUPPORT VECTOR MACHINE (LSSVM)

LSSVM was proposed by Suykens et al (2002). LSSVM is the statistical learning theory which adopts the least squares linear system as the loss function to the original SVM. LSSVM retains the SRM principle which leads to the improvement of speed than the classical SVM. It was achieved due to the varying inequality constraints into equations and takes the squared loss function. Hence, it solves system of equations instead of quadratic problems. LSSVM adopts the same inputs as that of SVM.

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Details of LSSVM

Consider a given training set of N data points $\left\{x_k, y_k\right\}_{k=1}^{N}$ with input data $x_k \in R^N$ and output $y_k \in r$ where R^N is the N-dimensional vector space and r is the one-dimensional vector space.

In feature space LSSVM models take the form

$$y(x) = w^T \phi(x) + b \tag{13}$$

where the nonlinear mapping $\phi(.)$ maps the input data into a higher dimensional feature space; $w \in R^n$; $b \in r$; w - adjustable weight vector; b - the scalar threshold.

In LSSVM for function estimation the following optimization problem is formulated:

$$\text{Minimize: } \frac{1}{2} w^T w + \gamma \frac{1}{2} \sum_{k=1}^{N} e_k^2$$

$$\text{Subjected to: } y(x) = w^T \phi(x_k) + b + e_k, \text{ k=1,…,N.} \tag{14}$$

where γ is the regularization parameter, determining the trade-off between the fitting error minimization and smoothness and e_k is error variable.

The Lagrangian ($L(w,b,e;\alpha)$) for the above optimization problem (14) is

$$L\left(w,b,e;\alpha\right) = \frac{1}{2} w^T w + \gamma \frac{1}{2} \sum e_i^2 - \sum \alpha_i \left\{w^T \phi\left(x_i\right) + b + e_i - y_i\right\} \tag{15}$$

with α_k Lagrange multipliers. The conditions for optimality are given by

$$\frac{\partial L}{\partial w} = 0 \Rightarrow w = \sum_{k=1}^{N} \alpha_k \phi(x_k)$$

$$\frac{\partial L}{\partial b} = 0 \Rightarrow \sum_{k=1}^{N} \alpha_k = 0$$

$$\frac{\partial L}{\partial e_k} = 0 \Rightarrow \alpha_k = \gamma e_k, \text{ k=1,…,N.}$$

$$\frac{\partial L}{\partial \alpha_k} = 0 \Rightarrow w^T \phi\left(x_k\right) + b + e_k - y_k = 0 \text{ , k=1,…,N.} \tag{16}$$

After elimination of e_k and w, the solution is given by the following set of linear equations

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$$\begin{bmatrix} 0 & 1^T \\ 1 & \Omega + \gamma^{-1}{}_I \end{bmatrix} \begin{bmatrix} b \\ \alpha \end{bmatrix} = \begin{bmatrix} 0 \\ y \end{bmatrix} \tag{17}$$

where $y=[y_1,\ldots,y_N]$, $1=[1,\ldots,]$, $\alpha=[\alpha_1,\ldots,\alpha_N]$ and Mercer's theorem (Vapnik, 1998; Smola and Scholkopf, 1998), is applied within the Ω matrix,

$$\Omega = \phi\left(x_k\right)^T \phi\left(x_l\right) = k\left(x_k, x_l\right), \text{ k,l=1,…,N}$$

where $k(x_k,x_l)$ is the kernel function. Choosing γ>0, ensures the matrix

$$\Phi = \begin{bmatrix} 0 & 1^T \\ 1 & \Omega + \gamma^{-1}{}_I \end{bmatrix}$$

is invertible. Then the analytical of α and b is given by

$$\begin{bmatrix} b \\ \alpha \end{bmatrix} = \Phi^{-1} \begin{bmatrix} 0 \\ y \end{bmatrix} \tag{18}$$

Radial basis function has been used as a kernel in this analysis. Radial basis function is given by

$$K\left(x_k, x_l\right) = \exp\left\{-\frac{\left(x_k - x_l\right)\left(x_k - x_l\right)^T}{2\sigma^2}\right\} \text{ k,l=1,…,N} \tag{19}$$

where σ is the width of radial basis function.

The resulting LSSVM model for rate of medical waste generation prediction becomes then

$$y\left(x\right) = \sum_{k=1}^{N} \alpha_k K\left(x, x_k\right) + b \tag{20}$$

LSSVM utilizes the same dataset which was used for developing SVM.

- **Training Dataset:** This is used to build the LSSVM model. In this article, 35 datasets out of 50 have been adopted as training dataset.
- **Testing Dataset:** This is used to verify the built LSSVM. This article uses the remaining 15 datasets as testing dataset.

The datasets are scaled between 0 and 1. The programming of LSSVM has been done by using MATLAB.

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GENETIC PROGRAMMING (GP)

Genetic Programming (GP) was proposed by Koza (1992). GP is one of the best parts of the evolutionary algorithm and also the specification of genetic algorithms (GA) (Goldberg, 1989). It helps in producing the clear prediction equations which satisfies the inabilities of some soft computing techniques (Adil et al., 2008). GP adopts Darwins concept of "survival of the fittest" and also some appropriate combination of computer programs. The computer program can be exposed in terms of parse tree. The explanation of parse tree was depicted in Figure 1.

Figure 1 explains the parse tree diagram of computer program for a simple equation $[(2a - 7b) + (3x + 6y)]$.

Details of GP

This section conveys the details of the GP. In 1st step, random populations of equations were created. Then the fitness value of each equation is determined in the sequential step. 'Parents' are selected in this step. 3rd step makes 'offspring's are created through the procedure of reproduction, mutation and crossover. In 4th step, the best equation is obtained. The following Figure 2 explains the technical procedure of GP.

Crossover is one of the genetic operators used to combine the population. This operator gently selects preferable parent's chromosome and couple them to produce an offspring. The crossover point was elected randomly. The following Figure 3 explains the process of crossover.

Mutation is another genetic operator which is identical to the crossover only in selecting the chromosomes of the parent's (i.e.) in the mutation selection point only. It changes the building blocks helping to breakout from the local minimal traps. The size of the mutation is also arbitrary, which helps to get the best individual (Figure 4).

GP adopts the same dataset which was used for developing SVM & LSSVM models. The programming of GP has been done by using MATLAB.

Figure 1. Example of parse tree

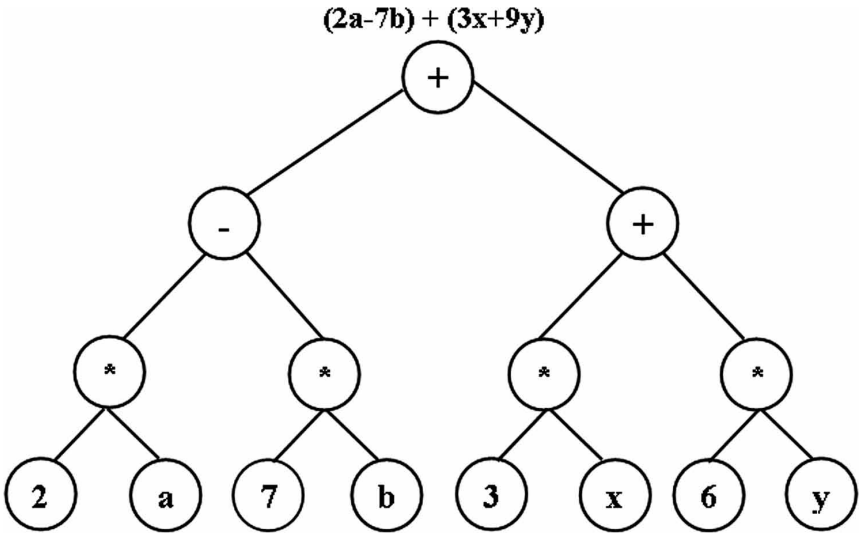

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Figure 2. Flowchart of a simplified GP

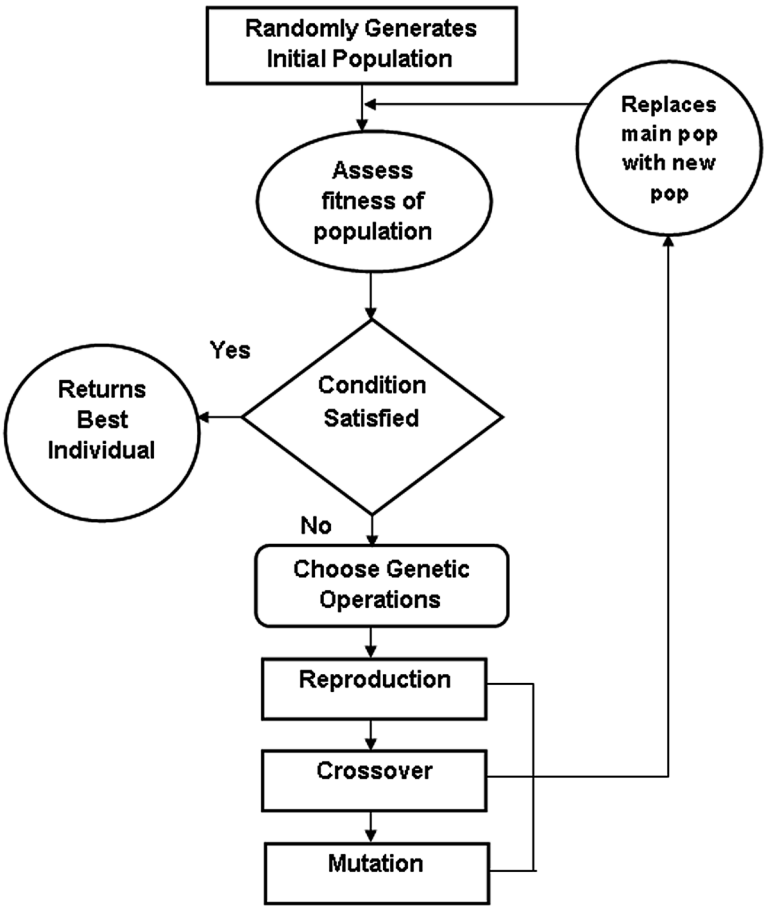

Figure 3. Process of crossover

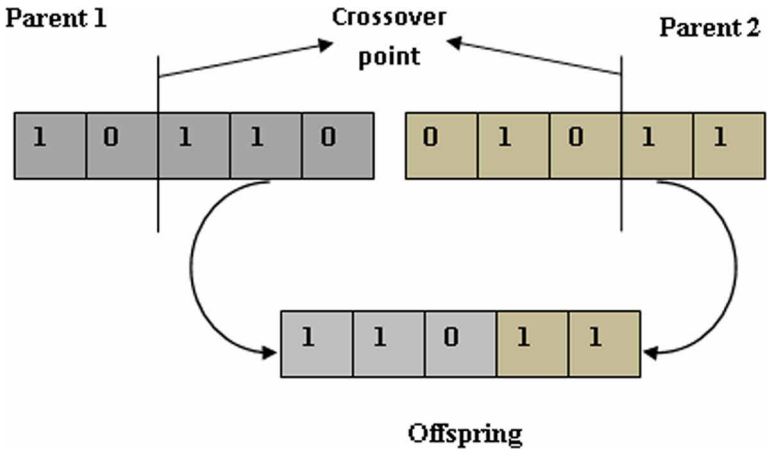

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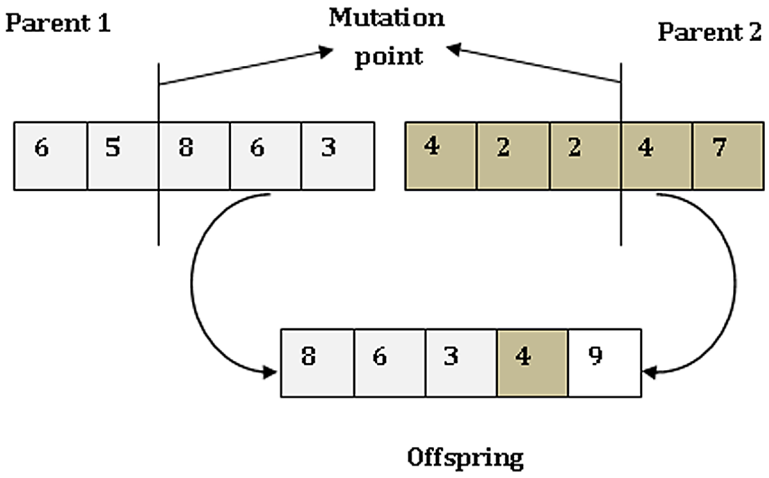
Figure 4. Methodology of mutation



RESULTS AND DISCUSSION

For developing the SVM model the design values of C, ε and σ are required. After several trials, the design values have been varied over a specific corresponding range in order to get better coefficient of correlation value. When the R value is close to one, then it is said to be a good model. At C=100, ε=0.001 and σ = 0.7, the R value is greater. Figure 5 and 6 describes the performance of training and testing datasets of the SVM model.

Therefore, the equation to determine w_t is as follows:

$$y = \sum_{i=1}^{31} w_i \exp\left\{-\frac{\left(x_i - x\right)^T \left(x_i - x\right)}{0.98}\right\} \tag{21}$$

The values of $(\alpha_i - \alpha_i^*)$ is shown in the following Figure 7.

For developing LSSVM, the design values of γ and σ have been determined by trial and error approach. The developed LSSVM gives best performance at γ=100 and σ=0.2. The performance of training and testing datasets has been determined by using the design values of γ and σ. Figures 5 and 6 illustrates the performance of LSSVM model. It can be seen from Figures 5 and 6 that the value of R is close to one.

The developed LSSVM give the following equation (by putting N=31, b=0.4258, σ=0.2, $y(x)=w_t$ and

$$K\left(x, x_k\right) = \exp\left[\frac{-\left(x - x_k\right)\left(x - x_k\right)}{2\sigma^2}\right]$$

in equation 20) for prediction of w_t.

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Figure 5. Performance of training dataset of SVM model

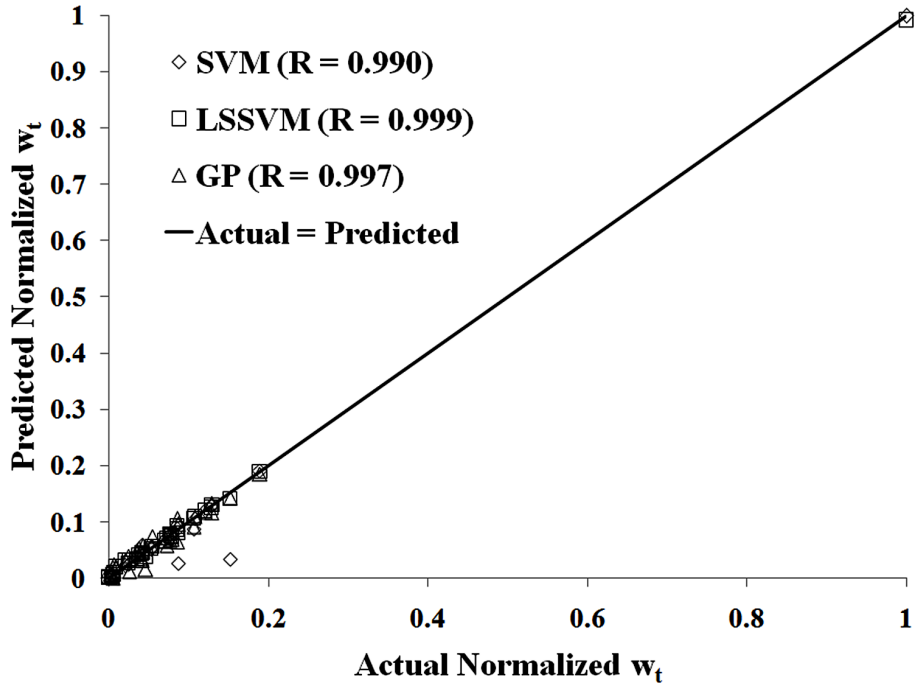

Figure 6. Performance of testing dataset of SVM model

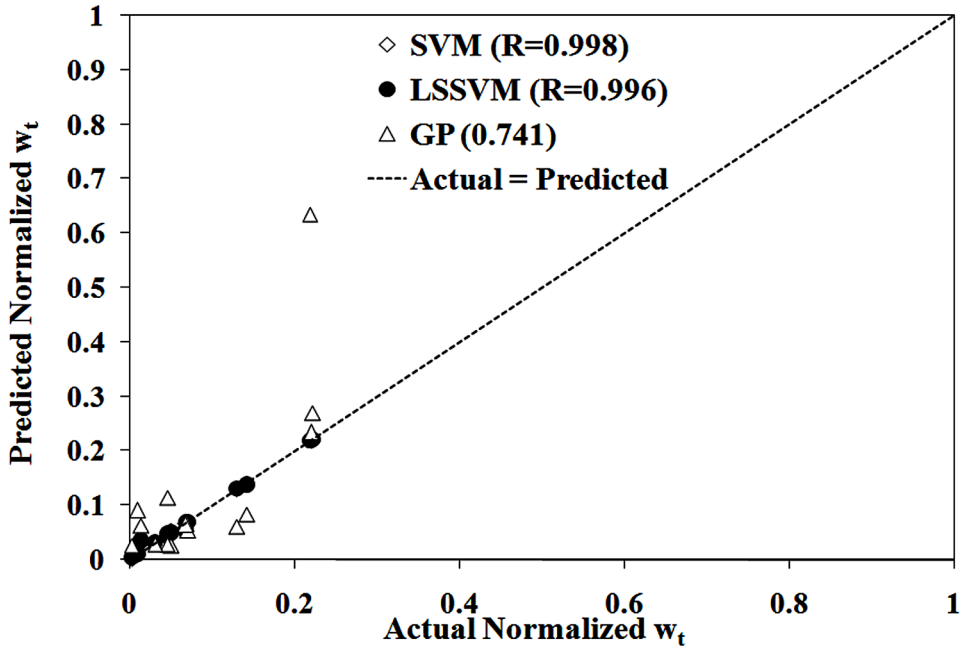

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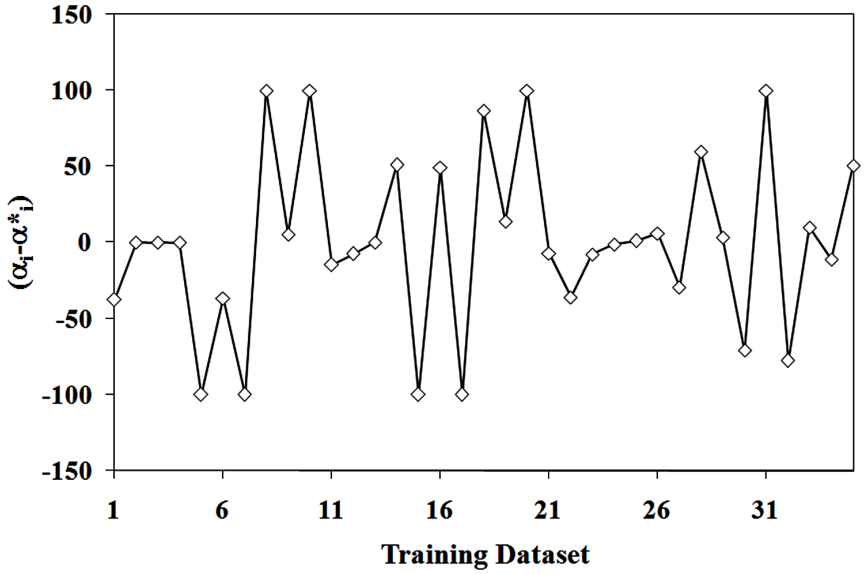
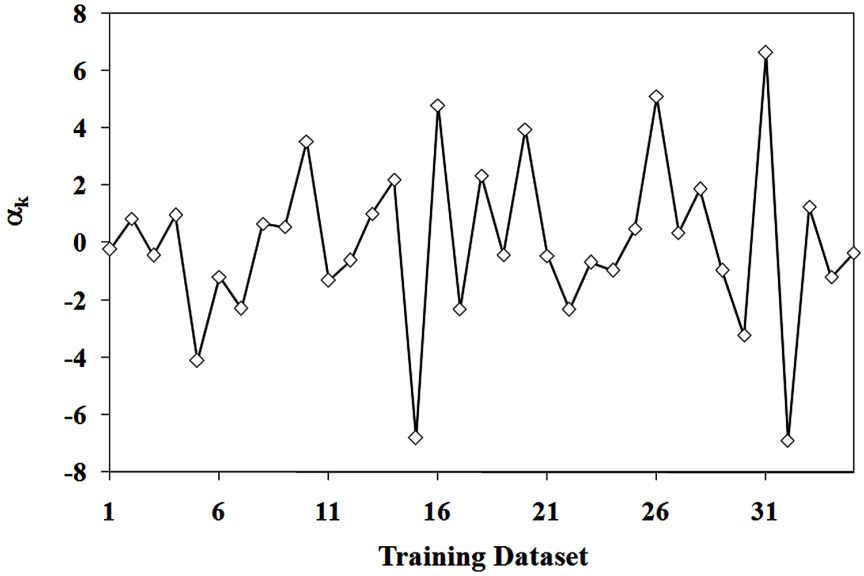
Figure 7. Values of $(\alpha_i - \alpha_i^*)$



$$d = \sum_{i=1}^{31} \alpha_k \exp\left[\frac{-\left(x - x_k\right)\left(x - x_k\right)^T}{0.08}\right] \tag{22}$$

Figure 8 shows the value of α_k.

Figure 8. Values of α_k



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The performance of the GP model was depicted in Figures 5 and 6. The merit of the GP model is that it conveys the direct equation. In order to determine the rate of medical waste generation the developed GP model generates the direct equation.

$$\begin{aligned} 0.2366\left(2x_1\right)^2 &- 0.02179\cos\left(-x_1 - 6.299x_2\right) - 0.01204x_6 \\ &+ 0.05986\sin\left(2x_2\left(x_5 - 8.176\right)\right) - 0.02338\sin\left(-8.729x_2 - 8.729x_6\right) \\ &- 0.03271\sin\left(-16.35x_2 - 16.35x_5\right) + 0.02408x_2\left(x_2 + x_5\right) + 0.04439 \end{aligned} \tag{23}$$

Different statistical criteria like Root Mean Square Error (RMSE), Mean Absolute Error (MAE), Coefficient of Efficiency (E), Root mean square error to observation's standard deviation ratio (RSR), Normalized Mean Biased Error (NMBE) and Performance Index (ρ) have been used to compare the developed model. The above mentioned statistical criteria have been determined by using the following equations.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(h_i - t_i\right)^2}{n}} \tag{24}$$

$$MAE = \frac{\sum_{i=1}^{n}\left|h_i - t_i\right|}{n} \tag{25}$$

$$E = 1 - \frac{\sum_{i=1}^{N}\left(h_i - t_i\right)^2}{\sum_{i=1}^{N}\left(hi - \overline{h}_i\right)^2} \tag{26}$$

$$RSR = \frac{RMSE}{\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(hi - \overline{h}_i\right)^2}} \tag{27}$$

$$NMBE = \frac{\sum_{i=1}^{n}\left(t_i - h_i\right)}{\overline{h}_i(n-p)} \tag{28}$$

$$\rho = \frac{RMSE}{\overline{h}_i}\frac{1}{R+1} \tag{29}$$

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where h_i and t_i are the actual and predicted values for the i^{th} output, $\overline{h_i}$ and $\overline{t_i}$ are the average of the measured and predicted outputs, n is the total number of data and p is the number of predictor variables.

By using the above equations the values have been determined and it is tabulated in the following Table 1.

SOLUTIONS AND RECOMMENDATIONS

The regression modeling procedures utilized in this chapter convey the equations for future estimation on rate of medical waste generation. It depicts the path for easy management on the generated medical wastes. With any number of inputs, the predicted equation will provide the outcomes directly without any conditions. By predicting the rate of waste generation in smart cities, the authorities can perform flawless planning for storing, transportation and disposal of medical wastes. This will lead to the prevention of harm effects to human and environmental pollution.

FUTURE RESEARCH DIRECTIONS

The variation in the dataset ranges may lead to the inappropriate results. This can be resolved by the researchers in upcoming years. Various datasets can be collected and utilize the different procedures for foretelling the rate of medical waste generations. It is also suggested for the scientists to adopt various the adopted techniques for foretelling the generation of some other wastes like solid wastes, electronic wastes, agricultural wastes, radioactive wastes, construction and demolition wastes, etc. to escape from the ill effects for the smart cities and its citizens.

CONCLUSION

This chapter examines the capability of SVM, LSSVM and GP for prediction of rate of medical waste generation based on type of hospital, capacity and bed occupancy. The dataset plays a prominent role in the regression techniques. The dataset which goes beyond the adopted range may lead to inappropri-

Table 1. Statistical criteria's for the developed models

	SVM		LSSVM		GP	
	Training	**Testing**	**Training**	**Testing**	**Training**	**Testing**
RMSE	0.0229	0.0211	0.0043	0.0304	0.0125	0.3296
MAE	0.0079	0.0088	0.0030	0.0146	0.0106	0.2483
E	0.9804	0.9962	0.9993	0.9922	0.9941	0.0811
RSR	0.1401	0.0613	0.0263	0.0884	0.0767	0.9586
NMBE(%)	-4.5931	1.2095	0.0362	-0.5208	-0.4643	-59.5678
ρ	0.1333	0.0267	0.0249	0.0385	0.0727	0.4790

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ate result which could be the practical difficulty. The researchers can try to overcome this difficulty in future. The developed SVM, LSSVM and GP give elegant and encouraging performances. GP uses four tuning parameters, whereas SVM and LSSVM use 3 and 2 parameters. SVM and LSSVM outperform the GP model. The developed equations can be used practically. This chapter issues the robust models based on SVM, LSSVM and GP for prediction of rate of medical waste generation.

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KEY TERMS AND DEFINITIONS

Artificial Neural Network: Artificial Neural Network is a structure framed with densely interconnected with artificial neurons that performs the parallel computations for data processing and knowledge representations.

Estimation: The action of forecasting or predicting something is called as estimation.

Genetic Programming: Genetic programming (GP) is a systematic, domain-independent, evolutionary computation technique for computational problem solving.

Least Square Support Vector Machine: Least Square Support Vector Machine (LSSVM) least squares version of SVM. In this, the solutions can be obtained by solving the set of linear equations.

Medical Waste: Medical waste is all waste materials generated at health care facilities, such as hospitals, clinics, physician's offices, dental practices, blood banks, and veterinary hospitals/clinics, as well as medical research facilities and laboratories.

Support Vector Machine: Support Vector Machine (SVM) is supervised learning algorithm used for analyzing data and recognizes designs, also used for classification and regression analysis.

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Chapter 46
Heavy Metal Pollution and its Management:
Bioremediation of Heavy Metal

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ABSTRACT

Environmental degradation has become a major societal issue thanks to uncontrolled anthropogenic activity, besides natural factors. Entry of toxic heavy metals and minerals in human system mainly through contaminated water, food and air, leads to overt and insidious health problems. Heavy metal pollution, a global concern today, can be managed by using bioremediation, an eco-friendly alternative. Bioremediation is one of the most promising technological approaches to the problem of hazardous waste. It is a technology for removing pollution from environment, restoring contaminated site and preventing future pollution. Bioremediation can be performed in situ or ex situ. Microorganisms directly degrade contaminants rather than merely transferring them from one medium to another, employ metabolic degradation pathways and can be used in situ to minimize disturbance of the cleanup site. Hence, microorganisms can be effective, economical and non-disruptive tools for eliminating hazardous chemicals. Its advantage generally outweigh the disadvantage, therefore may be used as management tool.

1. BACKGROUND

The rapid industrial developments have led to the generation of huge quantities of hazardous wastes, which have further aggravated the environmental problems in the country by depleting and polluting natural resources. Therefore, rational and sustainable utilization of natural resources and its protection from toxic releases is vital for sustainable socio-economic development (Chakrabarti, 2006). Hazardous waste management is a new concept for most of the Asian countries including India. The lack of technical and financial resources and the regulatory control for the management of hazardous wastes in the past had led to the unscientific disposal of hazardous wastes in India, which posed serious risks to

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human, animal and plant life. A huge quantity of pollutants in the form of domestic and industrial effluents is discharged directly or indirectly into the water bodies, which has severe impacts on its biotic and abiotic environment. During rain, surface water with soil, mud and humus enter into the river, tanks and other water bodies. The soil is the target of thousands of contaminants that vary in composition and in concentration. The contaminants enter the system as a result of a wide range of actions such as intentional applications, inadequate residue disposal, accidental wastes and inappropriate use. Some human activities have resulted in the accumulation of metals in the environment. The inorganic minerals like sodium, potassium, calcium, magnesium and heavy metals like iron, manganese, lead, mercury, chromium, cadmium, nickel, cobalt, beryllium copper etc., when reach to the river with water cause water pollution. The use of various types of pesticides and insecticides in agriculture also cause water pollution. The pathogenic organisms of these wastes transmit to the water and pose serious problems (Batley, 1989; Garbarino et al., 1995; Jogdand, 1995; Agarwal, 1998; Hakeem & Bhatnagar, 2010).

2. WASTE AND ITS TYPE

Waste is an unavoidable by product of most human activity. Waste can be, in the form of solid or liquid, posed the harmful nuisance. Most solid waste is either sent to landfills or to incinerators. Ocean dumping has also been a popular way for coastal communities to dispose of their solid wastes in which large barges carry waste out to sea and dump it into the ocean. Most municipal and non municipal waste is sent to landfills. Landfills are popular because they are relatively easy to operate and can handle of lot of waste material. There are two types of landfills, sanitary landfills and secure landfills. Each day after garbage is dumped in the landfill, it is covered with clay or plastic to prevent redistribution by animals or the wind. In natural system, there is no such thing as waste. Everything flows in a natural cycle of use and reuse. Living organisms consume materials and eventually return them to the environment, usually in a different form, for reuse. Solid waste refers to a variety of discarded materials, not liquid or gas that is deemed useless or worthless. However, what is worthless to one person may be of value to someone else and solid wastes can be considered to be misplaced resources. Solid wastes are all the waste arising from human and animal activities that are normally solid waste and that are discarded as useless or unwanted. The term is all inclusive and it encompasses the heterogeneous mass of throwaways from the urban community as well as the homogeneous accumulations of agricultural, industrial and mineral wastes (USAID, 2004; Rajor & Kunal, 2011).

Electronic waste, e-waste, e-scrap or Waste Electrical and Electronic Equipment (WEEE) describe loosely discarded, surplus, outdated, broken, electrical or electronic devices. Electronic waste may be defined as all secondary computers, entertainment device electronics, mobile phones and other items such as television sets and refrigerators, whether sold, donated or discarded by their original owners. The processing of electronic waste in developing countries causes serious health and pollution problems because electronic equipment contains some very serious contaminants such as lead, cadmium, beryllium and brominates flame retardants. Electronic waste processing systems have matured in recent years, following increased regulatory, public and commercial scrutiny and a proportionate increase in entrepreneurial interest. In developed countries, electronic waste processing usually involves dismantling the equipment into various parts like metal frames, power supplies, circuit boards, plastics, by hand. The advantages of this process are the human's ability to recognize and save working and repairable parts, including chips,

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transistors, RAM, etc. It is a major area of concern today that the wealthy countries are dumping large quantities of e waste into the developing world. According to BBC, currently the companies export 80 percent of the world's electronic trash to Asia. The problem of e-waste recycling in India involved the urgent need for educating consumers including the potential threat to public health and the environment posed by their products and for raising awareness for the proper waste management (Kesselman, 2007; Dogbevi, 2007; Beary, 2008; Mcphate, 2008; Toxic Links, 2008; Pinto, 2009).

Liquid waste can be defined as such fluids as wastewater, fats, oils, grease or used oil. The disposal of such waste, such as transmission fluid, cooking oil, spent oil, fats or grease can contaminate the groundwater or negatively impact the wastewater system. The liquid waste basically the waste water discharged from the industrial and domestic area. Wastewater is water that has been used for some purpose and is deemed unfit for further use. In fact, wastewater can be used for secondary purposes in most cases. Also, efficient use of water reduces the amount of wastewater generated. Sewage is created by residences, institutions, hospitals and commercial and industrial establishments. Raw influent or sewage includes household waste liquid from toilets, baths, showers, kitchens, sinks and so forth that is disposed of via sewers. In many areas, sewage also includes liquid waste from industry and commerce. As rainfall runs over the surface of roofs and the ground, it may pick up various contaminants including soil particles and other sediment, heavy metals, organic compounds, animal waste, oil and grease. It may be originated from various sites and by different uses (US EPA, 2000; Central New York Regional Planning and Development Board, 2004; Massoud & Ahmad, 2005).

Municipal waste water is the combination of liquid or water carried wastes originating in the sanitary conveniences of dwellings, commercial or industrial facilities and institutions, in addition to any groundwater, surface water and storm water that may be present. Wastewater is the flow of used water from a community. The characteristics of the wastewater discharges vary from location to location depending upon the population and industrial sector served, land uses, groundwater levels and degree of separation between storm water and sanitary wastes. Domestic wastewater includes typical wastes from the kitchen, bathroom and laundry, as well as any other wastes that people may accidentally or intentionally pour down the drain. Sanitary waste water consists of domestic wastewater as well as those discharged from commercial, institutional and similar facilities. Industrial wastes will be as varied as the industries that generate the wastes. Municipal waste water also contains a variety of inorganic substances from domestic and industrial sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc etc (Xie et al., 1996, Ferrari et al., 1999).

3. INDUSTRIAL EFFLUENTS AND SOIL POLLUTION

Toxic chemicals found in wastewater pass through wastewater treatment facilities that have not been designed to remove them and can interfere with their operation. In a biological treatment process toxic materials can upset a treatment process or even kill the biological community and make the process ineffective. To remove the toxic pollutants at the treatment facility can be very costly. Therefore, it is generally advantages to remove them at the source. Source control can be achieved by the use of municipal by laws limiting pollutant discharges to the sewerage system. The removal of toxic pollutants at the source can be achieved by requiring treatment prior to discharge, recycling of waste by products, manufacturing process changes and the substitution of raw material (Thorpe, 2009).

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The effluent of the industries goes into the water system and changes the physico-chemical quality of water and also makes it unfit for drinking and other uses. Since all natural waterways contain bacteria and nutrients, almost any waste compounds introduced into such waterways will initiate biochemical reactions. These biochemical reactions are measured as BOD and COD in the laboratory. Both have been widely adopted as a measure of pollution effect. Disposal of wastewaters from an industrial plant is a difficult and costly problem. Most petroleum refineries, chemical and petrochemical plants have onsite facilities to treat their wastewaters so that the pollutant concentrations in the treated wastewater comply with the local or national regulations regarding the disposal of wastewaters into community treatment plants or into rivers, lakes or oceans. The solids can be suspended 30% as well as dissolved solids which are about 70%. The dissolved solids can be precipitated by chemical and biological processes. Organic components may consist of carbohydrates, proteins, fats and greases, surfactants, oils, pesticides, phenols etc. From a physical point of view the suspended solids can lead to the development of sludge deposits and anaerobic conditions when discharged into the receiving environment. Physically, the wastewater is usually characterized by grey colour, musty odour, 0.1% solid content and 99.9% water content (Tchobanoglous, 1987; Tchobanoglous et al., 2003; Clair, 2003; Maiti, 2004).

The soil is the target of thousands of contaminants that vary in composition and in concentration. The contaminants enter the system as a result of a wide range of actions such as intentional applications, inadequate residue disposal, accidental wastes and inappropriate use. Soil pollution is defined as the buildup in soils of persistent toxic compounds, chemicals, salts, radioactive materials or disease causing agents, which have adverse effects on plant growth and animal health. Soil is the thin layer of organic and inorganic materials that covers the earth's rocky surface. The organic portion, derived from the decayed remains of plants and animals, is concentrated in the dark uppermost topsoil. The inorganic portion, made up of rock fragments, was formed over thousands of years by physical and chemical weathering of bedrock. Soil pollution is caused by the presence of manmade chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage links, application of pesticides and percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. This occurrence of this phenomenon is correlated with the degree of industrialization and intensities of chemical usage. The waste contaminates the soil. The solid waste includes garbage, domestic refuse and discarded solid materials such as those from commercial, industrial and agricultural operations. They contain increasing amounts of paper, cardboards, plastics, glass, old construction material, packaging material and toxic or otherwise hazardous substances (Knaebel et al., 1994; Franklin Associates, 1996).

Some human activities have resulted in the accumulation of metals in the environment. Both soil and aqueous effluents have been contaminated with heavy metals as the result of numerous industrial activities, including mining, smelting, jewelry, automobile battery production, vehicle emission and land filling of industrial waste and fly ash from incineration process. This contamination of the environment poses serious health threats to humans and animals, as these heavy metals tend to persist in the environment indefinitely. This kind of contamination presents a challenge, as the presence of heavy metals in soils and aqueous effluents leads to serious problems because they cannot be biodegraded. In this case, the metal ion can only be converted to the base metal, methylated, precipitated, volatilized or complexed with an organic ligand. The more common heavy metals associated with anthropogenic activities include

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lead, cadmium, copper, chromium, nickel, iron, mercury and zinc. Methods of treating the contaminated effluents currently consist of chemical precipitation, solvent extraction, dialysis, electrolytic extraction, cementation, reverse osmosis, evaporative methods, ion exchange resins, carbon adsorption and dilution (USEPA, 2000; European Union, 2002).

4. HEAVY METALS

Metals play an integral role in the life processes of living organisms. Some metals like Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni and Zn are essential, serve as micronutrients and are used for redox processes, to stabilize molecules through electrostatic interactions; as components of various enzymes and regulation of osmotic pressure. The essential metals must be present in a certain concentration range. Too low concentrations of heavy metals lead to a decrease in metabolic activity and too high concentrations, it leads to toxicity. While other metals like Ag, Al, Cd, Au, Pb and Hg have no biological role and they are non essential. Nonessential metals are tolerated at very low concentrations and inhibit metabolic activity at higher concentrations. They are potentially toxic to living organism specially microorganisms. Toxicity of non essential metals occurs through the displacement of essential metals from their native binding sites or through ligand interactions. The many uses of heavy metals in several applications lead to wide distribution in soil, silt, waste and waste water. Such pollution of the environment by toxic metals and radionuclide arises as a result of many human activities, largely industrial, although such sources as agriculture and sewage disposal also contribute. Heavy metal contamination can be a consequence of industrial activities that eliminate residues in the soil that in long terms, promote their accumulation. Heavy metals in wastewater come from industries and municipal sewage and they are one of the main causes of water and soil pollution. The majority of the sources are originated by human actions like metal manufacture and mining industries with storage, disposal and transportation problems. Among the metals found more frequently there are Cd, Pb, Co, Cu, Hg, Ni, Si and Zn. For Cd, Pb, Cu and Zn, their toxicity increases as follows: Pb < Zn < Cu < Cd, depending on countless abiotic and biotic factors (Lloyd et al., 2001; Glick, 2003; Zenker et al., 2005).

Both soil and aqueous effluents have been contaminated with heavy metals as the result of numerous industrial activities, including mining, smelting, jewelry, automobile battery production, vehicle emission and land filling of industrial waste and fly ash from incineration process. This contamination of the environment poses serious health threats to humans and animals, as these heavy metals tend to persist in the environment indefinitely. Metals play an integral role in the life processes of living organisms. Some metals like Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni and Zn are essential, serve as micronutrients and are used for redox processes, to stabilize molecules through electrostatic interactions; as components of various enzymes and regulation of osmotic pressure. The essential metals must be present in a certain concentration range. Too low concentrations of heavy metals lead to a decrease in metabolic activity and too high concentrations, it leads to toxicity. While other metals like Ag, Al, Cd, Au, Pb and Hg have no biological role and they are non essential. In order to survive in heavy metal polluted environments, many microorganisms have developed means of resistance to toxic metal ions. These mechanisms include metal exclusion by permeability barriers, active transport of the metal away from the cell organism, intracellular sequestration of the metal by protein binding, extracellular sequestration, enzymatic detoxification of the metal to a less toxic form and reduction in metal sensitivity of cellular targets. Most microorganisms are

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known to have specific genes for resistance to toxic ions of heavy metals. Mostly, the resistance genes are found on plasmids or on chromosomes. Plasmid encoded metal resistance determinants have been reported to be inducible (Nies & Silver, 1995; Rosen, 2002).

The intake of heavy metal ions by microbial strains normally includes a redox reaction involving the metal. Some bacteria use heavy metals for energy and their growth. Bacteria that are resistant to heavy metals also play an important role in biogeochemical cycling of metal ions. Since, the oxidation state of a metal ion may determine its solubility, many scientists have been attempting to use microbes that are capable to oxidize or reduce metals in order to remediate metal contaminated sites. Although, some heavy metals are important and essential trace elements and others are toxic at high concentrations to microbes, some microbes have adapted to tolerate the presence of metals or even to use them to grow. In addition, a number of interactions between microbial strains and metals have important environmental and health implications. Health problem due to heavy metals pollution in human being include nausea, vomiting, bone complications, nervous system impairments and even death become a major problem throughout many countries when metal ions concentration in the environment exceeded the admissible limits. Due to that, various treatment technologies had been searched to reduce the concentration of heavy metals in the environment (Nies, 1999; Lodeiro et. al., 2006).

It is needed to remove the heavy metals from the contaminated sites/waste. Several heavy metals removal technologies including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultra filtration and pyhtoremediation are commonly used in industries. However, these technologies are becoming uneconomical and unfavorable to remove heavy metals from industrial wastewaters. The development of new treatment method such as bioremediation to remove heavy metal ions from wastewater and solid waste which could be cost effective and more efficient has spurred to overcome the conventional method. Bioremediation technology has received much attention as it offered low cost technique and non hazardous biomaterials (Lovley, 1997; Ahalya et al., 2003).

5. BIOREMEDIATION

The history of bioremediation is considerably shorter and it reflects many upturns and downturns as a result of political and economic forces. Interest in use of microorganisms to degrade specific hazardous organic chemicals probably dates back to Gayle (1952), who proposed the microbial infallibility hypothesis. Gayle postulated that for any conceivable organic compound, there exists a microorganism that can degrade it under the right conditions. If not, evolution and adaptation would produce such a strain. This hypothesis cannot wrong, because failure to degrade a contaminant can be attributed to the researcher's failure to use the right strain under the right condition. In 1970s, environmental statutes of unprecedented scope passed, such as the Occupational Safety and Health Act (OSHA) of 1970, the Clean Air Act (CAA) of 1970, the Clean Water Act (CWA) of 1972, the Safe Drinking Water Act (SWA) of 1974 and the Toxic Substance Control Act (TSCA) of 1976. This regulatory pressure stimulated interest in site remediation technologies, including bioremediation. However, bioremediation failed to meet the expectations raised by many technology salespeople, who commonly advocated the addition of specialized bacteria to contaminated site i.e. bioaugmentation. Early proponents of this approach generally did not recognize that indigenous bacteria already present at a contaminated site where probably better predisposed physiologically and genetically to mediate the degradation of the target pollutants. The first patent for a biological remediation agent was registered in 1974, being a strain of *Pseudomonas putida*

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that was able to degrade petroleum. In 1991, about 70 microbial genera were reported to degrade petroleum compounds and almost an equal number has been added to the list in the successive two decades. Bioremediation can occur naturally or through intervention processes. Natural degradation of pollutants relies on indigenous microflora that is effective against specific contaminants and it usually occurs at a slow rate. With intervention processes, the rate of biodegradation is aided by encouraging growth of microorganisms, under optimized physico-chemical conditions. Microorganisms play a vital role in heavy metal contaminated soil and wastewater by the mechanisms of biosorption. Some microorganisms possess an astonishing catabolic versatility to degrade or transform such compounds. The need for economical, effective and safe methods for removing heavy metals from wastewater has resulted in the search for unconventional materials that may be useful in reducing the levels or accumulation of heavy metals in the environment (US Congress, 1991; Agarwal, 1998; Bouwer et al., 1998; Smith et al., 1998).

Bioremediation is the use of living microorganism to reduce the environmental pollution. It is a technology for removing pollution from the environment, restoring contaminated site and preventing future pollution. Bioremediation can be performed in situ or ex situ. With the onset of the Industrial Revolution, an ever increasing proportion of the earth's surface became contaminated with natural and xenobiotic toxic chemicals. The basic principle of bioremediation involves utilizing the activity of microorganisms naturally present in the soil and water or selected organisms inoculated into the environment, to biodegrade or detoxify contaminating compounds in situ. In the majority of cases a consortium of microorganisms will be involved in the biodegradation of the contaminant, rather than a single species. To optimize the process, promotion of the growth of indigenous microorganisms is necessary. It can be achieved by the addition of key nutrients such as nitrogen and phosphorus, which are normally present in growth limiting concentrations. This enables the natural microbial flora to develop and metabolize the contaminant (Vidali, 2001).

Alternatively, known biodegraders of the contaminant that have been identified, isolated and their activities optimized can be used as an inoculants. For example, a recent addition to the growing list of microorganisms able to sequester or reduce metals is *Geobacter metallireducens*. This bacterium can remove uranium, a radioactive waste, from drainage waters in mining operations and from contaminated ground waters. However, the most radiation resistant bacterium known is *Deinococcus radiodurans*; this organism is also being developed to help clean up soil and water contaminated by solvents, heavy metals and radioactive waste. A genetically engineered strain of *D. radiodurans* has been produced which can detoxify mercury (genes derived from *Escherichia coli*) and degrade toluene (genes derived from *Pseudomonas putida)* in radioactive environments (Bouwer & Zehnder, 1993; Bernard et al., 2007).

6. REQUIREMENTS OF BIOREMEDIATION

Bioremediation is a fairly new technology and holds the promise of becoming the solution to our polluted environment. This new technology gives us alternative routes to cleaning up contaminated sites was thought to be not possible previously. Nonetheless, the technology of bioremediation still has a long way more to go). Bioremediation faces several challenges and some of the most common ones are deficit of knowledge, lack of integrated research, lack of revenue and inadequate tool and infrastructure (Aksu, 1998; Vidali, 2001; Ahluwalia & Goyal, 2007). A deficit of knowledge on the different fundamental branches of sciences that are involved in the process of bioremediation hinders the progress of bioremediation. Examples of the different disciplines of sciences are such as structural and molecular biology,

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microbiology, genomics, geochemistry, along with hydrology and transport processes. To date, little is known on how introduced microorganisms interact with different hydrological environment. Research in each of the variety of fields is needed to further researchers' comprehension on the actual activity or rather, the chemistry that is involved and interactions between contaminants, native organisms on site and remedial organisms. There is still much to learn and gain from research as contaminated sites are complex systems, each composed of different types of contaminants, diverse organisms and dissimilar environment (Doyle, 1989; Prescott, 2002). Bioremediation is a multidisciplinary field and researchers from various fields need to integrate their knowledge. The success and efficiency of bioremediation requires the involvement of microbiologists, biochemists, engineers, geologists and soil scientists among others. Knowledge on the combined factors is not enough and mostly these are the rate limiting factors of the process of bioremediation. Interdisciplinary research of at the least two fields is unavoidable to advance this technology. Assimilation of scientific ideas across disciplines is most needed to optimize the potential of bioremediation (Blackburn & Hafker, 1993; Boopathy, 2000; Bernard & Jack, 2007). There is no doubt that governmental and private sectors are investing on biotechnology companies but not much of the revenue goes to the improvement of bioremediation. Lack of revenue is an obstruction to advancement in bioremediation as it prevents further research and discoveries from taking place. Thereupon, progress of bioremediation is delayed as a result of material deficiency (Gadd, 1988; Bouwer & Zehnder, 1993). Infrastructure and materials are needed to carry out research. Accuracy in experimental procedures is crucial to ensure successful treatment when introduced to contaminated site. However, there is inadequacy of infrastructure to analyze the conditions of contaminated sites as well as monitor the process of degradation that has been introduced to the site. Insufficiency of advanced tools specifically designed to aid research on bioremediation would also hold back development of research methodology and prevent discoveries from happening. Despite its shortcomings, its pertinence in this world is unquestionable in the light of present day environmental hazards. Bioremediation provides a technique for cleaning up pollution by enhancing the same biodegradation processes that occur in nature and potential for significant advances (Bouwer et al., 1998; Boopathy, 2000; Chatterjee et al., 2008; Shazia et al., 2009; Hakeem & Bhatnagar, 2010).

7. METAL TOXICITY AND MANAGEMENT

The pollution of the environment with toxic heavy metals is spreading throughout the world along with industrial progress. Effluents from textile, leather, tannery, electroplating, galvanizing, dyes and pigment, metallurgical industries and other metal processing and refining operations at small and large scale sector contains considerable amounts of toxic metal ions (White et al., 1995). Cadmium, chromium, cobalt, copper, iron, manganese, mercury, molybdenum, nickel, silver and zinc are known to be the most commonly heavy metals used and the more widespread contaminants of the environment (FWPCA, 1998). Traces of these heavy metals are necessary as co-factors of enzymatic reactions, but high levels of them may cause extreme toxicity to living organisms due to inhibition of metabolic reactions. Many compounds that are legally considered to be hazardous can be transformed to harmless products. This eliminates the chance of future liability associated with treatment and disposal of contaminated material. Instead of transferring contaminants from one environmental medium to another from land to water or air, the complete destruction of target pollutants is possible (Agarwal, 1998).

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Arbitrary and hysterical discharge of industrial and urban wastes into the environmental sink has become an issue of major global concern. Intensification of agriculture and manufacturing industries has resulted in increased release of a wide range of xenobiotic compounds to the environment. Excess loading of hazardous waste has led to scarcity of clean water and disturbances of soil, thus limiting crop production. Although enactment of stringent regulation has led to less indiscriminate disposal of organic and inorganic wastes, challenges remain that require other intervention (Hess et al., 1997). Waste comprises liquid waste discharged by domestic residences, institutions, hospitals, commercial properties, industry or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewater from different sources. Raw influent includes household waste liquid from toilets, baths, showers, kitchens, sinks and so forth that is disposed to the river via sewers. This affects the BOD, COD, turbidity and also causes the physico-chemical changes in the river. In many areas, sewage also includes liquid waste from industry and commerce. As rainfall runs over the surface of roofs and the ground, it may pick up various contaminants including soil particles and other sediment, heavy metals, organic compounds, animal waste and oil and grease (APHA, 1995; 1998; FWPCA, 1998). The metal ions from metal mining pose problems to the water environment by discharging mine water from underground and open pit mines (Knaebel, 1994). Leachate water and runoff water from overburden/waste rock dumps also contaminate nearby water streams (Ferrari et al., 1999). The principle pathways by which leached contaminants can enter into groundwater are leakage or spills from storage ponds, leach pad liners, storm water run on/off, uncontrolled leaching from heaps and dumps. These toxic metals ions not only cause potential human health hazards but also affect other life forms (Malik, 2004). Heavy metal pollution usually results from electroplating, plastic manufacturing, fertilizer, pigment industries, mining and metallurgical processes (Nirmal Kumar et al., 2009).

Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The major causes of emission are the anthropogenic sources specifically mining operations (Hutton & Symon, 1986; Nriagu, 1989). Much of the metal salts within the oceans, lakes, streams and estuaries are in the form of magnesium, calcium, potassium and sodium salts. While many other constituents are clearly available in solution, no element having a concentration less than 2 nmol in the ocean is generally considered essential for life. The metals cannot degraded to harmless products and hence persist in environmental indefinitely (Silver, 1996). The metals leached out and in sloppy areas, are carried by acid water downstream or run-off to the sea. Through mining activities, water bodies are most emphatically polluted (INECAR, 2000; European Union, 2002). The heavy metals refer to any metallic element that has a relatively high density than $5g/cm^3$, is toxic or poisonous even at low concentration and its pollution is the major concern faced by the society today (Aksu, 1998; Nies, 1999). Heavy metals are on the forefront of academic and regulatory concern, since millions of gallon of water containing toxic heavy metals are generated annually from several metal processing industries and discharged into the environment (Gardea et al., 2005).

Metals discharged into water bodies are not biodegraded but undergoes chemical or microbial transformations, creating large impact on the environment and public health. Heavy metals influence the microbial population by affecting their growth, morphology, biochemical activities and ultimately resulting in decreased biomass and diversity (Roane and Pepper, 2000). The microorganisms respond to the heavy metals by several processes; including transport across the cell membrane, biosorption to the cell walls and entrapment in extracellular capsules, precipitation, complexation and oxidation-reduction reactions (Veglio et al., 1997). The discharge of wastewater containing high concentrations of heavy metals

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to receiving water bodies has serious adverse environmental effects. Their occurrence and accumulation in the environment is a result of direct or indirect human activities, such as rapid industrialization, urbanization and anthropogenic sources (EPA, 2000; Hussein et al., 2005; Gardea et al., 2005). Metals, when present in our body, are capable of causing serious health problems by interfering with our normal body functions. Some metals are useful to the body in low concentrations like arsenic, copper, iron and nickel but are toxic at high concentrations. Other metals like aluminum, beryllium, cadmium, lead and mercury have no biological functions and are highly toxic disrupting bodily functions to a large extent (European Union, 2002).

The most metal ions have to enter the microbial cell for its physiological or toxic effect. Usually, microorganisms have solved the problem by using two types of uptake systems for metal ions. One is fast, unspecific and driven by the chemiosmotic gradient across the cytoplasmic membrane of bacteria. The second type of uptake system has high substrate specificity, is slower, generally uses ATP hydrolysis as the energy source and is only produced by the cell in times of need, starvation or a special metabolic situation (Nies & Silver, 1995; Nies, 1999). Heavy metals contamination is becoming a great concern to the environmental awareness and government policies. Several heavy metals removal technologies including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration and phytoremediation are commonly used in industries (Ahalya et al., 2003). However, these technologies are becoming uneconomical and unfavorable to remove heavy metals from industrial wastewaters. With increasing environmental attention and legal constraint on discharge effluents, a need of cost effective technologies are essential (Agarwal, 1998). Therefore, the search for efficient, eco-friendly and cost effective remedies for wastewater treatment has been initiated. In recent years, research attention has been focused on biological methods for the treatment of effluents, some of which are in the process of commercialization (Prasad and Freitas, 2003). Removal of heavy metals remains a major challenge in environmental biotechnology. The pollutants generally include organic wastes and heavy metals. Heavy metal removal is important for survival of the environment (Lenntech, 2004; Gardea et al., 2005).

There are three principle advantages of biological technologies for the removal of pollutants; first, biological processes can be carried out in situ at the contaminated site; second, bioprocess technologies are usually environmentally benign, no secondary pollution and third, they are cost effective. Of the different biological methods, bioaccumulation and biosorption have been demonstrated to possess good potential to replace conventional methods for the removal of metals (Volesky, 1995, King et al., 1997). Microorganisms are critical to nutrient recycling in ecosystems as they act as decomposers. Researchers develop a feasible method to accelerate the process of decay and removal by encouraging the microbial and associated flora and fauna within the ecosystem to accumulate, degrade and remove the pollutants from the identified sites (Vidali, 2001; Ahalya et al., 2003; Dubey, 2004). Bioremediation is the use of biological systems, almost invariably microorganisms to clean up a contaminated site. In bioremediation processes, microorganisms use the contaminants as nutrient or energy sources. Bioremediation uses naturally occurring or genetically engineered microorganisms such as bacteria and fungi to transform harmful substance into less toxic or non-toxic compounds. Compared to other methods, bioremediation is a more promising and less expensive way for cleaning up contaminated soil and water (Hess et al., 1997; Agarwal, 1998; USEPA, 1999; Kamaludeen et al., 2003; Tang et al., 2007).

In bioremediation, solubilization of heavy metal contaminants provides a means of removal from the solid substance. Some microbial species subject heavy metal ions to enzymatic reduction, the reduced form of heavy metal ions are quite insoluble and they precipitate out of solution (Nies, 1999). Most microorganisms can reproduce rapidly and microbes such as bacteria can also freely exchange genes

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by conjugation, transformation and transduction between widely divergent species. The organisms that are utilized vary, depending on the chemical nature of the polluting agents and are to be selected carefully as they only survive within a limited range of chemical contaminants (Shazia et al., 2009). Contaminant compounds are transformed by living organisms through reactions that take place as a part of their metabolic processes. Biodegradation of a compound is a result of the actions of multiple organisms. When microorganisms are imported to a contaminated site to enhance degradation, the process is known as bioaugmentation (Agarwal, 1998). Bioremediation is the process whereby organic wastes are biologically degraded under controlled conditions to an innocuous state or to levels below concentration limits established by regulatory authorities. Bioremediation is the elimination or reduction of toxic pollutant from the contaminated sites with the help of biological organisms such as bacteria, fungi and plants by degradation, assimilation or transpiration in the atmosphere. Moreover, the toxicity of heavy metals in wastewater was shown to be dependent on factors like metal species and concentration, pH, wastewater pollution load and solubility of the metal ions (Vidali, 2001; Strong and Burgess, 2008). Organic contaminants may be degraded biologically and CO_2 and H_2O are the final products, which are not hazardous and may be recycled. In contrast to toxic organic and inorganic substances, the metallic species released into the environment cannot be degraded biologically, chemically or physically (Singh and Ward, 2004). Bioaccumulation is the accumulation of materials which are not critical components of an organism by that organism. Usually, it refers to the accumulation of metals. Heavy metal ions accumulate in microbial cells through membrane transport proteins by active transport. Various microbial species including bacteria, fungi, algae and actinomycetes have been shown to be efficient in bioaccumulation of heavy metal ions from polluted effluents (Wong et al., 1993). The bioremediation of heavy metals using microorganisms has received a great deal of attention in recent years, not only as a scientific novelty but also for its potential application in industry. Metal accumulative bioprocess generally falls into one of two categories; biosorptive uptake by nonliving, non-growing biomass or biomass products and bioaccumulation by living cells (Aksu, 1998). Microbes can remove heavy metals from contaminated solutions either by bioaccumulation, precipitation or biosorption. In comparison with biosorption, bioaccumulation is a growth dependent process. Since, bioremediation is based on natural attenuation, therefore, it is considered more acceptable than other technologies. Most bioremediation systems are run under aerobic conditions, but running a system under anaerobic conditions may permit microbial organisms to degrade otherwise recalcitrant molecules (Bernard & Jack, 2007, Ke et al., 2009).

The foundation of bioremediation has been the natural ability of microorganisms to degrade organic compounds (Mostafa et al., 1992). This technology is based on the use of naturally occurring or genetically engineered microorganisms to restore contaminated sites and protect the environment. As bioremediation can be effective only where environmental conditions permit microbial growth and activity, its application involves the manipulation of environmental parameters to allow microbial growth and degradation to proceed at a faster rate. Like other technologies, bioremediation has its limitations (Teresa & Lee, 1994). Some contaminants, such as chlorinated organic or high aromatic hydrocarbons, are resistant to microbial attack. Most frequently, in situ bioremediation is applied to the degradation of contaminants in saturated soils and groundwater. It is a superior method to cleaning contaminated environments. Since, it is cheaper and uses harmless microbial organisms to degrade the chemicals. Chemotaxis is important to the study of in situ bioremediation because microbial organisms with chemotactic abilities can move into an area containing contaminants. So by enhancing the cells' chemotactic abilities, in situ bioremediation will become a safer method in degrading harmful compounds (Takehiko, 2004).

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Microbes able to degrade the contaminant increase in numbers when the contaminant is present and when the contaminant is degraded, the biodegradative population declines (Bernard and Jack, 2007). Theoretically, bioremediation is useful for the complete destruction of a wide variety of contaminants.

8. BIOLOGICAL TREATMENT

Recent studies in molecular biology and ecology offers numerous opportunities for more efficient biological processes. Notable accomplishments of the studies include the cleanup of polluted water and land areas. Bioremediation leads to changes in the solubility, sorption characteristics, transport properties and toxicity metals. It promotes the growth of microorganisms to degrade contaminants by utilizing those contaminants as carbon and energy sources (Teresa & Lee, 1994). The bioremediation systems in operation today rely on microorganisms native to contaminated sites, encouraging them to work by supplying them with the optimum levels of nutrients and other chemicals essentials for their metabolism (Shazia et al., 2009). Microorganisms can be isolated from almost any environmental conditions (Holt et al., 1994). The search for alternative and innovative treatment techniques has focused attention on the use of biological materials such as algae, fungi, yeast and bacteria for the removal and recovery technologies and has gained importance during recent years because of the better performance and low cost of the biological materials. Since, numerous types of pollutants are to be encountered in a contaminated site, diverse types of microorganisms are likely to be required for effective mediation (Gogoi et al., 2003). Microbes can adapt and grow at subzero temperatures, as well as extreme heat, desert conditions, in water, with an excess of oxygen and in anaerobic conditions, with the presence of hazardous compounds or on any waste stream. The main requirements are an energy source and a carbon source (Teresa & Lee, 1994). In situ biodegradation involves supplying oxygen and nutrients by circulating aqueous solutions through contaminated soils to stimulate naturally occurring bacteria to degrade organic contaminants. It can be used for soil and groundwater. *In situ* bioremediation means there is no need to excavate or remove soils or water in order to accomplish remediation. Generally, this technique includes conditions such as the infiltration of water containing nutrients and oxygen or other electron acceptors for groundwater treatment. Bioremediation can be carried out on site without causing a major disruption of normal activities (Thassitou & Arvanitoyannis, 2001). This also eliminates the need to transport quantities of waste off site and the potential threats to human health and the environment that can arise during transportation. Bioremediation can prove less expensive than other technologies that are used for clean-up of hazardous waste (Singh & Ward, 2004; Ramirez et al., 2009). The complex structure of microorganisms implies that there are many ways for the metal to be taken up by the microbial cell (Volesky & Holan, 1995). The presence and activity of microorganisms in biological wastewater treatment are vital to the process. With regard to microbial removal of heavy metals, biosorption phenomenon is crucial (Knauer et al., 1997). The mechanism by which microorganisms remove heavy metals can be divided into three categories; the first mechanism is the biosorption of metals ions on the cell surface, second intracellular uptake of metals ion and third chemical transformation of metal ions by microorganism (Pardo et al., 2003). Among the different technique employed for metals removal from multi elemental system, biosorption has been found to be highly selective. Furthermore, the metal accumulating bacteria can be used to remove, concentrate and recover metals from industrial effluents (Loick et al., 2009).

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9. BIOSORPTION

Biosorption is a metabolism independent binding of heavy metals to living cells, non living biomass or microbial extracellular pathways resulting in bioprecipitation of heavy metals or their mechanisms of removal (Cotoras et al., 1993). The mechanism of metal biosorption is a complicated process, mainly ion exchange, chelations, adsorption by physical forces, entrapment in inter and intrafibrilliar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes. In metal biosorption process by living cells, the metal ions are adsorbed to the surface of cells by interactions between metals and functional groups displayed on the surface of cells. All the metal ions before gaining access to the cell membrane and cell cytoplasm come across the cell wall. The cell wall consists of a variety of polysaccharides and proteins and which acts as active sites of binding metal ions. The mechanism of metal biosorption can be influenced by the status of biomass, living or non-living, types of biomaterials, properties of metal solution chemistry, ambient/ environmental conditions such as pH (Gee & Dudeney, 1998). There are several chemical groups that would attract and sequester the metals in biomass such as acetamido groups of chitin, structural polysaccharides of fungi, amino and phosphate groups in nucleic acids, amido, amino, sulphhydryl and carboxyl groups in proteins, hydroxyls in polysaccharide and mainly carboxyls and sulphates in polysaccharides of marine algae that belong to the divisions Phaeophyta, Rhodophyta and Chlorophyta (Diels et al., 2002). It does not necessarily mean that the presence of some functional group guarantees biosorption, perhaps due to steric, conformational or other barriers (Gunasekaran et al., 2003).

Difference in the cell wall composition among the different groups of microorganisms, viz. algae, bacteria, cyanobacteria and fungi, cause significant differences in the type and amount of metal ion binding to them. The potential metal binding groups in this class of microbes are carboxylates, amines, imidazoles, phosphates, sulfhydryls, sulfates and hydroxyls (Giller et al., 1998). The amines and imidazoles groups are positively charged when protonated and may build negatively charged metal complexes. Cell walls of bacteria are principally composed of peptidoglycans which consist of linear chains of the disaccharide N-acetylglucosamine (Gunasekaran et al., 2003). Heavy metal binding by biopolymers happens by chance and the relative removal efficiency depends upon the metal species and concentration, the reactivity of the available biopolymers or biomass and the composition of other wastewater components. Moreover, surface exposure of metal binding biopolymers improves the metal binding properties of microorganisms based not only on biosorption but also on microbial metabolic activities. Biosorption of heavy metals by microbial cells has been studied extensively as an alternative technology for the treatment of wastewaters. It is a promising process that can reduce capital costs by 20%, operational costs by 36% and total treatment costs by 28%, compared with conventional systems (Loukidou et al., 2004).

Microbes are exploited by people in biotechnology, both in traditional food and beverage preparation and in modern technologies based on genetic engineering (Giller et al., 1999). Bacteria, like the more complex eukaryotic organisms, have all the inner workings for cell function, cellular division and growth, genetic transcription, translation and energy production (Silver et al., 1990). All of this activity within a single bacterium typically takes place within a volume of 1.5-2.0 μm^3. How the bacteria alter their environment is equally important as how they are impacted by their surroundings. Much of this interaction takes place throughout and external to the outer structures. The enveloping layers that make up the outer structures of the bacterial cell consist of a cytoplasmic membrane, a capsule, sheaths, an S-layer and flagella (Beveridge, 1985). The cell wall consists primarily of a cytoplasmic membrane and a thick layer of peptidoglycan. All cells have a highly selective permeable barrier known as the cyto-

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plasmic membrane, separating the life sustaining metabolic activity of the cell from its environment and allowing all food materials, nutrients and waste products to pass (Silver, 1996). The metals can be captured in the outer portions of the cell such that the organism can be considered to be continuously enveloped in a brine of various ions. This phenomenon of capturing metals can act as the first step in the bacteria's active accumulation and assimilation of metals at various concentrations. This concentration of metal ions may have developed as a method for accumulating essential cations, if the bacteria find itself in a more dilute environment. The outer membrane may also immobilize heavy metals, thus preventing their penetration into the cell. Microorganisms' ability to oxidize metals plays an important role in the biological cycling of metals on a global scale. Microorganisms are also considered for their ability to accumulate metal ions within and on the membrane surface of the cell. Such interactions are so predominant that they can be utilized for economic or ecological gain (Sattelmacher, 2001).

Bacterial and fungal survival in the presence of toxic metals mainly depends on intrinsic biochemical and structural properties, physiological and genetically adaptation, including morphological changes and environmental modification of metal speciation, availability and toxicity, the relative importance of each being difficult to determine. It is probably more appropriate to define resistance by means of a mechanism produced in direct response to the metal species concerned, e.g. synthesis of metallothioneins (Eccles & Hunt, 1986; Gadd, 1992). Arbitrary terms such as resistance and tolerance which are used rather loosely and interchangeably in the literature are generally based on the ability to grow on a certain metal concentration in laboratory media (Ehrlich, 1997). Metal tolerance may be defined as the ability of an organism to survive metal toxicity by means of intrinsic properties and/or environmental modification of toxicity. Intrinsic properties that can determine survival include possession of impermeable pigmented cell walls, extracellular polysaccharide and metabolite excretion, especially where this leads to detoxification of the metal species by binding or perception (Aksu, 1998; Giller et al., 1999). However, in many cases distinctions are difficult because of the involvement of several direct and indirect physico-chemical and biological mechanisms implicated in fungal survival as distinct from environmental modification of toxicity include extracellular precipitation, complextion and crystallization, transformation of metal species by oxidation, reduction, methylation and dealkylation, biosorption to cell walls, pigments and extracellular polysaccharide, decreased transport or impermeability, efflux, intracellular compartmentation and precipitation and/or sequestration. A particular organism may directly and/or indirectly rely on several survival strategies (Peng et al., 2010).

The heavy metal removal from water and wastewater is crucial to protect the water environment from the heavy metal pollution. The heavy metal resistant microorganisms have significant role in bioremediation (Zouboulis et al., 2004; Peng et al., 2010). The metal and organic pollutants can be removed by the microbial flora. *Bacillus sp.* was very much efficient to remove the Au, Cd, Cr, Fe, Mn, Ni, Pb, U and Zn. It was recorded that *Bacillus sp.* can efficiently removed the metal pollutants from the waste or industrial effluents (Gunasekaran et al., 2003) and some aromatics, long chain alkanes, phenol, cresol (Cybulski et al., 2003). *Pseudomonas sp.* were reported to Cd, Cr, Cu, Ni, Pb, U and Zn (Sar and D'Souza, 2001; Tarangini, 2009). Ilhan et al., (2004) observed that *Staphylococcus saprophyticus* reduced Cr, Cu and Pb ions. The isolate was adsorbed 100% Pb ions at different pH range of 3-5 and at 27^0C temperature. *Corynebacterium sp.* and *Flavobacterium sp.* were reported for removal of organic contaminants and halogenated hydrocarbons, phenoxyacetaes and aromatic hydrocarbons (Jogdand, 1995). *Corynebacterium glutamicum* was able to reduce the thorium and uranium (Tarangini, 2009). The biosorption of heavy metal Cd and Cu by *Flavobacterium sp.* was reported by Rajbanshi, (2008) whereas, biosorption of Cu, Fe and Zn by *Corynebacterium sp.* was reported by Odokuma, (2009). Many investigators

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(Mattuschka et al., 1993; Jogdand, 1995; Tarangini 2009) reported that *Streptomyces sp.* can be used to remove the metal ions of Ag, Cd, Cu, Cr, Ni, Pb, U and Zn from the waste. *Streptomyces noursei* was able to reduce the metal ions in order Pb>Ag> Cu>Cr (Mattuschka et al., 1993). *Aspergillus niger* was reported to remove Ag, Au, Cd, Cu, Th, U and Zn (Townsley et al., 1986; Kuyucak & Volesky, 1988; Gunasekaran et al., 2003). *S. meliloti* has huge potential to reduce the toxicity from the environment reported by Chauhan (2015). Biosorption is being established as a useful alternative to conventional systems for the removal of toxic metals from industrial effluents/waste. Bioremediation provides a technique for cleaning up pollution by enhancing the natural biodegradation processes. So, by developing an understanding of microbial communities and their response to the natural environment and pollutants, expanding the knowledge of the genetics of the microbes to increase capabilities to degrade pollutants, conducting field trials of new bioremediation techniques which are cost effective and dedicating sites which are set aside for long term research purpose, these opportunities offer potential for significant advances (Sutar & Das, 2012).

More research is needed to assess the extent to which these products affect human health. Public awareness should be created. There should be monitoring and control over the concentration of heavy metals in cosmetics. The existence of metals in nano form or otherwise should be determined. Toxicity of metals bearing nano particles is a domain where systematic research needs to be carried out to establish or negate toxic factors. Susceptibility to toxicity is influenced by age, physiological status, nutrition status and genetic factors. More research is needed to study these interactions, particularly since malnutrition is rampant in India. Where specific interactions are known *e.g.* lead and calcium, fluoride and calcium, populations exposed to these toxic substances (factory workers, communities living near the factories) should receive periodic health check-up and nutritional support. Health monitoring of workers engaged in industries handling toxic metals/ minerals should be carried out regularly and nutritional support where necessary provided. Since toxicity is insidious, mechanisms for early detection of the problem at subclinical level through proper surveillance systems are needed. More research is needed to identify and develop bacteria, plant, and fish-based tests. Functional consequences which may not be too obvious, like effects on reproductive, neurological-cognitive and other functions have to be identified, through more research on animals and humans under controlled conditions. A few recommendations are given below to reduce the heavy metal pollution.

Anthropogenic pollution can be at the stage of fabrication or end use. Instead of pollute and clean; mitigation strategies should receive high priority. Regulatory standards for emission and discharges from process plants should be strictly enforced. Recycling/reprocessing of wastes containing toxic metals needs to be given greater emphasis not only from environmental and health considerations but also as a resource conservation measure. Monitoring of air, water and soil in the vicinity of the toxic metal processing units needs to be carried out more rigorously for the specific metal. Regional accredited laboratories for analyzing pollutants in various environmental compartments should be set up to help regulatory bodies. Guidelines for proper management of tailings and slags containing toxic metals should be prepared taking into consideration techno- economic feasibility. Tailings dumps and process wastes lying in locations close to the processing units need to be remediated on priority. Phytorestoration enhances ecological capital and provides biodiversity of choice suitable for the region where such restoration measures are undertaken. Attempt should be made to replace CFL bulbs with LED (Light emitting diode) bulbs Mercury-based medical devices and equipment should be totally phased out, since digital options are available. Presently there is emphasis on production and use of private vehicles-two wheelers, cars. This should change with emphasis on cleaner public transport systems to reduce the burden of

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road run off. CNG should replace petrol and diesel. Use of diesel should be confined to public transport and transport of goods. Manufacture of diesel cars should be stopped. Rich are taking the benefit of the subsidy on diesel. Periodic (six monthly) examination of water quality, particularly for detection of fluoride and arsenic is necessary in newer alluvium and flood plain areas in different parts of India. Water supplied by urban municipalities and rural panchayats, should be free of (or contain within safe levels) of biotic and abiotic toxicants including heavy metals and minerals. Inexpensive devises for purifying water at household level have to be developed. Creation of public awareness is very important. Greater interaction between scientists, technologists and media is needed to achieve that. School education can be a mechanism for creating awareness.

10. CONCLUSION

While anthropogenic activities are the major source of heavy metal pollution, natural sources contribute significantly to the burden of arsenic and fluoride. Apart from industries, road runoff is also an important source. The toxic elements enter the body mainly through water, food and air. Cosmetics, dental products, some drugs, particularly Ayurvaid and Unani drugs also contribute. Major pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. The lack of technical and financial resources and the regulatory control for the management of hazardous wastes in the past had led to the unscientific disposal of hazardous wastes, which posed serious risks to human, animal and plant life. A huge quantity of pollutants in the form of domestic and industrial effluents is discharged directly or indirectly into the soil/water bodies, which has severe impacts on its biotic and abiotic environment. During rain, surface water with soil, mud and humus enter into the river, tanks and other water bodies. The inorganic minerals like sodium, potassium, calcium, magnesium and heavy metals like iron, manganese, lead, mercury, chromium, cadmium, nickel, cobalt, copper etc., when reach to the soil/river water caused pollution. Heavy metal contamination is becoming a great concern to the environmental awareness and government policies. Several heavy metal removal technologies including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration and phytoremediation are commonly used in industries. However, these technologies are becoming uneconomical and unfavourable to remove heavy metal from contaminated sites or wastewater. With increasing environmental attention and legal constraint on discharge effluents, a need of cost effective technology is essential. Therefore, the search for efficient, eco-friendly and cost effective remedies for wastewater treatment has been initiated. In recent years, research attention has been focused on biological method, *e.g.* bioremediation, is in the process of commercialization. Bioremediation provides a technique for cleaning up pollution by enhancing the natural biodegradation processes. The bioremediation is one of the most promising technological approaches to the problem of hazardous waste. This process relies on microorganisms such as bacteria or fungi to transform hazardous chemicals into less toxic or nontoxic substances. Such biological transformation is more attractive than direct chemical or physical treatment. Microorganisms directly degrade contaminants rather than merely transferring them from one medium to another, employ metabolic degradation pathways and can be used in situ to minimize disturbance of the cleanup site. Hence, microorganisms can be effective, economical and non disruptive tools for eliminating hazardous chemicals. There is no doubt that bioremediation is in the process of paving a way to greater pastures. This technology offers an efficient and cost effective way to treat contaminated soil, waste and water. Its advantage generally outweigh the disadvantage, therefore may be used as management tool.

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Chapter 47
Leachate Treatment:
Case Studies in Selected European and Asian Countries

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ABSTRACT

Landfilling is one of the most important methods for disposal of solid waste in many countries. One of the most obvious problems associated with the landfilling practice is the generation of leachate. This chapter reviews case studies on the on-site treatment of leachates using various technologies in selected European and Asian countries. It was shown that the generation of leachate varies widely in both quantity and quality in European and Asian countries. Biological treatment and membrane technology show very high efficiencies in treating leachate generated from Odayeri landfill (in European side of Turkey) and Komurcuoda landfill (at Asian side of Turkey). Leachates from Arpley landfill (UK) and Bukit Tagar landfill (Malaysia) were successfully treated using sequence batch reactor (SBR). Fairly good treatment efficiencies were obtained using constructed wetlands (CWs) in treating Gdansk-Szadolki landfill leachate in Poland. Furthermore, the use of coagulation, filtration and membrane technologies has been proven effectively in treating Nonthaburi landfill leachate in Thailand.

INTRODUCTION

Landfill is one of the most popular and extensively used methods for the disposal of more than 90% of municipal solid waste (MSW) (Idris *et al*, 2009). Recent work done by Hoornweg and Bhada-Tata (2012) shows that the global MSW generation are expected to increase from the current 1.3 billion tonnes per year to approximately 2.2 billion tonnes per year by 2025. This corresponding to an increase in per capita waste generation rates from 1.2 to 1.42 kg per person per day in the next decade. The increasing trend represents for both developing and developed countries. Nevertheless, global averages are broad approximates only as rates may differ considerably by region, country, city, and even within cities.

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Due to the generation of solid waste is inevitable in daily activity of humans and animals, it leads to the generation of highly polluted wastewater which is called landfill leachate. The open dump landfill approach still remains the predominant MSW disposal option in developing countries. On the other hand, in developed countries, even though the development of landfill technology from uncontrolled to sophisticated and highly developed facilities, the generation of contaminated landfill leachate consistently leaving an unavoidable issue of the practice of waste disposal in landfills.

The generation landfill leachate creates a negative long-term impact on the surrounding environment and public health since it contains substantial amounts of dissolved organics (BOD and COD), xenobiotic organic compound (XOCs), inorganic salts, ammonia, heavy metals and other toxicants (Poznyak *et al.*, 2007 & Emenike *et al*., 2012). Through direct leachate contact, it can contaminate the surface and ground water, as well as soil (Panagos *et al.*, 2013) and this has become a foremost environmental concern worldwide. Therefore, it can be concluded that landfill leachates are, and will continue to be, a serious threat to the environment and quality of life unless proper treatments are taken. Various technologies of wastewater treatment have been employed to treat leachate in full scale on-site treatment system. By applying full scale on-site treatment system, it can avoid the cost of transporting leachate to wastewater treatment plants (WWTPs) (*i.e.* off-site treatment) (Robertson *et al*., 1995; Tsuzuki *et al*., 2009).

When installing a leachate treatment plant at a landfill, it is essential to consider leachate production rates and alterations in quality of the leachate when sizing the plant. Specific landfill site will determine the nature of both quantity and quality of the leachate, and both of the criteria will also varies throughout the life of a landfill site. As waste changes with time, so does the leachate quality. This is particularly, an evident in non-hazardous landfills that have received MSW (IPPC, 2007). As a point of reference, Table 1 shows the difference in quality (or typical characteristic) of landfill leachate from large landfills in the selected region/country. It was shown that Southeast Asia has the highest COD, TOC, alkalinity, chloride, conductivity, sulphate and magnesium, while phosphate, nitrate, and nitrite were found to be high in Hong Kong. In UK, it was shown to have highest BOD, iron and sodium.

Although landfilling represents one of the oldest, economic and most common methods of MSW disposal, however the cost of treatment of leachate is still high. Based on the quantity of the raw leachate generated, the operating costs were estimated to be almost US$6–8 per cubic metre of leachate (Yaman *et al.*, 2012). The treatment cost and as well as the successful of leachate treatment depend strongly on the quantity and quality of the leachate produced at the landfill site. On-site leachate treatment has been extensively practiced for many years in many countries, especially in European countries as an alternative to reduce cost and environmental risk of transporting leachate to WWTPs or off-site treatment. Some Asian countries have also been practising on-site leachate treatment. Many applicable technologies for on-site leachate treatment have been employed including a variety of physical/chemical processes and as well as biological processes. The purpose of this chapter is to present and evaluate the performance of full scale on-site treatment of landfill leachates using various technologies in selected European and Asian countries.

OVERVIEW ON LEACHATE TREATMENT IN EUROPE

In 2010, about 252 million tonnes of total MSW was produced in European countries (EU-27), whereby the MSW generation per capita is about 502 kg/cap. The analysis indicates large differences in MSW management performance between European countries. The majority of this waste (45%) is still sent to

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Table 1. Typical characteristic of landfill leachate from large landfills in selected region/country (Kiser, 2004; Abubakar, 2006)

Parameter	Units	South east Asia	Hong Kong	UK
pH	-	6.0–8.4	7.4–8.6	7.4–8.5
COD	mg/l	1,600–13,000	650–2,800	2,600–8,500
BOD_5	mg/l	-	45–400	90–3,000
TOC	mg/l	400–10,000	-	400–3,400
Alkalinity	mg/l	8,000–40,000	3,000–12,000	7,000–17,000
NH_3-N	mg/l	1,200–3,000	1,200–3,000	1,100–2,500
Chloride	mg/l	2,500–6,300	500–3,000	1,700–5,200
Conductivity	µS/cm	14,000–42,000	14,000–30,000	14,000–30,000
Nitrate-N	mg/l	< 1–12	< 0.1–22	< 0.3–2
Nitrite-N	mg/l	< 1 – < 2	< 0.1–3.6	< 0.1–2
Phosphate (as P)	mg/l	2–50	3–125	4–20
Sulphate (as SO_4)	mg/l	< 5–1200	-	< 5–150
Sodium	mg/l	1,500–3,000	200–2,100	1,700–4,000
Magnesium	mg/l	60–500	18–50	17–150
Iron	mg/l	1,000–20,000	5,000–9,000	3,000–72,000
Zinc	mg/l	150–1500	200–2,200	30–330
Lead	mg/l	< 300 – <1000	-	< 40-600

landfill, but an increasing amount is recycled (42%) or incinerated (5%). The general increase in recycling of MSW has led to a reduction in the percentage of MSW landfilled. Most countries reduced landfilling in the period 2001–2010 (Saki, 2012; EEA Report, 2013). Although alternative disposal methods for example recycling, incineration and composting are being encouraged, landfilling of MSW is still remains the predominant and crucial issues for waste management across Europe and other countries in the world. Since the protection of surface waters used for drinking water supply has been ruled under Directive 75/440/EEC (EC, 1975), significant progress has been achieved in identifying the contamination of aquatic ecosystem. Subsequently, landfill leachate need to be treated on-site to meet certain standards before it can be discharged into a sewer system or direct disposal into surface water.

Currently, there are more than 150,000 landfill sites across European countries and considerable funds have been spent on leachate treatment with an estimated annual cost of EUR 10 billion to 17 billion. It is predicted that leachate treatment will become a larger industry as Environmental Directives are implemented to improve water quality. At the moment, modern landfills are highly engineered and developed facilities designed to remove or minimize the adverse impact of the waste on the surrounding environment (Egner, 2013).

A large number of widely adopted processes have been used on-site for leachate treatment, either a single or in combinations with other method. Physicochemical has been widely adopted for leachate treatment, for example by using coagulation-flocculation, chemical oxidation, activated carbon adsorption, and membrane technology (MF, UF, NF and RO). In addition, biological methods have been commonly applied to remove organic matter and ammonium nitrogen from landfill leachate, for instance activated

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sludge process utilise an aerobic tank followed by a settlement tank. The sequence batch reactor (SBR) is one example of activated sludge treatment and this is the common technology used in the UK (Robinson, 2005). Furthermore, a specific treatment requirement for leachate may involve the use of primary, secondary, and tertiary processes. The use of on-site constructed wetland systems is might be one example. More than a decade ago, numerous on-site constructed wetland systems for landfill leachate treatment has been established in European countries (Wojciechowska, & Obarska-Pempkowiak, 2008). Three case studies of domestic on-site landfill leachates treatment in selected European countries are discussed in the next section in order to connect the processes effectiveness of full scale on-site treatment system to leachate characteristics and key contaminants treatability.

Case Study of Leachate Treatment Plant at the Odayeri Landfill Site on the European Side of Istanbul, Turkey

Istanbul is the largest city in Turkey. It is situated between the European and Asian regions, where about a third of its population lives in the Asian region. Having the largest population in Turkey, a large amount of solid wastes is being generated in Istanbul city. Currently, there are two operated landfill sites located both on its European (Odayeri landfill leachate treatment plant) and Asian (Komurcuoda landfill leachate treatment plant) regions (Yaman *et al*., 2012; Coban *et al.*, 2012). In this section, the case study of the European region of Istanbul city MSW landfill leachate treatment plant located at Odayeri, Turkey was discussed. Later, the case study of Komurcuoda landfill leachate treatment plant located at the Asian region will be discussed in this chapter.

Odayeri landfill site was originally opened in 1995 (Yaman *et al*., 2012) for the disposal of MSW generated from sixteen local residential wastes on the European side of Istanbul. Odayeri landfill site is 112-ha area covered with layers comprising gravel, coal, clay and sand in patches. The site continues to receive approximately 9,800 tons/daily of waste (Ozcan *et al*., 2006; Yaman, 2011). Over 2000 m^3 of leachate was generated from this Odayeri landfill site each day and the leachate collected was treated on site at the leachate treatment plant (Yaman *et al*., 2012). The analytical data of the raw leachate from Odayeri treatment plant shows that the leachate is characterized by high organics and ammonia concentration. Typical leachate characteristics measured in 2010 (in average) are COD (19,475 mg/l), TN (3,548 mg/l), NH_4-N (2,713 mg/l) and TP (14.8 mg/l) (Yaman *et al*., 2012). In addition, study reported by Campagna *et al.* (2013) shows that organic matter in raw Odayeri landfill leachate has hydrophilic character and approximately 37% of the COD in this raw leachate comprised of particulate/colloidal (>100 kDa) and 63% was soluble (<100 kDa). COD fractions were analysed to be 5%, 3%, 11% and 44% for molecular weight (MW) distributions of 100–10 kDa, 10–1 kDa, 1 kDa–500 Da and <500 Da, respectively. Based on the result obtained, it shows that significant parts of COD in Odayeri landfill leachate have very low MW distributions.

The units of the Odayeri landfill leachate treatment plant are consists of collecting basin (equalization basin), a pre-sedimentation unit, biological treatment (nitrification – denitrification), ultrafiltration membranes (UF), nanofiltration membranes (NF) and discharging channel. (Yaman, 2011; Yaman *et al*., 2012). As detailed out by Yaman *et al*. (2012), firstly, the raw leachate from collecting basin was pumped using three lift pumps (*i.e.* each have capacity of 125 m^3/l) to the pre-sedimentation unit (285 m^3) to eliminate settleable particulate matter from leachate. Then, the supernatant leachate at the top was sent to the biological treatment unit, which consists of anoxic and aerobic tanks. In the aerobic tank, ammonium in leachate with high concentrations will undergo nitrification process. In anoxic tank, deni-

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trification process occurred. To attain efficient and optimum biological treatment, the removal of COD taking place simultaneously during nitrification and denitrification processes at optimum condition of 20°C and pH 7.5–8.5. To supply oxygen and to ensure a homogenous mixture in the tanks, ten units of surface aerators and eight units of jet aerators were installed. Afterward, the treated leachate was pumped to UF and NF units. The typical UF membrane used is tubular membrane with nominal pore size of 30 nm, membrane area of 27 m^2 and it operates at a flux of 77 l/m.h, pressure of 6.4 bar and permeate flow rate of about 90–100 m^3/h. This UF membrane unit has the capability to treat 50 m^3/h leachate. Whereas, two units of NF membranes (consists of nine modules each) were used to receive the treated leachate released from UF membrane. The configuration of this membrane is spiral membrane having pore size of less than 1 nm and membrane area of 34 m^2. With the permeate flux of 17 l/m.h, these NF membranes unit has the capability to treat 22-23 m^3/h of leachate.

During the study carried out by Yaman *et al*. (2012), significant part of COD, TN, NH_4-N, and TP is removed at the rate of 99%, 94.5%, 99%, and 93.8%, respectively by this Odayeri landfill leachate treatment plant. UF and NF units have capability to remove most of the carbonaceous organic matter. The COD values after treated with UF membranes were within the range of 648−1635 mg/l and these values reduced again to 20−775 mg/l after pass through NF membranes. The maximum COD removal efficiency after treated with NF membranes was analyzed to be 99.9% and the minimum efficiency was analyzed to be 95.1%. As the results, the COD, TN, NH_4-N, and TP values of the treated water discharged from leachate treatment plant is still below the discharge limits required by regulations enforced in Turkey. In expenditure evaluation of Odayeri leachate treatment plant, the treatment and operational costs were estimated to be US$4.6–5.3 m^{-3} and US$6–8 m^{-3} leachate, respectively.

Furthermore, further investigation by Campagna *et al*. (2013) indicates that TOC concentration in raw Odayeri landfill leachate (*i.e.* about 5,075 mg/l) is able to be removed at 89% (574 mg/l) after released from UF membranes. Finally, after treated with NF membranes, the TOC concentration value was analyzed to be 227 mg/l, which mean about 40% of TOC was removed by NF membrane units. The obtained results show that Odayeri landfill leachate treatment plant was operated with high efficiency.

Case Study of Leachate Treatment Plant at the Arpley Landfill, Warrington, England

Arpley landfill has been established since 1988. It is located around 2.5 miles to the west of Warrington, off Liverpool Road, in Sankey Bridges, England. It is situated between the River Mersey and the Manchester Ship Canal. The site covers an area of circa 160 ha of land and formerly used for the disposal of dredging from each stream. Presently, the total Arpley landfill area covers more than 200 ha. Since 1999, Arpley landfill has been managed and operated by Waste Recycling Group (WRG), which is one of the leading UK waste management and energy recovery companies, after being acquired from Cheshire County Council (3C Waste). From the design, Arpley landfill only accepts non-hazardous and inert wastes arising from municipal, commercial and industrial sources and as well as inert materials. Since from the opening, the site has received more than 15 million tons of wastes. Arpley landfill site will continue to accept more than 800,000 tons/year of primary domestic waste (Robinson *et al*., 2008; FCC Environment, 2010).

In 2001, WRG has installed a full scale on-site leachate treatment plant at Arpley. The treatment plant began to operate after a successful commissioned during late 2001. The installation of this facility can ensure the leachate from the site is being treated to the required water quality standards before being

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released to the River Mersey. The plant is capable of treating raw landfill leachate containing of COD and NH_3-N of 8,000 mg/l and 2,500 mg/l, respectively. The plant capability can be increased up to 450 m^3/day for low characteristic of leachate generated from the site (Robinson *et al*., 2008).

The Arpley landfill leachate treatment plant consists of three large roofed sequencing batch reactors (SBR) tanks, each with automated control of nutrients dosing and pH value. The SBR treatment process has been developed and suitable for higher organic strength and NH_3-N concentrations as contained in raw landfill leachates. The higher volume of SBR tank makes the aeration process become more efficient, high rates of dilution of incoming leachates, and high resistance to the shock loading. Subsequently, the treated leachate from each SBR was pumped into the effluent balance tank, before being sent to dissolved air floatation (DAF) system to eliminate residual solids and colloidal materials. The installation of DAF system at Arpley landfill leachate treatment plant is the first UK application of DAF system to treat leachate. After being treated by DAF system, then it was pumped to a terraced reed beds (having an area of 3,000 m^2) for effluent polishing in order to achieve high effluent quality standards. Before being released to the River Mersey, the final effluent quality needs to fulfil the required limits (based on Water Resources Act 1991), such as the maximum daily rate is 600 m^3/day, pH value of 6−9, BOD_5 value of 30 mg/l, suspended solid of 45 mg/l, NH_3-N of 15 mg/l and non-detectable PCBs. BOD, COD, NH_3-N, iron, sodium and chloride are the example of substances that can be removed during the treatment processes (IPPC, 2007; Robinson *et al*., 2008).

According to Robinson *et al*. (2008), the main key factor of the leachate treatment process at Arpley is the pneumatic leachate collection system. This system is being designed to manage leachate levels through boreholes and wells at three distinct phases of the chosen sites, *i.e*. Birchwood, Lapwing and Walton. Different leachate strengths were measured at these three phases of the sites. At Birchwood phase, COD, NH_3-N and chloride fractions were analysed to be around 600 mg/l, 300-400 mg/l and 600 mg/l, respectively. While at Lapwing phase, the measured COD, NH_3-N and chloride fractions were about 5,000−10,000 mg/l, 1,000 mg/l and 2,500 mg/l, respectively. For Walton phase, approximately 6,000−20,000 mg/l, 1,500−2,200 mg/l and 3,500 mg/l were measured for COD, NH_3-N and chloride fractions, respectively.

From the major parameters measured during July 2007, Arpley landfill leachate treatment plant able to remove COD, BOD_5, TOC, and NH_3-N to give final effluent values of 835, 3.0, 140 and 0.4 mg/l, respectively. The pH and suspended values were around 8.03 and 3 mg/l, respectively. The treatment process was also able to reduce most of the heavy metals to below 0.5 mg/l. Results of the study conducted by Robinson *et al*. (2008) demonstrates that Arpley landfill leachate treatment plant was operated successfully to solve serious leachate problem in the UK.

Performance of Constructed Wetland Systems Treating Landfill Leachate in Gdansk-Szadolki, Northern Poland

In Poland, the extensive use of landfill is projected to continue and still the predominant waste management option in the future for disposal of MSW. Compared with other European countries, the composition of MSW produced in Poland is different. Due to the inadequately developed selection of waste materials, the generated MSW in Poland contains numerous organic components, metal, paper and hazardous materials as well (Slomczyńska & Slomczyński, 2004). In 2009, the majority collected MSW (85%) is still sent to landfill (Bialowiec, 2011). In the late 2005, there are about 762 legal landfills were operated in Poland. The available landfill sites in Poland need to be reduced to 200 landfill sites during 2005-

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2014. By year 2010, biodegradable MSW disposed in landfills should be reduced to 75% of amounts generated in 1995 (4,381 tons), then reduced to 50% in 2013, and by the end 2020 it was estimated to be reduced to 35% (The World Bank, 2011).

There are many sophisticated and highly developed leachate treatment technologies, however, most of these technologies are capital intensive and require constant operation and maintenance cost, hence, they are not well-suited at many landfill sites, especially in rural areas. The treatment of landfill leachates using natural systems appears to be environmentally sustainable for contaminants removal. Constructed wetlands (CWs) are engineered treatment systems which have similar contaminant removal mechanisms as in natural wetlands. CWs provide inexpensive capital and maintenance costs, simple in operation, have potential to remove contaminants and can provide green space or wildlife habitat (Liehr & Sloop, 1996).

In Poland, an increasing interest in CWs for sewage treatment was observed almost a decade ago, particularly serving individual households in rural areas. However, in the case of landfill leachate treatment, CWs are still in the developing stage (Obarska-Pempkowiak *et al*., 2013). In this section, the performance of CW systems treating landfill leachate in Gdansk-Szadolki, northern Poland was highlighted. The Gdansk-Szadolki landfill site was originally opened in 1973 which covers an area of approximately 60 ha for the disposal of local residential wastes. The annual leachate generation rates from this landfill site are approximately 9,000–9,500 m^3/year and the daily collected leachate flow varies from 6 to 240 m^3. In 2001, an on-site CW for leachate treatment was fabricated in this Gdansk-Szadolki landfill. The CW in Gdansk-Szadolki contains two parallel horizontal flow (HF)-CW beds, having an equal area of 50 x 50 m for each bed and the depth is 0.6 m. Using the info from the basis of filtration coefficients and the beds dimensions, the calculated total hydraulic capacity was equal to 0.994 m^3/day for bed 1 and 0.213 m^3/day for bed 2. Each bed was planted with common reed (*P. australis*) (Wojciechowska *et al*., 2009; Wojciechowska *et al*., 2010; Obarska-Pempkowiak *et al*., 2013).

The leachate composition form Gdansk-Szadolki landfill is very unstable and fluctuated over the time. The characteristics of raw leachate measured in 2008 (*in means*) are COD (445.2 mg/l), BOD_5 (115.9 mg/l), BOD/COD ratio (0.26), pH (7.2), TSS (84.2 mg/l) and total nitrogen (395.8 mg/l). However, these characteristic values were lower compared to measured parameters in 2004, which were COD (1,616.2 mg/l), BOD_5 (792.1 mg/l), BOD/COD ratio (0.49), pH (7.5), TSS (150.5 mg/l) and total nitrogen (433.3 mg/l). This is because the raw leachate generated was mixed with rainwater. The raw landfill leachate was pumped directly to the CW, without pre-treatment at the sedimentation tank. Thus, the CW contained high BOD, COD and ammonia nitrogen concentrations; this definitely gave significant effect on the treatment results. The reed beds 1 and 2 used to treat Gdansk-Szadolki landfill leachate shows very effective for BOD_5 removal (*i.e.* 95.7% for bed 1 and 79% for bed 2). However, low COD removal was observed (*i.e.* 78.5% for bed 1 and only 32% for bed 2). This is most probably due to high refractory compounds exist in the raw leachate, which has been shown by low BOD_5/COD ratio. The results indicate that nitrification occurred in both beds, where the ammonia nitrogen was characterised by only 0.5% and 1% from the total nitrogen in the effluents of beds 1 and 2, respectively. On the other hand, denitrification only occurred in bed 1. Overall, the average concentrations of contaminants in the effluent of bed 1 fulfil the required limits set by Polish environmental standards. On the contrary, the concentrations of COD, TSS and the total nitrogen in bed 2 exceed the limits. As a results, the CW in Gdansk-Szadolki provided fairly good treatment efficiencies of BOD_5 (bed 1), total nitrogen and ammonia nitrogen, regardless of clogging problems (Wojciechowska *et al*., 2010; Obarska-Pempkowiak *et al*., 2013).

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LEACHATE TREATMENT PRACTICES IN ASIA

In Asia, the major challenge in urban areas is solid waste management due to increasing generation rate of waste, especially MSW. The rate of MSW generation in rural areas can be as low as 0.15 kg/cap/day, while in the urban areas the rate can be above 1.0 kg/cap/day. In addition, due to economic growth, the quantitative and qualitative of MSW generated are difference between cities in Asian countries, especially if compared between smaller and major cities. For example, the rate of MSW generated in Katmandu city (Nepal) and Dhaka city (Bangladesh) is about 0.3 and 0.5 kg/cap/day, respectively. While in Singapore, Taipei city (Republic of China), and Penang (Malaysia), the MSW generation can more than 0.94, 0.95 and 0.98 kg/cap/day, respectively. Generally, the MSW contains more organic matters than other materials. The average percentages of organic matter can be ranged from 50% to 70% in major cities in Asian countries. The quantitative and qualitative of MSW are also be influenced by numerous factors like economics, culture, heritage, industrialization, and season (Hwa, 2007). In addition, most of MSW composition in the cities of developing countries is biodegradable organics (Dhokhikah & Trihadiningrum, 2012). On the other hand, in the Asian developed countries (such as in Japan, Singapore, Taiwan, and South Korea), the biodegradable organics composition commonly less than 45% (Shekdar, 2009).

At the moment, sanitary landfill seems to be the best option for Asian countries due to relatively simpler in technology. However, still many Asian developing countries practiced open dumping as their main disposal (70 – 90%), without to include on-site leachate treatment plant. The installation of leachate treatment plant is required in upgrading the existing dumpsites and landfills in Asia (Visvanathan *et al*., 2004). In this section, three case studies highlight the treatment technologies used in domestic on-site landfill leachates treatment facilities in selected Asian countries based on the characteristics of the leachate.

Case Study of Leachate Treatment Plant at the Komurcuoda Landfill Site on the Asian Side of Istanbul, Turkey

Komurcuoda landfill site is located at Anatolian (Asian) side of Istanbul and it has been under operation and receiving MSW since 1995. The site covers an area of approximately 89 ha of land. It is consists of six storage valleys and presently 17 million m^3 solid wastes have been collected and stored. Currently, it was estimated about 4.5 thousand tons of MSW is being collected daily (Yaman, 2011; Coban *et al*., 2012; Yuzer *et al*., 2012). The MSW collected in this landfill was received from the Hekimbasi and Aydinli transfer stations (Yazgan, 2013).

The on-site leachate treatment plant was built to receive and collect the leachate generated from Komurcuoda landfill site and has the capacity to treat about 1,200 m^3/day (Yaman, 2011; Coban *et al*., 2012). On daily average, the treatment plant was operated with a flowrate of 1,100 m^3/day (Yuzer *et al*., 2012). Similar with leachate treatment plant at the Odayeri landfill site, the current Komurcuoda on-site leachate treatment plant consists of ammonia stripping tank, primary sedimentation tank, aerobic/anoxic biological treatment followed by ultrafiltration membranes (UF) and nanofiltration membranes (NF) processes.

The characteristic of leachate form Komurcuoda landfill site is fluctuated over the time. From various parameters measured by Coban *et al*. (2012), it was found that COD, BOD_5, total nitrogen, and TSS were analysed to be around (with values ranging from minimum to maximum) 3,000−40,000 mg/l, 3,000−13,000 mg/l, 2,000−5,000 mg/l and 300−1,500 mg/l, respectively. The on-site Komurcuoda

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leachate treatment plant shows a very effective treatment for COD removal, with the final removal rate of almost 99% after pass through NF membranes (*i.e.* treated to the level of 250 mg/l from the average influent COD of the leachate of around 24,000 mg/l). Apart from that, from the average influent of total nitrogen of around 2,890 mg/l, the total nitrogen was treated to the final level of 121 mg/l which gave the removal rate of around 96%. In addition, this Komurcuoda leachate treatment plant is also able to reduce NH_4-N from 2,313 mg/l (average influent) to 35 mg/l with the removal rate of about 98% (Coban *et al*., 2012). The results pointed out that Komurcuoda leachate treatment plant was operated with high efficiency, due to integrated membrane processes.

Case Study of Leachate Treatment Plant at the Nonthaburi Disposal Site, Thailand

Bangkok (as a capital city of Thailand) and also other urban areas in Thailand have generated about 61% MSW in 2010, while the remaining 39% of MSW was generated from the rural areas. Organic waste from food (64%) is the main component of MSW component in Thailand, followed by plastic (17%) and paper (8%) (Cherdsatirkul, 2012; Pollution Control Department, 2015a; Pollution Control Department, 2015b). In 2010, the generation of MSW in Thailand reached 15.11 million tons, of which 84% is being collected (*i.e.* 12.69 million tons). From that amount, 5.97 million tons of MSW (*i.e.* 47%) was disposed properly into sanitary landfills, while the rest was not disposed in a proper way. Further, the MSW generation in 2011 slightly increased to 15.97 tons (*i.e.* increase by 5.5%). While in Bangkok alone, it was estimated about 9,497 tons of MSW is being generated daily. From a number of MSW disposal facilities in Thailand, sanitary landfill (*i.e.* 131 sites) is still the most popular methods for the disposal of MSW (Jacob *et al*., 2013).

From many disposal sites, Nonthaburi landfill site (located in Sai Noi District, Nonthaburi Province) is one of largest solid waste disposal sites in Thailand. The site continues to receive more than 800 tons of MSW daily. The composition of collected MSW mainly consists of 27.9–56.6% of degraded organic wastes and 24.6–44.8% of plastic wastes (Chiemchaisri *et al*., 2010). The Nonthaburi landfill site was originally started in 1982 which covers an area of nearly 10.9 ha prior to the rehabilitation activities to occupy a total area of 38.6 ha. At the beginning, no integrated leachate treatment plant available at Nonthaburi landfill site. The leachate generated is not released from the site, but it is being collected through an open pipe system to be stored and treated in the stabilization pond located near the site. Until now, more than 300,000 m^3 of leachate is being generated (Theepharaksapan *et al*., 2011).

In order to treat the generated leachate, a full scale on-site leachate treatment with intake capacity of 1,000 m^3/day has been installed. This leachate treatment plant consists of coagulation unit, pressurized sand filtration unit, microfiltration (MF) unit and reverse osmosis (RO) membrane processes. In chemical coagulation unit, $FeCl_3$ in two open jet clarifiers (with a total volume of 113 m^3) was dosed to raw leachate. These clarifiers operated at an overflow velocity of 1.5 m/h and hydraulic retention time of 160 min. Then, the leachate was sent to the pressurized sand filtration units at a filtration rate of 6.4 m/h. The pressurized sand filter consisted of two tanks with total filter area of 6.6 m^2. Subsequently, after being pretreated using 5μm catridge MF unit, the treated leachate was pumped to RO unit. This unit consisted of six pressure vessels each containing seven RO membrane modules (0.20 m in diameter) and operated at a maximum pressure of 2.5 MPa with recovery rate of 50% (Theepharaksapan *et al*., 2011; Rukapan *et al*., 2012; Rukapan *et al*., 2014).

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During the analysis carried out by Theepharaksapan *et al*. (2011), the raw leachate contained very high organic matters in terms of COD, BOD_5, and TOC with values (in average) of 52,650 mg/l, 47,274 mg/l and 25,320 mg/l, respectively. It was also found that the raw leachate is very acidic (3.97) and contained high concentration of total dissolved solid (32,500 mg/l), suspended solid (27,500 mg/l) and total nitrogen (430 mg/l). After treated with chemical coagulation and pressurized sand filtration units, both biodegradable and recalcitrant compounds, in term of COD, BOD_5, TOC and as well as total nitrogen and suspended solid were reduced significantly to the level of 510 mg/l, 24 mg/l, 152 mg/l, 59 mg/l and 190 mg/l, respectively. Additional treatment with MF and RO units reduced again most contaminant concentrations to below the standard limit. From this full scale on-site leachate treatment, it was also noticed that most of the COD and ammonia were removed at chemical coagulation and membrane processes, respectively. At the final stage, the maximum COD, ammonia nitrogen and heavy metals removal efficiencies were measured more than 99%, 97% and 90%, respectively.

However, further investigation by Rukapan *et al*. (2012) and Rukapan *et al*. (2014) shows that membrane fouling is still the main task to be solved when reverse osmosis (RO) membrane is to be applied to full-scale on-site leachate treatment plant. Study by Rukapan *et al*. (2012) revealed that in long-term operation (2 years), the deposited foulants (*i.e.* ferric element with particle size of 0.45–0.70 μm) on RO membrane increased by 7–10 fold as compared to short-term operation (6 months). The degree of fouling was also higher on the first membrane module. Successive chemical cleaning using alkaline (NaOH) followed by acid solution (HCl) gave the best results in removing foulants on the membrane surface.

Case Study of Leachate Treatment Plant at Bukit Tagar Sanitary Landfill, Malaysia

Due to rapid development especially in urban areas, MSW generation in Malaysia has increased more than 91% over the past decade. The population in urban areas is the main waste generator which constitutes more than 65% of the total population (Periathamby *et al*., 2009). Currently, landfill is one of the most preferred methods for solid waste disposal in Malaysia. According to a report by JPSPN (2013), currently there are about 296 landfill sites in Malaysia of which 165 of them are currently operating and the rest are non-operational landfill sites. The site covers an area between 8 and 60 ha. Nevertheless, most of these sites are open dumpsites, and the capacity has been overloaded.

Among sanitary landfills operated in Malaysia, Bukit Tagar sanitary landfill (located in Hulu Selangor district) is one of the largest and modern landfills equipped with sophisticated and highly developed facilities. The landfill site occupied in a total 1,700 acres land area, surrounded by palm plantation and situated approximately 50 km from Kuala Lumpur. The site construction began in 2004 and opened in April 2005 to receive its first load of MSW of about 0.5 Mtonnes. Currently, Bukit Tagar sanitary landfill receives around 3,000 tons of waste per day. Bukit Tagar sanitary landfill has been classified as a fully engineered level IV landfill with complete high density polyethylene (HDPE) membrane liner. It was also equipped with leachate collection and treatment systems which accomplish all the standards according to the Malaysian Technical Guideline. The generated leachate was collected and treated on-site leachate treatment plant located not far away from the site in order to achieve the requirements of water quality standards required by the environmental agency. The treated effluent is flowed to plantation land within the landfill site (Kortegast *et al*., 2007; Zakaria, 2007; Taha *et al*., 2011; Ghazali *et al*., 2014). The

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leachate treatment facility at the Bukit Tagar sanitary landfill has been designed to treat 1,000 m^3/day of raw leachate and allow modular expansion up to 3,000 m^3/day. At this time, this leachate treatment facility handles 300 to 500 m^3/day of leachate (Malek *et al*., 2008; Taha *et al*., 2011).

The generated leachate is collected and stored at four leachate holding ponds, having a total storage capacity of 180,000 m^3 and these ponds act as pre-treatment of the raw leachate. Then, four sequential batch reactor (SBR) lagoons (with a capacity of 5000 m^3 and equipped with 24 aerators in total) will be used for biological treatment to remove biodegradable COD and as well as nitrification of ammoniacal-N. These SBR lagoons are expected to operate in sequence on a 24-hour cycle, receiving inputs of leachate from a single large raw leachate balance tank (RLBT). The process was arranged for releasing the treated leachate for every 6 hours for each SBR lagoon into a treated leachate balance tank (TLBT). Thereafter, it was pumped to a dissolved air flotation (DAF) tank to eliminate all residual suspended solids and some colloidal COD compounds. Optimization of the process was carried out by on-site testing through dosing with polyelectrolyte and flocculent solution. Final polishing process take places in the reed beds (*i.e.* four reed beds with 1 ha of area in total), consists of *phragmites* plant which capable of absorbing the remaining contaminants in treated leachate in order to improve its quality (Kortegast *et al*., 2007; Malek *et al*., 2008).

From the study carried out by Kortegast *et al*. (2007), it was found that the raw leachate characteristics has been changed in composition during storage in the leachate holding ponds (*i.e.* Pond 3) due to development of methanogenic conditions occurred by anaerobic degradation which subsequently reduce the major contaminants values. After measured at four different times (*i.e.* from March 15, 2006 to December 12, 2006) the COD, BOD_5, TOC, suspended solid, and ammoniacal-N values were (from maximum to minimum) 33,268- 4,636 mg/l, 17,630- 1,834 mg/l, 6,804- 540 mg/l, 930- 350 mg/l and 1,923- 1,239 mg/l, respectively. The pH was also changed from 5.4 to 8.5. As a result, when transferring this storage raw leachate to the treatment process, it had transformed to methanogenic conditions. After went through biological process (SBR), the analysis at TLBT shows that COD, BOD_5, TOC, suspended solid, and ammoniacal-N values were decreased to 450 mg/l, 23 mg/l, 194 mg/l, 93 mg/l and 3.2 mg/l, respectively. Then, after treated with DAF and reed beds processes, the final effluent have the COD, BOD_5, TOC, suspended solid, ammoniacal-N, and pH values of 403 mg/l, 16 mg/l, 60 mg/l, 16 mg/l, 0.9 mg/l, and 6.8, respectively. The results demonstrated the effectiveness and reliable treatment for leachate to comply the required discharge standard. Although some parameter like COD has exceed the limit, thus, other methods using for example activated carbon or membrane process should be applied to reduce again this parameter.

PERFORMANCE COMPARISON OF ON-SITE LEACHATE TREATMENT

In summary, the comparison of on-site leachate treatment in selected European countries is given in Table 2. From the data obtained, it shows that the leachate generated from Odayeri landfill (Turkey) and Arpley landfill (UK) is characterized by high concentration of organics and ammonia, while the leachate generated from Gdansk-Szadolki landfill (Poland) is characterized by relatively low organics and ammonia concentration. These variations in leachate characteristics are caused mainly due to different type of solid wastes being disposed of, different climate conditions, site hydrogeology, and the landfill design and operation. From the view of on-site treatment, biological treatment combined with membrane based technology has been used successfully to treat leachate generated from Odayeri landfill (Turkey),whereas

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the SBR treatment process has been developed and become the common technology used to treat leachate in UK. Leachate from Arpley landfill has been effectively treated using this technology in combination with DAF and reed beds. Constructed wetlands (CWs) are another type of on-site treatment that has been applied to treat leachate generated from Gdansk-Szadolki landfill (Poland). Although the results show that CWs provided quite good treatment efficiency, however, possibility of clogging are present which lead to reduce the hydraulic conductivity of the beds, resulted in slightly lower treatment efficiency in the second bed. Therefore, it is likely to be essential to have some type of pretreatment before passing leachate to a CW treatment system.

Table 2. Comparison of leachate characteristic and treatment performance at selected European countries

		Europe		
		Odayeri landfill, Turkey (Yaman *et al*., 2012)	**Arpley landfill, UK (Robinson *et al*., 2008)**	**Gdansk-Szadolki landfill, Poland (Obarska-Pempkowiak *et al*., 2013)**
Landfill site	Started (year)	1995	1988	1973
	Area covered	112 ha	> 200 ha	60 ha
	MSW received	9,800 tons/day	> 800,000 tons/year	
	Leachate generation	2,000 m^3/day		9,000 – 9,500 m^3/year
Characteristic of leachate feeding	COD (mg/l)	19,475[(a)]	576 – 22,440	445.2[(b)]
	BOD_5 (mg/l)		14 – 9,632	115.9[(b)]
	TOC(mg/l)		117 – 6,200	
	TN (mg/l)	3,548[(a)]		395.8[(b)]
	NH_4-N (mg/l)	2,713[(a)]		
	TP (mg/l)	14.8[(a)]		
	NH_3-N (mg/l)		278 – 1,919	
	TSS (mg/l)			84.2[(b)]
Technology used		Pre-sedimentation unit, nitrification-denitrification unit, ultrafiltration membranes, & nanofiltration membranes	Sequencing batch reactors (SBR), dissolved air floatation (DAF) unit, & terraced reed beds.	Horizontal flow-constructed wetlands (HF-CW)
Treatment capacity		2,000 m^3/day	450 m^3/day	Bed-1: 0.994 m^3/day Bed-2: 0.213 m^3/day
Performance (% removal/ final effluent)		COD = 99% TN = 94.5%, NH_4-N = 99% TP = 93.8%	COD = 835 mg/l[(c)] BOD_5 = 3.0 mg/l[(c)] TOC = 140 mg/l[(c)] NH_3-N = 0.4 mg/l[(c)]	Bed-1: BOD_5 (95.7%), COD (78.5%) Bed-2: BOD_5 (79%), COD (32%)
Comply with discharge limit		Yes	Yes	Bed-1: Yes Bed-2: COD, TSS & TN exceed the limits.

[(a)]Average,[(b)]Mean, [(c)]Effluent from SBR

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Furthermore, there are similarities between the on-site leachate treatment in selected European and Asian countries. Table 3 shows the summary of on-site leachate treatment in selected Asian countries. Komurcuoda landfill leachate treatment plant (at Asian side of Turkey) uses the same technology with Odayeri landfill leachate treatment plant (at European side of Turkey). Similar treatment performance was also observed from these treatment plants although Komurcuoda landfill leachate treatment plant has lower treatment capacity and the landfill only received nearly half of MSW as compared to Odayeri landfill. On the other hand, Bukit Tagar sanitary landfill (Malaysia) adopted the same technology with Arpley landfill leachate treatment plant (UK) to treat the leachate. With almost similar treatment capacity, Bukit Tagar sanitary landfill leachate treatment plant is capable to treat the leachate with higher treat-

Table 3. Comparison of leachate characteristic and treatment performance at selected Asian countries

		Asia		
		Komurcuoda landfill, Turkey (Coban *et al*., 2012)	**Nonthaburi landfill, Thailand (Theepharaksapan *et al*., 2011)**	**Bukit Tagar Landfill, Malaysia (Kortegast *et al*., 2007)**
Landfill site	Started (year)	1995	1982	2005
	Area covered	89 ha	38.6 ha	1,700 acres (688 ha)
	MSW received	4,500 tons/day	> 800 tons/day	3,000 tons/day
	Leachate generation	1,200 m^3/day		
Characteristic of leachate feeding	COD (mg/l)	3,000 – 40,000	52,650[(a)]	4,636 – 33,268
	BOD_5 (mg/l)	3,000 – 13,000	47,274[(a)]	1,834 – 17,630
	TOC(mg/l)		25,320[(a)]	540 – 6,804
	TN (mg/l)	2,000 – 5,000	430[(a)]	
	NH_3-N (mg/l)		240[(a)]	1,239 – 1,923
	TSS (mg/l)	300 – 1,500		
	SS (mg/l)		27,500[(a)]	350 – 930
	TDS (mg/l)		32,500[(a)]	
Technology used		Ammonia stripping unit, primary sedimentation unit, aerobic/anoxic units, ultrafiltration membranes, & nanofiltration membranes	Coagulation unit, pressurized sand filtration unit, microfiltration unit and reverse osmosis membranes	Sequencing batch reactors (SBR), dissolved air floatation (DAF) unit, & reed beds
Treatment capacity		1,200 m^3/day	1,000 m^3/day	300 – 500 m^3/day (Design: 1,000 m^3/day)
Performance (% removal/ final effluent)		COD = 99% TN = 96% NH_4-N = 98%	COD = 99% NH_3-N = 97% Heavy metals = 90%	COD = 403 mg/l BOD_5 = 16 mg/l TOC = 60 mg/l SS = 16 mg/l NH_3-N = 0.9 mg/l
Comply with discharge limit		Yes	Yes	Yes, except COD

[(a)]Average

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ment efficiency (except for COD parameter), although having higher organics and ammonia concentration as compared to Arpley landfill leachate treatment plant. While in Nonthaburi landfill (Thailand), the generated leachate has higher concentration of organics and suspended solid, but lower ammonia concentration as compared to Komurcuoda landfill and Bukit Tagar landfill. Using coagulation and filtration processes together with membrane technology, Nonthaburi landfill leachate treatment plant able to achieve high and reliable treatment efficiencies for leachate to fulfil the required discharge standard.

CONCLUSION

Few case studies have been reported on the on-site treatment of landfill leachates using various technologies in selected European (*i.e.* Turkey at European side, England and Poland) and Asian countries (*i.e.* Turkey at Asian side, Thailand and Malaysia). This case study was reported in order to connect the various treatments effectiveness to leachate characteristics and key contaminants treatability. The characteristic and generation of leachate become the key elements in designing and performing on-site leachate treatment. From selected case studies, it was revealed that biological treatment combined with membrane based technology have been applied on-site leachate treatment plant and has high capability in treating leachate from Odayeri landfill (at European side of Turkey) and Komurcuoda landfill (at Asian side of Turkey). Biological treatment has also been combined with dissolved air floatation (DAF) system to successfully treat leachate from Arpley landfill (UK) and Bukit Tagar landfill (Malaysia), although have different leachate characteristics. Apart from that, significant efficiencies were shown when coagulation and filtration methods were used with membrane based technology to treat Nonthaburi landfill leachate in Thailand. Although there are increasing interests in constructed wetlands (CWs), however, it is important that the system is designed adequately for leachate treatment based on the site-specific leachate composition to comply the required discharge standard. In addition, few problems need to be solved, especially related to clogging problems and membrane fouling.

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Chapter 48
On-Site Sanitation Systems for Low-Income Countries:
Technical Guidelines for Groundwater Pollution and Nuisance Control

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ABSTRACT

On-site sanitation systems, the commonest sanitation technologies in low-income countries, are central to the elimination of open defecation in such countries. Nevertheless, their selection and application in the physical and socio-economic environment of low-income settings could be a complex and challenging task. Poorly designed and constructed facilities could pollute groundwater resources and create nuisances to the user and the general public. Meanwhile, local authorities in these countries often lack the human resource with the requisite technical capacity to analyse situations and recommend appropriate solutions. This calls for guidance in the most crucial technical decisions that affect the safe usage and environmental sustainability of on-site sanitation technologies. This Chapter reviews salient standards and guidelines for the selection of appropriate technologies, prevention of groundwater pollution, control of odor and fly nuisance, structural stability and safety of the latrine user.

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INTRODUCTION

Improved sanitation technologies or latrines play a central role in public health management by serving as a barrier to the transmission of pathogenic agents (Mara et al., 2010). As a determinant of health, access to improved sanitation enhances poverty reduction and other Millennium Development Goals especially those related to gender and mortality (United Nations Department for Economic and Social Affairs [UNDESA], 2007). Nevertheless, some 2.5 billion people, mostly in low-income countries, lack access to improved sanitation (Joint Monitoring Program [JMP], 2014). This makes the sanitation MDG practically unachievable and exposes the health of these billions of people to the risks posed by open defecation (JMP, 2013).

In low-income countries, on-site sanitation systems are the most affordable and the most technically feasible for many households. When properly constructed, operated and maintained in accordance with appropriate technical standards and guidelines, they can offer most of the benefits of water-borne sewerage to their users. On the other hand, poorly constructed and maintained on-site sanitation systems could pose a major threat to groundwater resources. Groundwater happens to be a major source of drinking water for most households in these countries, especially those in peri-urban and rural areas that are often not connected to conventional water supply systems. Aside from groundwater pollution, poorly constructed and maintained on-site sanitation systems, especially simple pit latrines, tend to offer a very low level of hygiene that may be comparable to open defecation. Consequently, some prospective users of available facilities may avoid using them and resort to the practice of open defecation which is recognized as the riskiest sanitation practice (United Nations Children's Fund [UNICEF], 2010).

To serve their intended purpose, latrines should be constructed to fulfil basic scientific and engineering principles. Moreover, the choice of a technology should be such that its requirements for sustainable operation and maintenance could be met within a given environment or socio-economic context at an affordable cost. In view of this, various national and international institutions have developed standards and guidelines to assist technical practitioners and lay people in the choice of latrine technologies, their design and construction, as well as the best operation and maintenance practices. Such standards and guidelines are usually aimed at controlling the risks of pollution and nuisances to the general public, especially those of offensive odor and fly breeding.

Although rigid compliance to conservative design codes has been criticized as a setback to innovation in technology development and adaptation in resource-constraint settings (Jenkins & Sudgen, 2006), the availability of flexible standards and guidelines can enhance the technical judgment of sanitation professionals. This is especially imperative in low-income countries where governments are faced with challenges in developing or attracting adequate human resources with the required technical capacity for the sanitation sector. In Ghana, for instance, 2008 statistics indicated that out of 430 engineers and other professionals required in the various local authorities, only eight were available at post nationwide (Obeng & Filho, 2010). Consequently, the practice of environmental sanitation fell in the hands of sub-professionals and low-capacity technical officers. In such cases, the availability of technical guidelines and toolkits would make a significant contribution to the appropriateness of technical decision-making.

Furthermore, in low-income countries technical decisions are required to be taken within the boundaries of infrastructural and socio-economic limitations that make the technical decision-making process very complex and challenging (Katukiza et al., 2010). These challenges that are particularly more prevalent in peri-urban areas of low-income countries include poor physical planning, unreliable water supply and low income levels (Ministry of Water Resources Works and Housing [MWRWH], 2007; Ministry of Local

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Government and Rural Development [MLGRD], 2010; Katukiza et al., 2010). Where such constraints and low human resource capacity exist, there is the need for technical standards and guidelines to direct the implementation or adaptation of available technical solutions without compromising user safety or the integrity of the environment (Mara, 2006; Paterson et al., 2007).

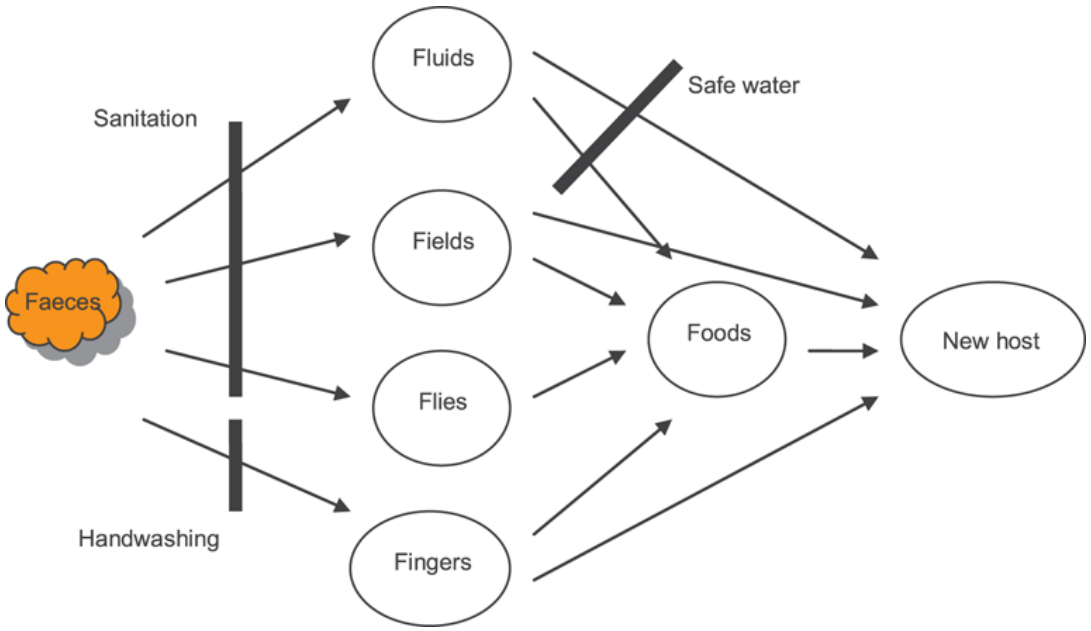
The purpose of this chapter is to review salient technical standards and guidelines for sanitation technologies commonly used in low-income countries with a specific focus on selection of appropriate technologies, prevention of groundwater pollution, control of odor and fly nuisances, structural stability and safety of the latrine user. The chapter identifies potential challenges that may be encountered in the application or enforcement of some standards and guidelines in specific difficult areas such as peri-urban settings and how they may be overcome. To facilitate an appreciation of the various standards and guidelines, the review is preceded with an overview of typologies and basic descriptions of the pro-poor sanitation technologies commonly used in low-income countries.

BACKGROUND

Sanitation Technology as a Barrier to Disease Transmission

Figure 1. illustrates the role of sanitation in breaking the routes of fecal-oral disease transmission. Of all types of human excreta, feces pose the greatest risk to health (Mara, 2010). It is estimated that one gram of fresh infected feces can contain 10^6—10^8 bacterial pathogens, 10^4 protozoan cysts or oocytes, 10^6 viral pathogens and 10—10^4 helminthes eggs (Feachem et al., 1983). When infected feces is indiscriminately disposed of, pathogens may be deposited in the soil, washed by water or carried by flies; it may also come into contact with human hands.

Figure 1. Sanitation technology as a barrier to fecal-oral disease transmission (Source: Mara et al. (2010))



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Through any of these routes, pathogens may be transferred to food and, ultimately, into the body of a new host. A person may also directly contract pathogens through contact with contaminated soil or drinking of polluted water. The result could be death or morbidity. Consequently, diarrheal diseases are the second cause of death in children under five years old, killing an estimated 760,000 yearly (World Health Organization [WHO], 2013).

Sanitation is a proven effective barrier that breaks these routes and prevents the transmission of gastro-intestinal diseases. Mara et al. (2010) accredits the first scientific notice of the relationship between disease transmission and the lack of sanitation to Chadwick's 'Report on an inquiry into the sanitary condition of the laboring population of Great Britain' (Chadwick, 1842). Since then, further scientific evidence has confirmed that gastro-intestinal diseases can be prevented or efficiently controlled through effective sanitation or its combination with water supply and hygiene. For instance, improved sanitation has been found to reduce the rate of diarrheal diseases by 32% – 37% (Waddington & Snilstveit, 2009; Fewtrell et al., 2005). Significantly, the impact of improved sanitation has been found to be even higher where baseline conditions were extremely poor. Examples of such cases were reported by Norman et al. (2010) and Barreto et al. (2007).

Emphasis on Simplicity and Affordability in Low-Income Countries

In low-income countries, cost and simplicity are key considered factors in choosing sanitation technology options (Murphy et al., 2009). On the basis of cost and simplicity, excreta disposal systems may be classified as either pro-poor or advanced (Heron, 2007; Paterson et al., 2007). Pro-poor or affordable sanitation technologies are often described by various terms such as low-cost technologies, appropriate technologies, sustainable technologies. Common examples include the pit latrines, the pour-flush latrine, the aqua privy and the septic tank with a water closet system. On the other hand, conventional sewerage is recognized as advanced or anti-poor (Paterson et al., 2007). Because some cost is saved by eliminating the need to transport excreta to a remote destination for completion of the sanitation chain, on-site sanitation technologies are commonly classified as pro-poor as compared to off-site technologies. However, it has been argued that simplified sewerage that relaxes the conservative design codes used in conventional sewerage can be cheaper than on-site sanitation in peri-urban areas where high population densities create economies of scale (Paterson et al., 2007). Notwithstanding, this chapter is restricted to on-site sanitation technology options.

The most important features of pro-poor sanitation technologies are that they are simple and inexpensive to construct, operate and maintain. It is important, however, that their simplicity and low-cost do not compromise the main sanitation function or the key requirement of an improved sanitation facility, i.e. the prevention of fecal-oral disease transmission (UN Millennium Project, 2005)

Basic Technology Options

Although recent attempts to adapt one technology or another to some specific local context have given rise to several technology options, sanitation systems commonly found in low-income countries are based on the following water-dependent and non-water-dependent technologies.

The most common non-water-dependent (dry) on-site sanitation systems are:

1. The simple pit latrine

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2. The ventilated improved pit (VIP) latrine
3. The composting latrine

The water-dependent (wet) on-site sanitation systems have water-seals and these include:

1. The pour-flush latrine
2. The aqua privy latrine
3. The septic tank with water closet

Recent technological innovations include the development of the bucket and cartage and the worm digester toilet with water closet. The feasibility and technical performance of these recent technologies are still being researched and are not discussed further in this chapter. For the above listed dry and wet sanitation systems, detailed technical descriptions, advantages and disadvantages have been thoroughly discussed in several works (e.g. Brikke & Bredero, 2003; Cotton et al., 1995; Feacham et al., 1983; Franceys et al., 1992; Harvey al, 2003; Kalbermatten et al., 1980; Mara, 1984, 1985; Tilley et al., 2008). From these existing works, the salient features of the technologies are summarized below to facilitate an appreciation of the significance of the various technical guidelines applicable to them.

Simple Pit Latrines

As a basic characteristic of all types of pit latrines, the simple or traditional pit latrine retains excreta, anal cleansing material and, in some cases, sullage and refuse (Franceys et al., 1992) in a hole dug in the ground. Pathogens are killed as excreta decompose to produce humus-like solids, water and gases. Liquids in the pit are allowed to percolate into the surrounding soil while gases dissipate into the air, leaving a solid residue in the pit. To be regarded as an improved sanitation option, the pit is covered with a slab (JMP, 2006). The cover slab bears a hole or a seat through which the user defecates. A superstructure is provided to ensure user privacy and protection from the elements of the weather. When the pit is full, it is covered and another one constructed using as much of the previous latrine's materials as possible.

Pit latrines are widely used in low-income countries because of their affordability and simplicity in construction and operation. They represent the cheapest form of sanitation possible (Franceys et al., 1992). Their main disadvantage is that they generate offensive odors and are associated with the breeding of insects especially house flies, mosquitoes and cockroaches. At their worst, their level of sanitary hygiene is only a little better than open defecation (Cotton et al., 1995). Like all other pit latrines, they could also pose health risks to the use of groundwater as a drinking water source. Their use in urban slums and high density peri-urban areas is limited as land may not be available for digging a second pit when the first one is full.

Ventilated Improved Pit Latrines

Ventilated improved pit (VIP) latrines are designed to overcome the challenges of intense odor and fly nuisance associated with the simple pit latrine. The main difference with the simple pit latrine is that the pit cover slab is fitted with a vent pipe that is covered at the top with a fly screen to control odor and fly nuisance. Odor control is achieved through the chimney effect that allows the circulation of air from the superstructure into the pit via the squat hole and out via the vent pipe as shown in Figure 2. The vent

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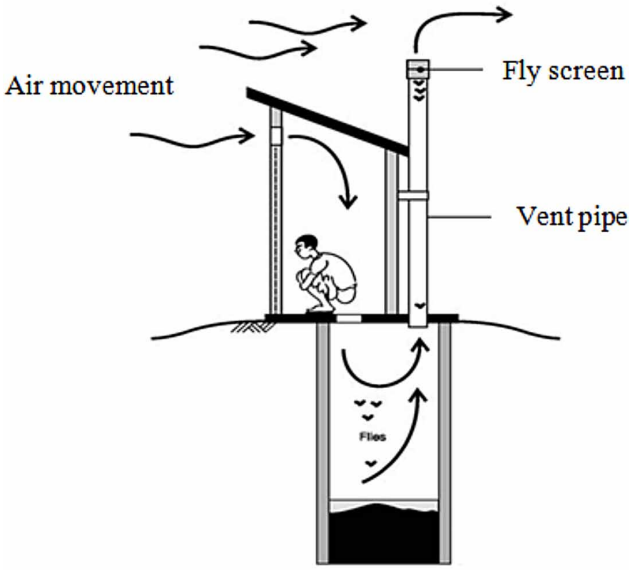
Figure 2. The chimney effect in a VIP latrine (Source: Harvey et al., 2002)



pipe is also responsible for directing flies produced in the pit to the external bright light at the top of the pipe. Flies are prevented from escaping through the vent pipe by the fly screen and die of dehydration (Brikke & Bredero, 2003) or fall back into the pit to die eventually. External flies attracted to the odor emitted from the top of the vent pipe are also denied entry by the fly screen.

The VIP latrine can be designed for permanent use by constructing a double pit (dividing a single pit with an impermeable wall), under the same superstructure, with each pit having its own squat hole and vent pipe. Developed in Kumasi, Ghana by staff of the Civil Engineering Department of the Kwame Nkrumah University of Science and Technology, it is popular in that country where it is locally known as the Kumasi Ventilated Improved Pit Latrine (KVIP). Only one pit is used at a time. When the first pit becomes full, it is covered and the second pit is used. Pit sizes are designed to allow adequate retention time, usually 2 years (Mara, 1984), so that by the time the second pit becomes full the content of the first pit would have decomposed and may be emptied by manual means. By alternating the two pits, the double-pit VIP can be used indefinitely. VIP latrines may also be designed with multiple pits under two or more cubicles.

With a proper superstructure and vent pipe design, odor and flies can be effectively controlled and the VIP can provide most of the health benefits and conveniences of conventional sewerage at a relatively much lower cost (Kalbermatten et al., 1980; Ryan & Mara, 1983). They are, however, more expensive to construct than simple pit latrines and require a greater operational input from the user, especially the double-pit VIPs (Franceys et al., 1992). As in simple pit latrines, the risk of groundwater pollution is a major concern. For low-income households, the additional materials required for the vent pipe and pit division may make the VIP less affordable as compared to the simple pit latrine.

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Composting Latrines

There are two types of composting latrines depending on whether the latrine employs a continuous or a batch composting mechanism (Franceys et al., 1992; Kalbermatten, 1980). The continuous and batch composting latrines employ aerobic and anaerobic composting processes respectively (Harvey et al., 2002). The continuous composting latrine consists of a watertight sloping chamber directly below the drop hole, into which feces and urine fall. Inverted U- or V-shaped ducts and ventilation pipes are used to create aerobic conditions by promoting the passage of air through the mass of excreta and to allow excess moisture to evaporate (Franceys et al., 1992). After each use, the feces are covered with an absorbent usually in the form of dry organic wastes such as sawdust, ash, grass or household refuse. The absorbent deodorizes the decomposing feces, absorbs excess moisture and maintains an appropriate carbon-nitrogen ratio suitable for composting. As new material enters at the top, old material gradually slides on the sloppy floor into a humus vault from where the humus is periodically collected and used as a soil conditioner.

In the batch or anaerobic composting latrine, the decomposing excreta is retained in the chamber without periodic removal until the chamber is about three-fourths full. At this stage, it is topped with earth and sealed for the composting process to continue under anaerobic conditions. In many cases, urine is collected separately and used as a fertilizer. The most common type of the batch composting latrine is the double-vault composting latrine that employs two chambers or vaults used alternatively like a double-pit VIP latrine.

The obvious advantage of the composting latrine is the production of a soil conditioner that may be a useful farm input where it is socially acceptable and a demand exists. Besides, the use of watertight chambers substantially minimizes the risk of groundwater pollution as compared to the pit latrines. This makes the technology more suitable where the water table is high or groundwater is a major source of drinking water. Nevertheless, the technology requires a careful operation to prevent excessive odors and fly proliferation (Franceys et al., 1992). There is the need for household awareness on the rate of absorbent addition and, in the case of the continuous composting latrine, the rate at which the compost is removed. Besides, the requirement for organic wastes or grass limits their use to areas where households may have gardens and the compost may be required for agriculture. Even in these areas, their use may still be limited unless excreta reuse in agriculture is culturally acceptable.

Pour-Flush Latrines

The simplest form of the pour-flush latrine is a modification of the simple pit latrine which incorporates into the latrine cover slab a pan (commonly referred to as a pour-flush bowl) fitted with a shallow U-bend trap that provides a water seal as shown in Fig. 3a. After defecation, a few liters of water, about 1—4 liters depending on the geometry of the bowl and trap (Franceys et al., 1992), is poured into the bowl to flush the excreta into the pit. In another design, referred to as the offset pour-flush latrine, the pit is completely displaced from the latrine superstructure, as shown in Fig. 3b, and the bowl is connected to the pit with a short pipe of about 100 millimeter diameter (Kalabermatten et al., 1980). In its simplest form, the pit is sealed when it becomes full and another one is dug, but the offset design allows two pits to be used alternatively as in the double-pit VIP.

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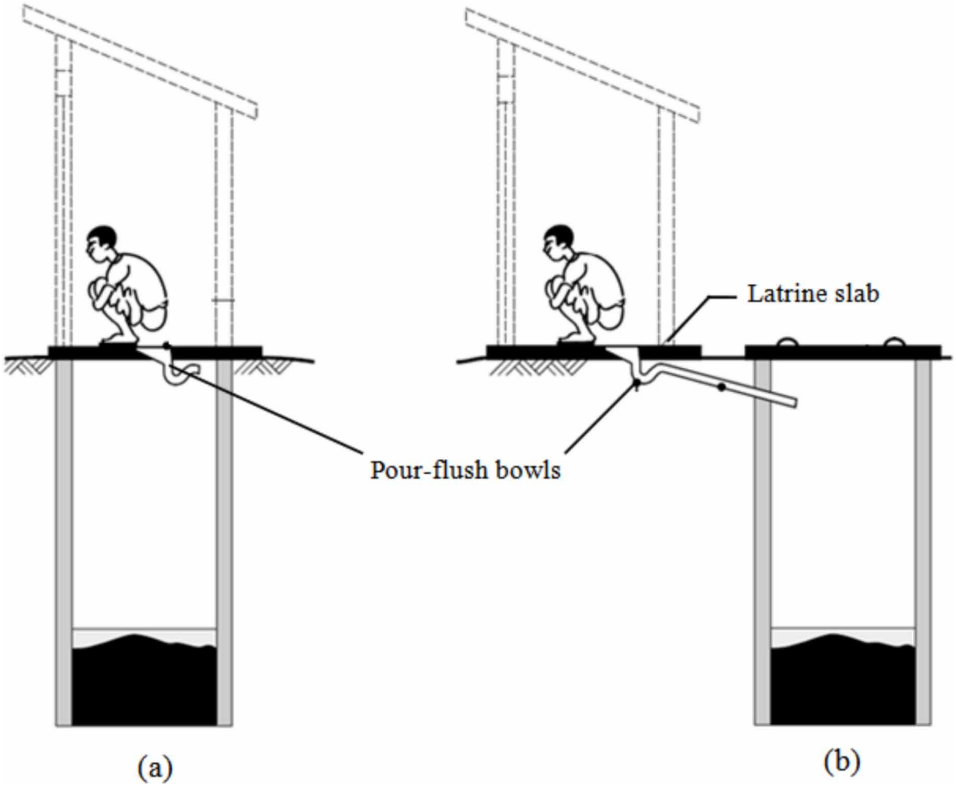
Figure 3. Pour-flush latrines (Source: Adapted from Harvey et al., 2002)



If properly constructed and maintained, the pour flush latrine can effectively reduce the nuisance of odor and flies. The offset pour-flush latrine can be conveniently provided inside a dwelling with the pit located outside (Heron, 2006). They are particularly suitable where water is used for anal cleansing and squatting to defecate is preferred. However, poor design or improper use can easily lead to blockage of the water trap. Besides, the requirement of water for flushing can be a setback where water is fetched from a communal source.

Aqua Privy Latrines

An aqua privy latrine (Figure 4) has a watertight underground tank directly below the latrine floor. The tank is filled with water above the level of excreta to maintain a water seal. Excreta are dropped into the tank through a chute which is fitted to the base of the drop hole and extends into the water in the tank. The user needs to flush sufficient water to replace any water losses due to leakages and evaporation in order to maintain the water level in the tank and to clear out the chute of any blockage by excreta. The aqua privy operates essentially as a small septic tank. Usually, effluent is allowed to infiltrate into the soil through a soak pit while the sludge in the tank is removed periodically by a cesspit emptier.

If the level of water in the tank is properly maintained, i.e. above the sludge, the aqua privy eliminates the problems of odor and flies. In practice, however, the water level is often found to be improperly maintained either because users are not aware of its relevance to the operation of the system or are reluctant

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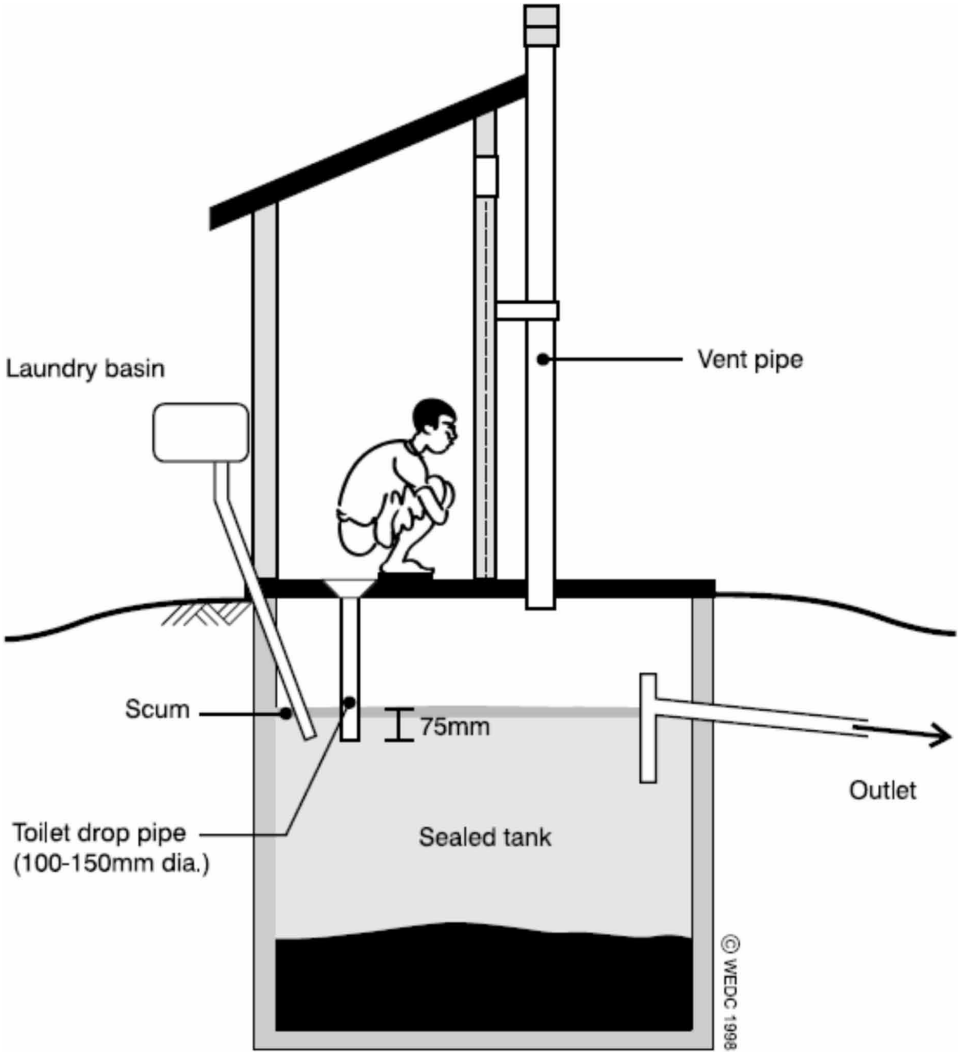
Figure 4. Aqua privy latrine (Source: Harvey et al., 2002)



to expend or carry the water to the toilet (Kalbermatten, 1980). Besides, the requirement of a watertight tank and regular use of water make the aqua privy a more expensive technology to construct and operate than the dry sanitation systems described above or the pour-flush latrine (Franceys et al., 1992; Heron, 2007). Furthermore, the use of a soak pit or a drain field could pollute groundwater resources.

The Septic Tank with Water Closet

The septic tank is a watertight settling chamber built just below the ground level to receive raw sewage via a pipe connected to a water closet toilet with a water seal. It is suitable where the volume of wastewater produced is too large to be disposed of in pit latrines and a central sewerage system is unaffordable (Harvey et al., 2002). The solids in the sewage settle in about 1—3 days of hydraulic retention time and are digested anaerobically in the tank (Kabermatten et al., 1980). Sludge and scum are required to be

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removed periodically using a cesspit emptier but the liquid effluent is usually disposed of by infiltration in a soak pit or drain field. Hence, the system works more efficiently where the soil is well permeable and not prone to flooding or waterlogging. The main difference with an aqua privy is that the septic tank is completely offset from the toilet superstructure while the aqua privy is built directly under the superstructure (Heron, 2007).

A well maintained septic tank with a water closet system provides all the convenience of conventional sewerage. However, about 7—12 liters of water is required for flushing when full-flush water closet systems are used. This, coupled with the large space requirement and high cost of construction, makes the septic tank the most expensive on-site sanitation system (Brikke & Bredero, 2003).

GUIDELINES FOR TECHNOLOGY SELECTION

Frequently, the failure of sanitation facilities leading to environmental pollution and cause for nuisance can be traced to the wrong choice of technology for the given context. Generally, guidelines for selection of sanitation technologies emphasize the need for the chosen technology option to be sustainable. This means the technology can be constructed with readily available materials; will be accepted and regularly used by the intended users; and can be operated to achieve the overall goal of preventing fecal-oral transmission at an affordable cost (Howard et al., 2003; Ngoc and Schnitzer, 2009; Ottoson and Stenström, 2003). To achieve this goal, some general and specific guidelines need to be observed.

General Guidelines for Selecting Sustainable Sanitation Technologies

To select sustainable sanitation technology options for any given locality or household, the following general guidelines have to be observed:

Performance of the Basic Sanitation Function

Within the conditions of the existing natural and built environment, the chosen technology should be able to satisfy the basic requirement of disposing of excreta in a manner that reduces the risk of fecal-oral transmission to its users and the environment (Mara et al., 2010, UN Millennium Project, 2005). On this basis, bucket latrines, pit latrines without slab, flush or pour–flush to the open environment and open defecation in bushes or beaches are ruled out as improved sanitation options (JMP, 2006).

Acceptance by the Intended Users

For a given sanitation technology to be regularly used, it should be acceptable in the light of the cultural values of the intended user groups (Garfi & Ferrer-Marti, 2011). In view of this, it is highly recommended to involve the intended users in the process of technology selection (Ntim, 1988).

Use of Locally Available Materials

As a general rule, technology options that make use of locally available materials are more sustainable than those that require importation of materials (Mitchell, 1980). This is because the use of locally avail-

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able materials eliminates dependence on external sources of material supply and mostly reduces the cost of the technology (Murphy et al., 2009). Besides, facilities constructed with locally available materials by local tradesmen can be easily repaired in the event of any breakdown (Garfi & Ferrer-Marti, 2011).

Affordability

Affordability is a basic requirement for technology uptake because most people who need sanitation in low-income countries are poor (Jenkins & Sugden, 2006). Therefore, a sustainable sanitation option for a low-income setting should be affordable to the majority of intended users (Murphy et al., 2009). However, a sustainable technology option for a given context need not necessarily represent the least-cost solution. The most important consideration is to ensure that the cost of the technology is closely matched to how much the intended users are willing and capable of paying (Murphy, 2009).

Requirements of Operation and Maintenance

To ensure constant availability and regular usage, the skills and services required for operation and maintenance should be readily available. Priority should be given to technologies that local people will be capable of maintaining and repairing (Darrow & Saxenian, 1993; Garfi & Ferrer-Marti, 2011). Maintenance support services, where necessary, should be accessible. For instance, the use of a septic tank should only be recommended where cesspit emptying services are available and the proposed latrine location will be accessible to a cesspit emptier.

Guidelines on Specific Factors Affecting Technology Selection

In addition to the above general guidelines for selecting sustainable sanitation technologies, guidelines are available to support sanitation practitioners on how the following specific factors may influence the choice of technology options:

Water Consumption/Availability

It is widely accepted that a minimum of 20 liters per person per day is required for drinking and personal hygiene in order to derive maximum benefits from hygienic excreta disposal irrespective of the sanitation technology chosen (JMP, 2006; WHO, 2008). Thus, wet sanitation systems should only be considered when available water supply is in excess of 20 liters per capita per day. Table 1 shows guidelines for minimum water requirements for various wet sanitation technologies:

In the absence of data on water consumption or availability, it is recommend that wet systems are avoided where water is only available from communal sources but not within individual compounds, with the exception of the pour-flush technology that may be feasible in such situations if water is used for anal cleansing (Kalbermatten et al., 1980). A yard or compound connection makes systems employing a water-seal feasible but caution must be exercised against the use of full-flush cistern systems (Kalbermatten et al., 1980). This may be attributed to their inefficient operation under conditions where water is not piped directly to the toilet location in the house.

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Table 1. Minimum water requirement for wet on-site sanitation systems

Sanitation technology	Minimum water requirement for flushing (liters per person per day)
Pour-flush (direct on pit)	3—6
Pour flush (offset)	6—10
Aqua privy	6—10
Septic tank with cistern flush water closet	10—20

Sources: Kalbermatten et al., 1980; Mara, 1985; Gleick, 1996

Housing Density

As a guide, the pit latrines, pour-flush and septic tanks with soakaways are not suitable in densely populated areas where the population density exceeds 300 persons per hectare (approximately 110,000 square feet) for single-story homes (Kalbermatten et al., 1980; Mara, 1984). It should be noted that the low-population status of peri-urban areas of low-income countries can no longer be taken for granted due to recent rises in their population densities (Barrios et al., 2006; Paterson et al., 2007).

Nature of Soils

Generally, all systems requiring on-site effluent disposal by infiltration such as the pit latrines, pour-flush latrines and septic tanks require permeable soils for efficient operation (Brikke & Bredero, 2003; Fraceys et al., 1992; Kalbermaaten, 1980). Mara, 1984 recommends a minimum of 2 millimeters per hour for VIP latrines. Obviously, wet systems such as pour-flush and septic tanks or aqua privies with soakaways would require no less infiltration rate than this.

PREVENTION OF GROUNDWATER POLLUTION

General Guidelines for Prevention of Groundwater Pollution

Groundwater pollution is perhaps the most crucial concern for the use of on-site sanitation systems, especially pit latrines and other systems in which liquids are allowed to seep into the surrounding soil (Graham & Polizzotto, 2013; Katukiza et al., 2012). To prevent groundwater pollution, minimum distances are recommended for the vertical clearance between pit bases and the groundwater table, as well as the lateral clearance between the latrine location and groundwater abstraction points. To prevent groundwater pollution, the section of unconsolidated soils between the bottom of a pit latrine and the groundwater table has been identified as the most important line of defense against bacteria and viruses (Mara, 1984). There is a general consensus that a minimum of 2 meters of this section offers protection against pathogenic organisms (Banks et al., 2002; Franceys et al., 1992; Lewis et al., 1982). However, it has been suggested that 1.5 meters may be tolerated (Banks et al., 2002).

Guidelines on the minimum lateral distance between latrine locations and groundwater abstraction points are widely varied, ranging between 8 and 75 meters. A minimum distance of 15 meters was found

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by Lewis et al. (1982) in a comprehensive review as being safe and traditional. Shorter distances have been recommended for some more favorable conditions. According to the WHO, 15 meters is satisfactory where the latrine is upstream to the groundwater abstraction point but could be reduced if the latrine is located downstream, though no minimum distance is suggested by the WHO for the latter case (Franceys et al., 1992). Also, where the soil is fine, it has been suggested that the distance could be reduced to 8 meters (Wegelin-Schuringa, 1991). Moreover, Cotton et al. (1995) note that where a minimum of 2 meters of unsaturated zone can be maintained between the pit base and the water table throughout the year, a well or borehole may be cited a few meters away from a latrine but no specific minimum distance has been specified for such situations. Nevertheless, some national agencies require that latrines are located at longer distances from drinking water sources. Examples include 30 meters for Haiti (Reed, 2010), 50 meters for Ghana (CWSA, 2010) and 75 meters for South Africa (Still & Nash, 2002). For areas with rocky soils and shallow groundwater tables, it has been recommended that pit latrines should not be used at all (Nichols et al., 1983; Pujari, et al., 2012).

Special Measures Under Difficult Conditions

For some localities such as peri-urban settings in low-income areas, it may be a challenge to meet a minimum distance between latrine locations and groundwater abstraction points. This is due to the likelihood of the need to site both groundwater sources and latrines on the same compound. Low-income peri-urban areas receive a disproportionately inadequate piped water supply (Paterson et al., 2007) that makes most households rely on usually untreated groundwater via wells and boreholes (Cotton et al., 1995; Rosa & Clasen, 2010; United Nations, 2008). Meanwhile, restrictions are often placed on the siting of latrines by lack of space that may be attributable to high population densities and poor physical planning (Paterson et al., 2007). Consequently, it may be challenging accommodating a latrine and a groundwater abstraction point at 15 meters apart on the compound of a household.

In such difficult situations, a possible solution may be the raising of latrines above the ground level to increase the vertical separation between the pit base and the water table to a minimum of 2 meters (Dzwairo et al., 2007; Graham & Polizzotto, 2013) to compensate for a shorter lateral separation between latrine location and a water source. If the effective size (E.S.) of soil particles is 0.2 mm or less and an unsaturated section of 2 meters can be maintained throughout the year, even pour-flush latrines that discharge more effluent than pit latrines can be located at 3 meters away from water sources (Roy et al., 1984). The same distance can be maintained for soils of an effective size larger than 0.2 millimeters, provided the bottom of the pit is sealed off with an impervious material such as a plastic sheet or puddle clay while an envelope of fine sand (E.S. $<$ 0.2 millimeters) is provided around the pit up to a thickness of 500 millimeters (Harvey et al., 2002; Roy et al., 1984). A greater challenge may be faced in coastal peri-urban settings and other places where a higher water table may make it impossible to maintain 2 meters of the unsaturated zone above the water table. In such cases, a minimum distance of 10 meters instead of 3 meters should be maintained with the same precautions taken as described above if the soil sizes are larger than 0.2 millimeters (Roy et al., 1984).

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CONTROL OF ODOR AND FLY NUISANCES

Odor Control Mechanisms

Intense odor is one of the major challenges associated with the most basic sanitation technologies such as the simple pit latrine (Brikke & Bredero, 2003; Franceys et al., 1992). To control the emission of odor, both structural and operational solutions have been recommended. Identified odor control solutions include structural designs to improve ventilation, use of a water seal and addition of substances. Relevant guidelines for these solutions are discussed below:

Structural Designs for Improving Ventilation

The problem of intense odor with the simple pit latrine is addressed in the ventilated improved pit latrine (VIP) with structural modifications that enhance the exchange of air between the pit and the external environment via the superstructure and vent pipe. The VIP achieves odorless conditions when airflow rate through the vent pipe reaches 10 cubic meters per hour, but 20 cubic meters per hour is recommended for permanent (emptiable) toilets sited close to homes in urban centers (Ryan & Mara, 1983). Table 2 summarizes the sizes of vent pipes recommended to achieve these levels of ventilation while additional guidelines are summarized in Box 1.

Although adherence to these technical recommendations in Table 2 and Box 1 has been found to effectively control odor (Feacham et al., 1983; Franceys et al., 1992), their level of complexity may be above the capacity of many households in low-income peri-urban areas. The double-pit VIP developed with these guidelines in Ghana where it is locally known as the Kumasi Ventilated Improved Pit (KVIP) latrine has been particularly noted as being too complex and expensive (Jenkins & Sudgen, 2006). Such level of complexity may lead to poorly constructed latrines as households may lack knowledge of all relevant guidelines or seek to minimize cost. Poorly constructed latrines that fail to adequately control odor would discourage regular patronage by the prospective users and adoption by other households. To address these concerns, it would be necessary to assist households with technical support services through the local government system or use of community structures to train local artisans in latrine construction.

The above guidelines were found to achieve good odor control, mostly based on the feedback of users of the latrines studied. However, no studies have reported the use of modern gas detectors to quantify the actual levels of various odorous gases that can be maintained in latrines constructed in accordance with these guidelines. This could make research on odor control less subjective and contribute to the development of permissible levels for public health regulation, especially monitoring of public toilets in low-income countries.

Table 2. Minimum sizes of vent pipes

Type of vent pipe	Minimum size for 10 cubic meters per hour ventilation rate	Minimum size for 20 cubic meters per hour ventilation rate
Asbestos cement (AC) or polyvinyl chloride (PVC) pipe	100 millimeter diameter	150 millimeter diameter
Cement-rendered, bamboo or other rural vent pipes	200 millimeter diameter	230 millimeter diameter
Brickwork	180 millimeter square	230 millimeter square

Sources: Ryan & Mara, 1983; Mara, 1984

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Box 1. Guidelines for odor control in VIP latrines

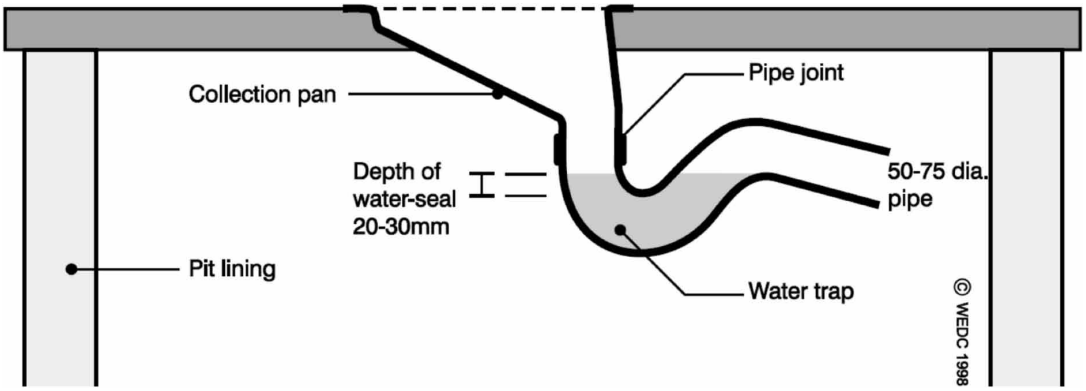
1. The vent pipe should be installed to a minimum height of 500 millimeters above a flat roof or the highest point of a sloping roof; for conical roofs, the vent pipe should be at least as high as the apex of the roof.
2. Where local wind speeds exceed 3 meters per second, the diameter of asbestos cement (AC) and polyvinyl (PVC) vent pipes may be reduced to 100 millimeters while those of other types may be reduced to 200 millimeters instead of the dimensions stated in Table 2 for a 20 cubic meter per hour ventilation rate.
3. For vent pipes serving two adjacent pits as in double-pit VIPs, the dimensions stated in Table 2 for a 20 cubic meter per hour ventilation should be maintained irrespective of the local wind speed.
4. For multiple alternating pits such as those used as communal latrines, a minimum of 200 millimeter diameter AC or PVC vent pipe should be provided
5. Where local wind speeds are less than 0.5 meter per second, the vent pipe should be painted black to enhance thermally induced ventilation.
6. The vent pipe should be located on the windward side of the superstructure.
7. Openings of a total area not less than 3 times the cross-sectional area of the vent pipe should be provided on the windward side of the superstructure; if both openings and vent pipe cannot be located on the windward size, preference should be given to openings on the windward side.
8. Openings in the opposite side to the windward direction should be avoided to avoid a drastic reduction in the pressure difference required to cause up-draught in the vent pipe.
9. The squat hole or toilet seat should not be covered to allow air flow through the superstructure into the pit.
(Cotton et al., 1995; Feacham et al., 1983; Franceys et al., 1992; Mara, 1984; Ryan & Mara, 1983)

Use of a Water Seal

Technologies such as the pour-flush, aqua privies and septic tanks make use of a water seal to prevent odorous gases from reaching the superstructure. For effective odor prevention, the following recommendations have been made:

1. The depth of the water seal, in a pour-flush latrine should be 20—30 millimeters in a 50—70 millimeter diameter water trap as shown in Figure 5 (Harvey et al., 2002; Roy et al., 1984)
2. The chute of an aqua privy latrine should extend to 50—75 millimeters below the water surface in the tank to effectively seal off odors (Brikke & Bredero, 2003; Franceys et al., 1992; Harvey et al., 2002). This requires that the water level above the sludge should be at least 75 millimeters (Brikke & Bredero, 2003).

Figure 5. Cross-section of a typical pour-flush pan with a water-trap (Source: Harvey et al., 2002)



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Addition of Substances

Various substances have been reported as being added to excreta by latrine owners in low-income countries to reduce odor (Rheinlander et al., 2013). Substances that have been recognized by experts as inhibiting odors and commonly recommended for use in composting latrines are mostly absorbents such as sawdust, wood ash, dry grass, husks, peat moss, etc. (Brikke & Bredero, 2003; Fraceys et al., 1992; Kalbermatten et al., 1980). Most of these substances were thought to be readily available at an affordable price or at no cost in the peri-urban environment where latrine owners may keep gardens (Kalbermatten et al., 1980). However, recent sharp rises in population densities in peri-urban areas (Barrios et al., 2006; Paterson et al., 2007) make this claim contestable.

No guidelines were found on the optimum quantities of the various substances required to achieve an acceptable level of odor control for any given excreta loading rate. Such data would be useful to help households achieve a good level of odor control with minimal material doses. Given the bulky nature of some of these materials, applying optimum quantities is absolutely necessary to avoid compromising the excreta storage capacity of latrines.

Fly Control Measures

The installation of a vent pipe and water traps as discussed above are also meant to control the proliferation of flies in latrines. For the VIP latrine, the following specific measures are recommended for controlling flies and other insects (Curtis & Hawkins, 1982; Franceys et al., 1992; Mara, 1984; Ryan & Mara, 1983):

1. The vent pipe should be installed as vertical as possible to easily direct flies in the pit to the light of the sky.
2. The top of the vent pipe should be covered with an insect screen having apertures not exceeding 1.2 x 1.5 millimeters to prevent entry of flies and mosquitoes.
3. The toilet room should be kept as dark as possible so that flies in the pit would not be attracted to light in the toilet room.
4. The door should be closed when the toilet is not in use to keep the room dark.
5. An insect screen may be used to cover the squat hole when not in use.

In recent times, efforts to improve the VIP have replaced masonry seats with prefabricated porcelain bowls fitted with plastic seats and covers like those used in water closet toilets. In addition to its aesthetic value, the smooth surface of the porcelain bowl allows easy cleaning while the plastic seat offers a more comfortable seating arrangement. Also, the plastic cover supposedly prevents flies from entering or leaving the bowl or pit. However, complete covering of the toilet seat is known to disrupt the chimney effect as noted above. Based on successful use of insect traps over VIP squat holes in Tanzania (Curtis, 1981), a potential improvement could be the replacement of the solid cover with an insect screen fitted in a plastic frame. However, the introduction of screened seat covers could also interfere with the chimney effect due to the reduced flow area and head losses associated with airflow through the fly screen (Ryan & Mara, 1983). Such interference may be compensated for by a revision of existing guidelines on vent pipe dimensions but no such investigation has been reported.

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STRUCTURAL STABILITY AND USER SAFETY

Safety concerns over the use of on-site sanitation mostly arise from possible collapse of the pit, the cover slab or superstructure. Structural stability is of a greater concern where the latrine is built in unstable soils. Beside these, there is also the fear of entry by rodents and reptiles and the risk of the user falling into the pit through the squat hole. Relevant guidelines on assessing soil stability and addressing safety concerns are discussed in this section.

Soil Stability Criteria

Soil stability may be assessed in terms of the particle size distribution or undrained sheer strength as described in, for example, British Standards BS 2004: 1972 (Mara, 1984). Soils are considered stable if they contain more than 30 per cent clay (E.S < 0.002 millimeters) or a combined sand and silt (E.S. > 0.002 millimeters) fraction not exceeding 70 per cent; on the other hand, soils with undrained shear strength of 20 kilonewton per square meter or above can be considered stable enough to support normal superstructures and cover slab loads (Mara, 1984).

In low-income countries, such scientific assessments of soil stability would most likely be unaffordable to individual households. In such situations, Mara (1984) recommends a simple improvised evaluation of the soil's stability by collecting samples by hand-auguring at 0.5 meter intervals to a depth of 3 meters. A rough cylinder of approximately 5 centimeters in length and 2 centimeter diameter is then formed from each sample by hand-rolling. When the sample is gently crushed between the thumb and fingers after sun-drying for two days (or oven-drying at 100 degrees Celsius for two hours where possible), unstable soils are found to crush easily while stable, cohesive ones do not. Obviously, this test is subjective and requires experience after practice with soils of known particle size distribution and undrained sheer strength.

In addition to the above, it can be reasonably assumed that if other excavations in the locality such as hand-dug wells have not been lined and they have been self-supporting for a number of years, then it will be fairly safe to leave pit latrines unlined (Franceys et al., 1992, Harvey et al., 2002).

Pit Lining

Aside from systems such as septic tanks and aqua privies that require watertight chambers that must always be lined (Franceys et al., 1992), pit lining is recommended as a safety measure where the soils are unstable (Fraceys et al., 1992; Mara, 1984). Even in stable soils, it is recommended to always line the top 0.5 meter of the pit as a precautionary measure against pit collapse due to, for example, gradual release of pore water pressure (Franceys et al., 1992; Harvey et al., 2002; Mara, 1984). According to Mara (1984), this could be in the form of partial lining by plastering the soil faces with 10 millimeter thick cement mortar using 1 part cement and 5 parts sand. However, Franceys et al. (1992) recommend full lining at the top 0.3—0.5 meter to support the slab in all cases.

In unstable soils, pits should be fully lined with suitable materials such as fired bricks, concrete blocks, cast in-situ concrete, perforated oil drums, ferrocement, etc, with perforations or unmortared joints left below a depth of 0.5 meter to allow for infiltration (Franceys et al., 1992; Harvey et al., 2002; Mara, 1984). In wet pits, lining can be done by inserting short-length concrete pipes as excavation proceeds (Mara, 1984).

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Stability of the Cover Slab

The cover slab may be made of concrete, wood, ferrocement and plastic but concrete is the most preferred material due to its durability, low cost and ease of cleaning (Harvey et al., 2002). As a basic requirement, the cover slab should not deflect noticeably and should be strong enough to support the weight of the superstructure, a vent pipe (in the case of VIPs), a pedestal seat (if used) and the user (Franceys et al., 1992; Mara, 1984). When concrete is used, it is necessary to reinforce it with steel bars placed at the lower side of the slab to prevent the development of tension cracks and eventual collapse. Adequate strength may be achieved with different combinations of slab thickness, diameter of steel bars and spacing intervals. The spacing of steel bars to be provided along the length and breadth of the cover slab are shown for different steel bar diameters and slab thickness in Table 3.

In low-income settings, the cost of reinforcing the cover slab, which is usually the most expensive component of a pit latrine (Harvey et al., 2002), can be a major setback to households. As an alternative to reinforcement, the concrete may be cast in a dome shape which transmits the imposed weights to the supporting ground, leaving the underside of the slab in compression and therefore requires no reinforcement (Franceys et al., 1992; Harvey et al., 2002; Mara, 1984)

Size of Drop Holes

To minimize the risk of falling into the pit, especially for children, Mara (1984) recommends the use of a key- or pear-shaped opening with a maximum width of 200 millimeters. Harvey et al., however, recommend a maximum of 250 millimeters and a minimum of 160 millimeters to avoid users fouling the floor with feces and urine. Perhaps, latrines to be used by children should have a maximum drop hole width of 200 millimeters. Further research in the determination of an appropriate size of drop holes need to consider the squatting positions of men, women and children of different ages, height and weight.

Prevention of Entry by Rodents and Reptiles

In Nepal, rats have been reported to burrow into double-pit latrines through holes allowed in the lining for infiltration (Fraceys et al., 1992). Rodents and reptiles may also enter the superstructure through openings allowed for ventilation. Although a full lining of the top 0.5—1 meter of pits has been recommended for preventing entry by rats (Franceys et al., 1992), not much detailed guidelines exist on how to effectively prevent other rodents and reptiles from entering the superstructure through openings

Table 3. Spacing for steel reinforcement bars in pit latrine cover slabs

Slab thickness (millimeters)	Steel bar diameter (millimeters)	Spacing of steel bars (millimeters) in each direction for minimum slab span of:				
		1 meter	*1.25 meters*	*1.5 meters*	*1.75 meters*	*2 meters*
65	6	150	150	125	75	50
	8	250	250	200	150	125
80	6	150	150	150	125	75
	8	250	250	250	200	150

Source: Franceys et al., 1992; Harvey et al., 2002

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provided for ventilation. Provision of special netting at openings could be a solution but its effect on the rate of ventilation due to loss of air pressure across the net needs to be investigated. It also calls for an investigation into the necessary compensation in the recommended size of openings, i.e. three times the cross-sectional area of the vent pipe, as recommended by Mara (1984).

FUTURE RESEARCH DIRECTION

Adapting existing guidelines on on-site sanitation systems to the evolving conditions of urban slums and peri-urban areas of low-income areas requires much attention in future research. Future research needs to explore opportunities for relaxing or modifying existing design codes to respond to the infrastructural limitations of these areas. Notably, population explosions in these areas and the inability of governments to match population growth with public infrastructure, especially water supply, place constraints on the selection and design of some sanitation technologies. For instance, lack of regular water supply implies that most households have to depend on dry sanitation systems, with the ventilated improved pit (VIP) latrine becoming increasingly popular in these areas. However, the performance of this technology is very sensitive to environmental factors such as wind speed and direction that are influenced by uncontrolled land development. Particularly, multiple extensions to houses in response to increasing demand for residential accommodation tend to alter the circulation of air within the neighborhood and lead to situations where existing VIP latrines that were originally built with openings facing the wind direction later become disoriented as the wind direction changes. In such cases, future research needs to explore the feasibility of a 'direction-free' VIP that would be independent of the direction of wind as well as improved designs of dry sanitation systems, in general, to eliminate or minimize the development of odors.

CONCLUSION

On-site sanitation technologies can effectively perform the basic function of raising a barrier against fecal-oral disease transmission and afford households in low-income countries all the health benefits of conventional sewerage provided relevant technical guidelines are observed in the choice of technology options, the design and construction of facilities and their operation and maintenance. Perhaps, the most crucial requirement for the long-term sustainability of facilities is the appropriate choice of a technology option to suit a given physical and socio-cultural environment. This chapter provides the most critical principles and considerations. Thus, the technology option should be capable of raising an effective barrier to disease transmission; it should be accepted and used regularly by the intended users; and it should be affordable in terms of the cost of construction and maintenance. To safeguard human health and environmental sustainability, the prevention of groundwater pollution is an overriding factor. This chapter has discussed minimum distances recommended for the vertical clearance between pit bases and the groundwater table, as well as the lateral clearance between the latrine location and groundwater abstraction points. Beside these, issues relating to the comfort and safety of the latrine user are key to consistent usage of facilities and, hence, the prevention of open defecation. Guidelines have been discussed for the control of odor and fly nuisances and the structural stability of facilities.

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However, the guidelines provided in this chapter should not be taken as being exhaustive or the final word of authority. Frequently, local experiences may require the development of specific guidelines by local experts in response to prevailing needs and challenges. In applying these guidelines, there is the need for flexibility and innovation. Nevertheless, such innovation should not compromise the safety of the latrine user and the prevention of fecal-oral disease transmission.

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KEY TERMS AND DEFINITIONS

Bucket and Cartage Toilet: A reinvention of the age-old sanitation system in which excreta are stored in the home in waste buckets or other containers that are collected regularly by a cleaning team and carted or transported to a central disposal or treatment site. The new system, which is referred to as porta potty in some countries, has a specially designed container that allows the separation of urine from feces.

Chimney Effect: The movement of air through chimneys and vent pipes as a result of buoyancy or difference in the densities of hot and cold air. In a ventilated improved pit latrine, external cold air entering the pit through the superstructure displaces hot air in the pit of a relatively lower density. The hot air then rises through the vent pipe.

Ferrocement: A thin-shell construction material consisting of cement mortar reinforced with wire mesh or small-diameter steel rods.

Guideline: A principle, code or recommendation to inspire a sound practice. Following guidelines is usually advisory rather than mandatory.

On-Site Sanitation: A type of sanitation system that retains all the components of a sanitation system within the premises or surroundings of the excreta generating entity. It may, however, require periodic removal of fecal sludge from the holding tank, pit or vault.

Sanitation System: An assemblage of structures and appurtenances for the collection, storage, transportation, treatment and disposal of excreta. Some sanitation systems may not involve all of the above components. In a broader sense, sanitation may be defined as the protection of human settlements from diseases associated with waste generated by humans. However, this chapter focused on sanitation as safe disposal of human excreta.

Shear Strength: The property of a material which measures its ability to resist forces that attempt to cause its internal structure to slide against itself in a plane that is parallel to the direction of the force.

Soakaway: A constructed drain field, usually consisting of a pit or a channel filled with crushed rock, in which waste water slowly infiltrates into the adjoining ground.

Soil Stability: The property of a soil that determines its tendency to be self-supporting, especially in the absence of an embankment.

Standard: A mandatory code of practice required to be followed in a particular vocation or service. A standard is meant to be enforced by an appropriate authority.

Structural Stability: The property of being stable or resistant to collapse.

Sullage: Any type of domestic wastewater generated from cooking, washing and cleaning that does not contain excreta. It is sometimes referred to as grey water.

Water Seal: A layer or section of water used to trap volatile substances or prevent them from escaping from a closed system.

Worm Digester with Water Closet Toilet: A sanitation system in which a digester containing macro-invertebrates (red worms) is connected to a micro-flush or full-flush water closet system to provide stabilization and reduction of excreta. The effluent is disposed of in a drain field or soakaway pit.

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Chapter 49
Mining Spatial Patterns of Distribution of Uranium in Surface and Ground Waters in Ukraine

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ABSTRACT

A variety of geovisualization and spatial statistical methods can reveal spatial patterns in the distribution of chemical elements in surface and groundwater, and also identify major factors which define those patterns. This chapter describes a combination of modeling techniques to enhance understanding of large-scale spatial distribution of uranium in groundwater in Ukraine, by linking spatial patterns of several indicators and predictors. Factor, correlation, and regression analysis, including their spatial implementations, were used to describe the impacts of several environmental variables on spatial distribution of uranium. Local factor analysis (or Geographically Weighted Factor Analysis, GWFA) was proposed to identify major environmental factors which define the distribution of uranium, and to discover and map their spatial relationships. The study resulted in a series of maps to help visualize and explore the relationships between uranium and several environmental indicators.

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INTRODUCTION

Surface and ground waters are important resources for drinking water supplies. Ukraine river flow is 1,000 m^3 per capita, which is one of the lowest indicators in Europe, so availability of quality drinking water is a very important issue for the country. Drinking water quality is determined by chemical and biological content of the water and depends on several factors, including radioactivity of surface and groundwater associated with various natural and anthropogenic processes.

Natural radioactivity and groundwater contamination is often studied in areas of the extraction and processing of minerals, including uranium and oil. Natural radioactivity of oil and gas was first registered in 1904 in Canada, and later found in many places worldwide (Schneider, 1990; Makarenko, 2000). Several areas in Ukraine have high concentrations of uranium, so surface and groundwater in these areas can be potentially unsafe as a source of drinking water. Concentrations of uranium of 0.08 Mg/L and higher are potentially dangerous to human health, therefore, investigation of the impacts of uranium on groundwater (and thus, on the quality of drinking water) is an important scientific problem (Canadian soil quality, 2007; Nacional'nij atlas, 2007; Uranium in Drinking-water, 2011).

Multiple studies suggest that geological structure is the main natural factor which determines the content of natural radionuclides in ground and surface waters (Hakonson-Hayes et. al., 2002; Myers et. al., 1982; Sami & Druzynski, 2003; Skeppstrom & Olofsson, 2007). There is a wide body of research on this topic, but the most relevant to Ukraine are studies implemented in Sweden, Finland, and Canada, as geological structures in these countries are similar to those in Ukraine; they are all located on Precambrian crystalline shields, Baltic and Canadian.

Ukraine is located in the central and southeast regions of Central Europe, with a population of about 47 million people. It spreads from the southwest of the Eastern European Plain, through the Ukrainian Carpathians and the Crimean Mountains, with its shores in the south washed by the Black and Azov Seas. About 95% of the country is relatively flat (with an average elevation of about 170m), and the Carpathians and Crimean Mountains occupy about 5% of its territory.

Ukraine is located within two major tectonic structures: the East European platform and the Alpine geosynclinal (folded) region. The plateau part of Ukraine is a rigid, slightly shifting tectonic structure with ancient crystalline rock covered by sediments (sand, clay, limestone, etc.). The Alpine geosynclinal region is dominated by sedimentary rocks. The system is relatively young (25-100 million years), and exhibits intense tectonic movements.

Ukraine has a complicated geological structure, comprising the following genetically related geostructural regions: the Ukrainian Shield, Volyn-Podolsk Upland, Dnieper-Donetsk Basin, Donetsk folded structure within the East European Platform, and Carpathian and Crimean folded systems and Scythian Platform within the Alpine geosynclinal region. An interesting geological structure, the Black Sea Depression, stands out in the entire system. The structure lies in the merging areas of the old East European and younger Scythian Platform.

Apart from radioactive elements in rocks, concentration of radioactive elements in natural waters is defined by hydrogeological and climatic conditions, physical properties of rocks, chemical composition and electrochemical properties of natural waters, migration of radioactive isotopes during their transition from rocks into the water and further transportation with water, as occurs mostly in faults or other permeable surfaces. On average, river water has less total natural radioactivity than the sea and underground waters, except for rivers in regions with highly radioactive rocks (Uranium in Drinking-water, 2011). Levels of radioactivity in rivers vary depending on seasonal changes; levels reduce in spring and rise

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during the low-water periods of summer due to an increase in the concentration of natural radionuclides. Higher levels of uranium are found in rivers with catchment areas composed of granites.

Another significant factor affecting water quality is climate. Climate change impacts all components of the environment, resulting in reorganization of geochemical processes. Climate plays a major role in rock weathering, and rocks, in turn, serve as a transportation channel for radioactive elements in natural water. For example, a large amount of precipitation leads to leaching of uranium from radioactive minerals, dilution of groundwater enriched with radioactive elements, and transportation of radioisotopes away from the source of natural concentration. Substantial saturation of rocks containing radioactive elements may result in accumulations of uranium and radon in groundwater. Chemical composition of water is another important factor. Acidity, gas composition, and oxidation are important elements defining the mineralization of water, which is directly related to concentration of uranium in groundwater.

In summary, major environmental and natural indicators affecting concentration of uranium in ground and surface waters can be grouped into four categories: geological structure and geomorphology, geochemical composition, mineralogical composition, and climate (Salih et. al., 2002). Geological and geomorphological factors include types and mineral structure of rocks, relief of the territory (elevation), structure of the relief (slope, exposure), and deepness of bedrock. Geochemical factors are characterized by distribution of rare earth elements in the water, which are often found in conjunction with uranium. These include arsenic, fluoride, chromium, copper, and zinc. Mineralogical indicators are divided into two groups: characteristics of water and those of soil. These indicators are the product of interaction between climate and geological structures. Mineralogical markers in water include common indicators of mineralization, hardness, chloride, sulphate, magnesium, and calcium. Concentrations of humus were used to characterize soil. Climatic factors studied were characterized by average annual rainfall, and average annual values of temperature and evaporation.

Figure 1 illustrates distribution of uranium in Ukraine. Two different symbolization methods for categorization of the source data were used to illustrate spatial distribution of uranium. While the areas of low concentration (below 0.04 Mg/L) and transitional types of uranium have been clearly identified using quintile categorization (Figure 1, center), geometric interval-based categorization were used to illustrate the distribution of high levels of uranium concentration (0.04-0.145 Mg/L, Figure 1, right). Zones of low concentration (Polesia, the Carpathian Montains, and Transcarpathia) are characterized by a percolative water regime and high level of precipitation. Low concentrations of uranium were observed in the Dnieper River valley in northern Ukraine and near the delta in the south. The highest concentrations were associated with the structures of the Ukrainian Crystalline Shield in central Ukraine and also observed near the coast of the Azov Sea.

Geographical distribution of uranium in surface and ground waters in Ukraine indicates that concentration increases from North-West to South-East. This trend is associated with arrangement of geologic structures (granite) in the Ukrainian Crystalline Shield, mineralization of water, and certain fluctuations of climate, such as increased evaporation (Shiraishi et.al., 1994). There are six uranium provinces in Ukraine with different geologic structures and features of concentration of uranium in rocks (Nacional'nij atlas Ukraïni, 2007). The northern and western regions of Ukraine are characterized by relatively low amounts of uranium. The main concentration of uranium is found in the Ukrainian Crystalline Shield, with the mining industry located mainly in Kirovohrad and Dnipropetrovsk regions. These areas exhibit high concentrations of uranium deposits. Another area of high concentration of uranium in waters is in eastern Ukraine, in the Donetsk fold region and partly in the Black Sea lowlands. Surface and ground water in this area are characterized by high levels of mineralization (Makarenko, 2000).

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Figure 1. Distribution of natural uranium in Ukraine, by geological survey points (left) and categorization parameters, quintile (center), and geometrical interval (right)
Data courtesy of State Enterprise "Kirovgeologiya" (Prirodni ta antropogenni, 2004)

The goal of this study is to explore various geostatistical methods to model spatial dependencies between several environmental variables and distribution of uranium in groundwater. The study is focused on comparative analysis of using several techniques to identify the most robust method to describe spatial distribution of uranium in groundwater in Ukraine. The analysis was conducted using tools available in SPSS, ArcGIS, and GeoDa packages.

BACKGROUND

This study is based on the results of geological surveys in Ukraine carried out by State Enterprise "Kirovgeologiya" (Prirodni ta antropogenni, 2004; Makarenko, 2000). The database consists of 23 environmental indicators collected in 9353 sample points in Ukraine and neighboring territories of Russia, Belarus, and Moldova. Unfortunately, not all environmental indicators are available for all neighboring territories, limiting the research by using only the complete dataset available for Ukraine (6546 sample points).Variables included in the source dataset are listed in Table 1. Several spatial statistical methods were used to discover patterns of spatial distribution of natural uranium. (Note on terminology: the terms 'natural variables,' or 'environmental indicators,' are widely used in this study to describe various natural and environmental factors, for example, mineralization, precipitation, relief, and many others. Some models use 'predictors' with the same meaning as 'variables.')

The following spatial analyses and cartographic visualization workflow was used to describe the impact of several environmental variables on spatial distribution of uranium.

Exploratory spatial data analysis (ESDA) was used for initial data analysis, such as checking for statistical distribution, linearity, multicollinearity, and presence (or absence) of a pattern (both in spatial and non-spatial domains). Based on initial hypotheses and results of ESDA, further statistical data exploration can be developed by building correlation, regression, and factor models.

Many methods of regression are based on the assumption that the distribution of the dependent variable is normal. Figure 2 displays the histogram of uranium concentration (left), which clearly shows that statistical distribution of the source data does not meet criteria for normality. However, logarithmic transformation brings the dataset closer to normal (Figure 2, center and right).

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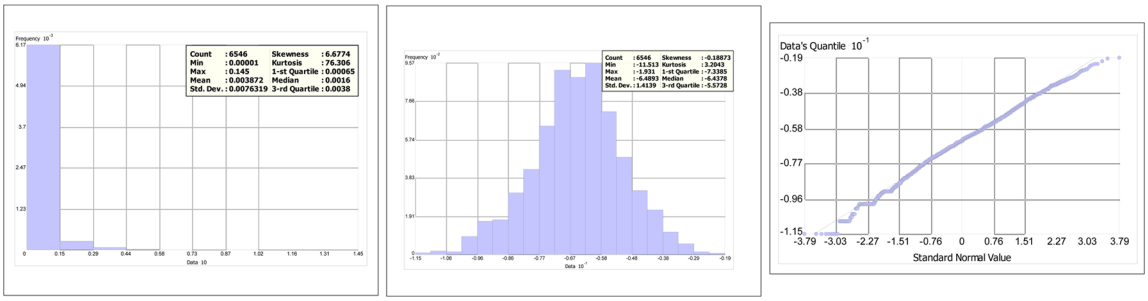
Figure 2. Histograms of the source (left), and normalized data (center), and normal QQPlot after applying logarithmic transformation (right)



For linear regression models, the relationship between a dependent variable and each independent variable should be linear. For example, the curve estimation procedure shows that the relationship between uranium and mineralization of waters is more exponential than linear; this would require nonlinear regression modeling. (However, implementation of multiple nonlinear regressions for these variables can be problematic.)

Independent variables can be significantly correlated (multicollinear) and produce unstable and unreliable multiple regression models. Several variables in the source dataset exhibit multicollinearity and require appropriate treatment.

Spatial autocorrelation methods were used to identify patterns in spatial measurements of uranium concentration. According to Moran's *I* and Getis-Ord analysis (Getis & Ord, 1992; Moran, 1950), the distribution of uranium can be described as highly clustered with statistical significance. Moran's *I* index is 0.5475 (p-value = 0.0) and Observed General G = 0.00007 (p-value = 0.0). There is positive spatial autocorrelation, as Moran's *I* is positive and greater than expected IndexE(*I*) = -0.00015. Thus, spatial patterns in observations of uranium should be taken into account in correlation, regression, and factors models to avoid bias due to over-counting (Anselin, 1995).

In the second step, quantitative measure of global correlation is used to confirm or reject several hypotheses of relationship between the dependent variable (uranium) and independent variables (environmental indicators). The analysis should identify natural variables which define high concentration of uranium, taking into account multicollineaity and clustered nature of the data.

The classical global Pearson correlation coefficient *r* is used as a measure of global correlation. The coefficient is defined as:

$$r = \frac{\sum_{i=1}^{n}\left(u_i - \overline{u}\right) * \left(v_i - \overline{v}\right)}{(n-1) * S_u * S_v}, \tag{1}$$

where *r* is the correlation coefficient; u_i and v_i are the individual observations; $\overline{u}$ and $\overline{v}$ are the means of the two variables; *n* is the sample size; and S_u and S_v are the standard deviations of the two variables.

In the next step, global factor analysis is applied as an attempt to identify underlying indicators and factors that explain the pattern of correlations within a set of natural variables. Factor analysis is used

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to identify a smaller number of natural variables that define most of the variance of uranium distribution. This study utilizes factor analysis based on the principal components using Varimax rotation with Kaiser normalization (Harman, 1976).

In the factor analysis model based on factor *p* is:

$$\Lambda_p = \Omega_p \Gamma_p^{1/2}, \tag{2}$$

where Λ_p is the matrix of factor loadings based on factor *p;* Ω_p is the diagonal matrix of ϖ_i that are the corresponding eigenvectors of *R*, where *R* is the correlation *n*×*n* matrix *or* eigenvectors of Σ, where $\Sigma=[\sigma_{ij}]_{n\times n}$ is the covariance *n*×*n* matrix of natural variables; and Γ is the matrix of eigenvalues. Here, *n* represents the number of variables and *p* is the number of factors. It is also assumed that each factor has unit variance and the factors are independent of each other.

After a varimax rotation, each original variable tends to be associated with one (or a small number) of components, and each component represents only a small number of variables. This simplifies interpretation of resultant factors and their associations with the variables. In addition, components can often be interpreted from the opposition of few variables with positive loadings to few variables with negative loadings. Varimax searches for a linear combination of the original factors, such that the variance of the squared loadings, are maximized, which amounts to maximizing (Harman, 1976).

The most significant natural variables, as identified from factor and global correlation analysis, were used to demonstrate spatial non-stationarity of correlation between uranium and natural variables. This was done by implementing local correlation analysis (or geographically weighted correlation, GWC). In this study, a local form of bilinear regression with optimized bandwidth was used to model spatially-varying relationships between uranium and natural variables.

The geographically weighted local Pearson correlation coefficient $r_i(x_k,y_k)$ is used, and defined as:

$$r_i(x_k, y_k) = \frac{\sum_{j=1}^{n} \varpi_j * \left(u_j - \overline{u}\right) * \left(v_j - \overline{v}\right)}{(n-1) * S_u * S_v} = \beta_1(x_k, y_k) \frac{S_u}{S_v}, \tag{3}$$

where $r_i(x_k,y_k)$ is the correlation coefficient, x_k,y_k is the location of observation *i*; u_j and v_j are the individual observations; $\overline{u}$ and $\overline{v}$ are the means of the two variables, ϖ_j is the weight assigned to each observation that based on a distance decay function centered on the observation *i; n* is the sample size; and S_u and S_v are the standard deviations of the two variables; $\beta_1(x_k,y_k)$ is the estimated parameter for the bivariate local least-squares regression on observation *i.*

Relationships between the dependent variable and all explanatory variables, as identified from the factor analysis, were modeled by using stepwise linear multivariate regression analysis (or ordinary least squares regression, OLS regression). Then, several most significant explanatory variables identified from the stepwise multivariate regression analysis were used to build local linear multivariate regression models (or geographically weighted regression, GWR) with the optimized bandwidth (Fotheringham et. al., 2002).

Explanatory variables in the spatial regression model have consistent relationships with the dependent variables both in geographic space and in data space. The following requirements of linear multiple regression have to be addressed (Tabachnick & Fidell, 2012):

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- Variables have a linear association.
- It is important not to miss significant explanatory variables (misspecification must be avoided).
- Explanatory variables should not be redundant (multicollinearity must be avoided).
- For every value of a dependent variable, the distribution of its residuals should be normal, and the mean of the residuals should equal zero.
- Residuals have a constant variance across all the values of the statistical variables (non-stationarity or spatial heterogeneity must be considered).
- The value of each residual is independent of all other residual values (spatial autocorrelation must be considered).

The OLS global regression formula was applied to the explanatory independent variables v_p to best predict the dependent variable *u*, and defined as:

$$u = \beta_0 + \beta_1 * v_1 + \beta_2 * v_2 + ... + \beta_p * v_p + \varepsilon \,, \tag{4}$$

where *y* is the dependent variable, x_p are the explanatory variables, β_p are global regression coefficients, *p* is number of variables, and $\varepsilon$is random error or residual.

A stepwise approach was used to build multivariate regression models. At each step, the independent variable not included in the equation had the smallest probability of *F-statistic*, if that probability is sufficiently small. Variables already in the regression equation are removed if their probability of *F-statistic* becomes sufficiently large. The method terminates when no more variables are eligible for inclusion or removal. The Akaike Information Criterion and *adjusted* R^2 are used to estimate the models' performance. The method also insures that Variance Inflation Factors among explanatory variables are low, to avoid measures redundancy or multicollinearity among explanatory variables.

There is a possibility to improve model results by applying local Geographically Weighted Regression (GWR), which takes into account the effect of heteroskedasticity (Fotheringham et. al., 2002; Ord & Getis, 1995).

The geographically weighted local regression (Fotheringham et. al., 2002), defined as:

$$u_i(x_k, y_k) = \beta_{0i}(x_k, y_k) + \beta_{1i}(x_k, y_k) * v_{1i} + \beta_{2i}(x_k, y_k) * v_{2i} + ... + \beta_{pi}(x_k, y_k) * v_{pi} + \varepsilon_i \,, \tag{5}$$

on observation *i*, where $u_i(x_k,y_k)$ is the dependent variable estimated in location *i*; v_{pi} are the explanatory variables; $\beta_p(x_k,y_k)$ are the local regression coefficients; *p* is the number of variables, and ε_i is the residual estimated in location *i*. Each local regression $u_i(x_k,y_k)$ equation is solved using a different weighting of the observations that based on a distance decay function centered on observation *i.*

GWR accounts for spatial non-stationarity in parameter estimates, but it does not directly address autocorrelation (Jetz, 2005). In addition, GWR models tend to have large numbers of parameters, which are not easy to empirically estimate.

If strong autocorrelation is present in the residuals of global multivariate regression models, further actions can be taken by using autoregressive models of spatial econometrics. The spatial lag model and spatial error model were used (Anselin, 2006).

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General expression for the spatial lag model is:

$$u = \rho * W * u + \beta * v + \varepsilon, \tag{6}$$

where u is a vector of dependent observations, W is a spatial weight matrix, ρ is a spatial autoregressive parameter, v is a matrix of explanatory variables, β are the respective regression coefficients, and ε is a vector of independent disturbances.

General expression for the spatial error model is:

$$u=\beta*v+\varepsilon \text{ with } \varepsilon=\lambda*W*\varepsilon+\zeta, \tag{7}$$

where λ is the coefficient of spatially lagged autoregressive errors and ζ is a vector of independently distributed errors.

A spatial error model is appropriate when there appears to be structure in the residual term, and a spatial lag model is appropriate when spatial structure is present in the variables of the model (Anselin, 2001, 2006).

Finally, local factor analysis (or geographically weighted factor analysis, GWFA) with the optimized bandwidth (Harris et. al., 2011) was used to generate linear multivariate regression models for the dependent variable (uranium), and six major factors were produced in the global factor analysis.

The geographically weighted local factor/regression models, defined as:

$$u_i(x_k, y_k) = \beta_{0i}(x_k, y_k) + \beta_{1i}(x_k, y_k) * F_{1i} + \beta_2(x_k, y_k) * F_{2i} + ... + \beta_{pi}(x_k, y_k) * F_{pi} + \varepsilon_i, \tag{8}$$

on observation i, where $u_i(x_k,y_k)$ is the dependent variable estimated in location i; F_p are the factors from principal components extraction; $\beta_p(x_k,y_k)$ are the local regression coefficients; p is the number of variables, and ε_i is the residual estimated in location i. Each local regression $u_i(x_k,y_k)$ equation is solved using a different weighting of the observations.

GLOBAL AND LOCAL SPATIAL CORRELATION ANALYSIS OF DISTRIBUTION OF URANIUM

The overall distribution of uranium depends on several factors defined by geographical conditions of the area. The most significant factors can be identified using global correlation of uranium with all indicators from the four defined groups: geological, geochemical, mineralogical, and climatic (see Table 1).

The highest global correlation coefficients of uranium were obtained for humus (r=0.52), temperature (r=0.51), precipitation (r=-0.50), and volume of natural groundwater resources (r=-0.56). Uranium also has significant correlation with the overall water mineralization (r=0.49) and its components: SO_4 (r=0.45), Cl (r=0.44), and hardness of water (r=0.49). These indicators are interdependent and highly correlated. Geomorphic indicators, which include relief (r=-0.24), sediment thickness (r=0.02), and slope of terrain (r=-0.08), were less associated with the distribution of uranium. Although there is a

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direct association between granite rocks represented in relief uplifts and uranium concentration in water, correlation analysis identifies certain relationships between uranium and mineralization of water and variations in climatic conditions.

Each factor affecting concentration of uranium has its own spatial distribution, forming certain allocations in geographic space. Local correlations for different indicators can form complex spatial patterns and anomalies. Moran's I and Getis-Ord analyses confirm that the distribution pattern of uranium is highly clustered. Thus, values of correlation coefficients inherit high non-stationarity and should be modeled by using local methods. For example, global coefficient of correlation shows very low relationship between uranium and isopachs (only r=0.02), but local coefficients of correlation range from -0.71 up to 0.42 indicating very high association between these two variables (see southwest area of Bessarabia region in Figure 3).

Global Factor Analysis of the Relationship Between Natural Variables and Uranium

There are many natural variables which influence the distribution of uranium. Factor analysis has been used to find the impact of a particular variable on the distribution of uranium in Ukraine. Analysis of 23 different natural variables has revealed six principal components which shape the distribution of uranium (see Table 1). In this case, the analysis involved the independent variables excluding uranium.

The first major component is characterized by mineralization of water, with the most important issue being the total salinity and hardness of water. The second component largely comprises metals dissolved in water (copper, iron, magnesium, and zinc). The third component describes climatic conditions of the territory and formation of surface and ground water. The fourth component is associated with the presence of organic compounds in water. The fifth component describes geomorphological characteristics, and the sixth component is associated with mineral compounds and metals which often accompany uranium ('satellites').

The analysis shows that all six identified principal components largely coincide with the four groups of natural variables outlined in the hypothesis of uranium distribution in Ukraine (see Table 2).

It should be mentioned, that factor analysis on all variables including uranium indicates that uranium belongs to the first mineralogical group.

Figure 3. Uranium (left), isopachs (center), and their correlation (right). This is an example of low global correlation (r=-0.02) with high values in local variations (r=-0.70, blue, and r=-0.42, red)

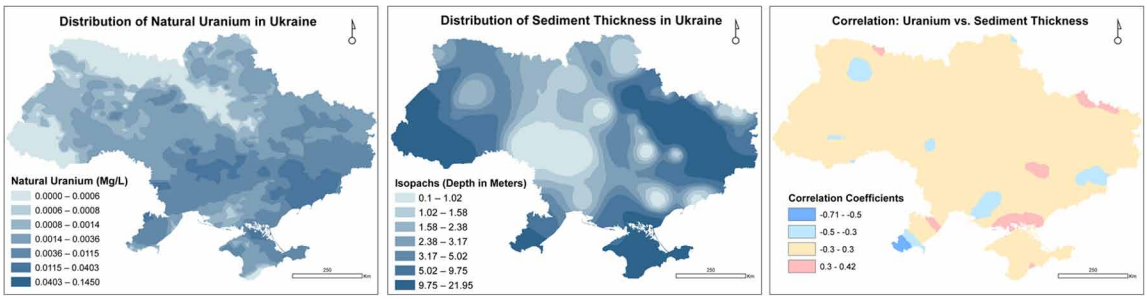

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Table 1. Principal components of environmental indicators

	Global Correlation Coefficient	Component					
		1	2	3	4	5	6
Explained variance (cumulative) %		30.2	44.2	54.1	62.3	68.0	72.5
SO_4	0.45	0.95	0.14	-0.09	-0.05	0.10	0.09
Mineralization of water	0.49	0.95	0.11	-0.16	0.00	0.13	0.15
Hardness of water	0.49	0.94	0.04	-0.17	0.01	0.06	0.17
Cl	0.44	0.92	0.07	-0.15	0.02	0.15	0.13
NO_3	0.27	0.63	-0.18	0.20	0.37	0.35	-0.06
Cu	-0.07	0.03	0.89	0.10	0.07	0.04	0.04
Fe	-0.15	0.01	0.85	0.29	0.00	0.07	-0.01
Mg	0.12	0.39	0.72	0.01	-0.09	0.09	0.00
Zn	0.01	-0.10	0.61	-0.42	0.10	-0.10	0.10
Precipitation	-0.50	-0.33	0.24	0.76	0.16	-0.16	-0.28
Relief	-0.24	-0.15	0.08	0.70	0.07	-0.01	-0.06
Slope	-0.08	-0.01	-0.05	0.62	-0.14	0.24	0.09
Temperature	0.51	0.43	-0.35	-0.52	-0.33	0.29	0.22
NH_4	-0.13	-0.03	0.04	0.17	0.82	-0.16	-0.04
NO_2	0.29	0.53	-0.01	-0.13	0.67	0.23	0.06
PO_4	0.17	0.04	0.21	-0.33	0.63	0.33	0.20
Cr	-0.39	-0.35	-0.23	0.25	0.59	-0.49	-0.22
Isopach (depth in meters)	0.02	0.13	0.08	0.29	0.07	0.70	-0.15
Humus	0.52	0.37	0.06	-0.08	-0.02	0.65	0.31
Volume of natural groundwater resources	-0.56	-0.43	0.26	0.38	0.26	-0.51	-0.29
HCO_3	0.16	0.13	-0.02	0.08	0.04	-0.23	0.78
F	0.35	0.21	0.05	-0.23	-0.04	0.13	0.55
As	0.23	0.03	0.05	-0.04	0.02	0.30	0.47

Table 2. Principal components and groups of environmental indicators

Component	Natural Variable	Group
1	Mineralization and hardness of water	Mineralogical
2	Metals dissolved in water	Geochemical
3	Climatic conditions of territory and formation of surface and ground water	Climatic
4	Organic compounds in water	Mineralogical
5	Geomorphological characteristics	Geological structure and geomorphology
6	Mineral compounds and satellite elements of uranium	Geochemical

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Local Spatial Correlation

Results of factor analysis were used to explore patterns of local spatial correlation of particular indicators with uranium. The local correlation analysis was carried out for the most significant elements from each component (highlighted in Table 1).

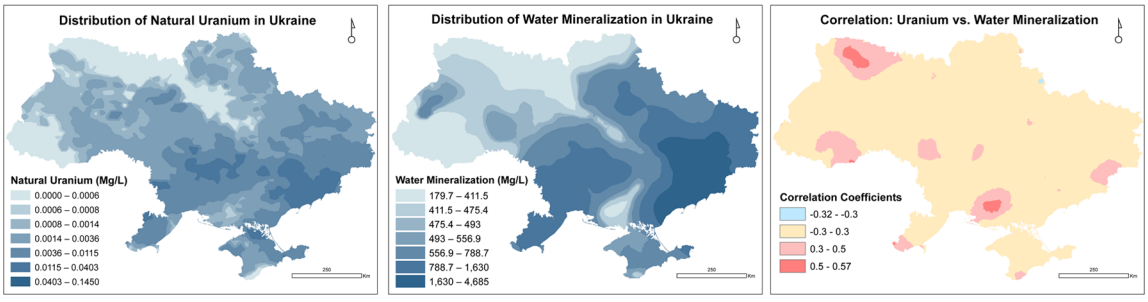
Component 1

Uranium exhibits positive correlation with total mineralization of water reaching r=0.56 in certain areas (Figure 4). The relationships strengthen in the north, center, and south of Ukraine, and weaken in the forest-steppe zone.

The total salinity of surface and groundwater gradually increases from the northwest to the southeast (Gorev, et. al., 1995), which is associated with climatic changes of the balance between precipitation and evaporation. Atlantic air masses soften the climate of the western part of Ukraine, increasing rainfall, and decreasing the temperature range and the total number of active temperatures. This is clearly articulated in the area of the Carpathian Mountains, where active migration of Atlantic air brings the maximum precipitation to Ukraine and the Western Polesie. The eastern Ukraine has more continental climate, defined by continental air masses of the eastern European part of Russia, and even Siberia. These air masses are characterized by low humidity and predominant anticyclonic activity when the balance between precipitation and evaporation is shifted towards evaporation. There is also a natural zonal increase in insolation from the north to the south.

Both mineralization and uranium are less exposed in the northern and western parts of Ukraine, but still exhibit relatively high correlation. The amount of mineralization of water in the forest-steppe zone is increased, but uranium does not show the same pattern, which results in weakening of correlation. High concentration of uranium in the area of the Ukrainian Crystalline Shield contributes to higher correlation with mineralization of water. In the south, the correlation is increased due to the increase of mineralization and concentration of uranium. However, correlation weakens in the western part of the Black Sea Lowland. High mineralization is associated with low values of uranium, which is found in small quantities in these sedimentary rocks. Overall, the correlation analysis highlights significant global association between uranium and water mineralization, with strong local correlation in certain

Figure 4. Uranium (left), water mineralization (center), and distribution of local correlation (right). Global correlation r=0.49



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areas in Ukraine. A strong relationship is defined mostly by climate parameters, geological formation, and distribution of large river basins. Weakening of correlation is associated with transition from the mixed forest to steppe zone with specific balance of temperature and precipitation.

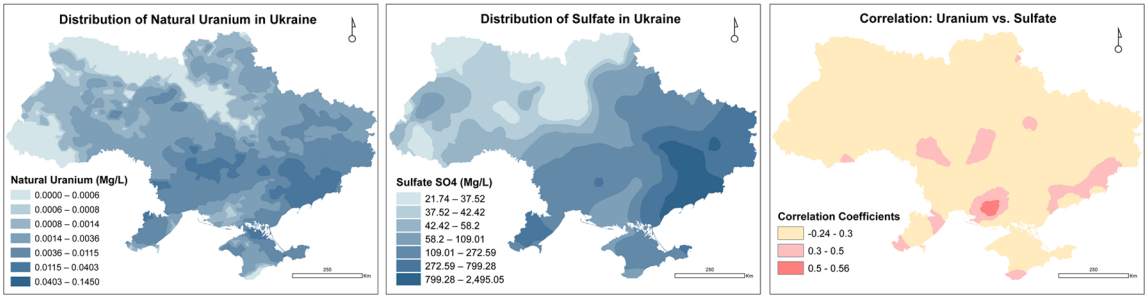
Total mineralization of water is closely related to water hardness, SO_4, and Cl. Water hardness exhibits correlation patterns very similar to that of mineralization, but with slightly higher maximum values of the local correlation (r=0.59). There is also a clearly defined relationship of uranium with folded structures of the Donetsk range in the east part of Ukraine, which may be associated with higher natural hardness of groundwater in this area.

Group SO_4 is characterized by a somewhat more evident zonal relationship with uranium, which strengthens in the Ukrainian Crystalline Shield and Azov Upland (Figure 5). This indicates that this group is more dependent on the geochemistry of the environment than the total mineralization, and so it is not a significant factor in local geochemical anomalies.

Uranium can probably correlate with sulfate in the karst areas (for example, in the west Ukraine or in the Crimea). The distribution of uranium and sulfates in groundwater in the Dnieper-Donets Basin is influenced by deposits of hydrocarbon (Penkov, 1989) that occur in sedimentary rocks of the geological depression along the Eastern wing of the Ukrainian shield. Oil fields are mostly found in the northern part of the region; the central and southeastern areas are rich with natural gas. (Note on the physical processes in areas of hydrocarbon deposits: anaerobic bacteria cause desulfurization of groundwater (decrease of SO_4^{2-}), enrichment of carbon dioxide and hydrocarbons. This pattern has been found in local shale gas in the Kirovograd region. Concentration of ammonium sulfide, hydrogen sulfide, and the total gas saturation can decrease with the distance from the area of hydrocarbon deposits.)

Local correlation of uranium with chlorides is similar to the patterns of correlation with mineralization. The difference in values of global correlation and maximum coefficients of local correlation is less than in the case of mineralization, which indicates a relatively weak connection with uranium. Areas of high correlation with chloride are smaller and, there, distribution does not have any pronounced trend to the south. This may indicate that the chlorides can better explain the general patterns of distribution of uranium, but do not reflect local geochemical anomalies.

Figure 5. Uranium (left), SO_4 (center), and distribution of local correlation (right). Global correlation r=0.45



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Component 2

The second component is largely formed by metals with the highest global correlation of uranium with iron (r=-0.15), and the widest range in local correlation revealed by magnesium (r=-0.34…0.63). In association with uranium, metals exhibit noticeable local correlation in relatively small areas, associating mainly with bedrocks and geochemical anomalies. Another feature of environmental variables in this component group is that the main element is usually accompanied by a constellation of certain metals ('satellites'). Copper has been placed in the first place in this component group, but has the lowest global correlation with uranium (r=-0.07). Iron shows low global correlation (r=-0.15), but the local correlation spans from r=-0.40 to r=0.49 (Figure 6). Iron shows moderate to high correlation with uranium in the Black Sea Lowland, which may be related to iron ore deposits in the Ukrainian Crystalline Shield.

Elevated concentration of iron in Northern Ukraine (Polesye) can be associated with large wetland areas. Swamp waters are rich with iron and other microelements. The correlation between the iron and uranium here depends on the type of wetland. In Southern Ukraine, areas of increased concentration of iron and accompanying uranium are likely impacted by iron ore mining and processing industry of the Kryvyi Rih iron ore basin. This area has a significant number of registered cancer patients (in the town of Yellow Waters in particular) (Bagriy et. al., 2005). Concentration of iron in the mountain rivers of the Crimea is low (0.00-0.05 mg/dm^3), increasing to 0.6 mg/dm^3 during the floods. This can also indicate the impact of karst.

Similar patterns were observed for copper and zinc.

Magnesium shows strong correlation with uranium only in the southern part of Ukraine, with the maximum value r=0.63 (Figure 7). This clustered pattern might be associated with the proximity of the sea, and as a predictor, magnesium can be taken into account only in the Black Sea province.

Component 3

Among the natural variables of the second largest component, precipitation and temperature play important roles, but are highly correlated between themselves. Temperature shows the highest global correlation coefficient (r=0.51), and displays distribution with the highest values in local correlation (r=-0.52…0.53). Temperature is highly correlated with uranium in the southeast areas (Figure 8).

Figure 6. Uranium (left), iron (center), and distribution of local correlation (right). Global correlation r=-0.15

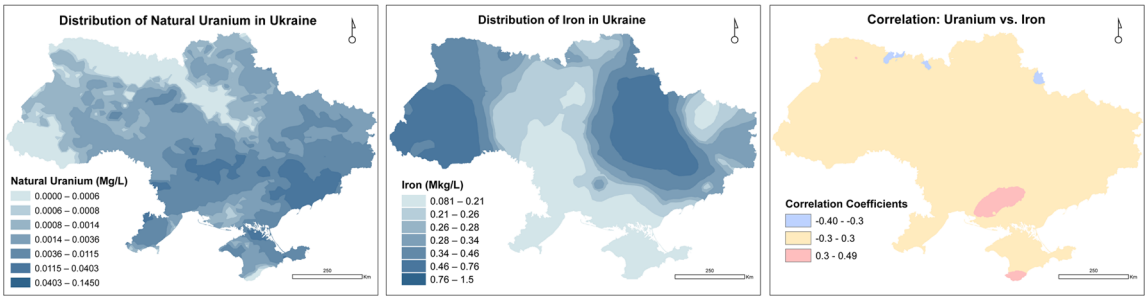

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Figure 7. Uranium (left), magnesium (center), and distribution of local correlation (right). Global correlation r=0.12

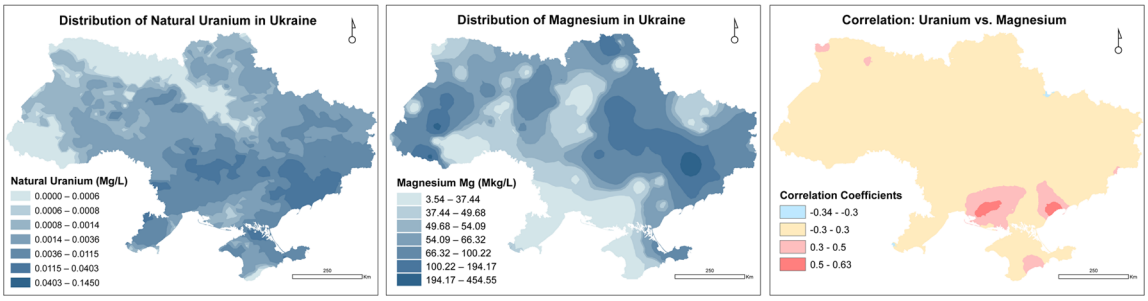
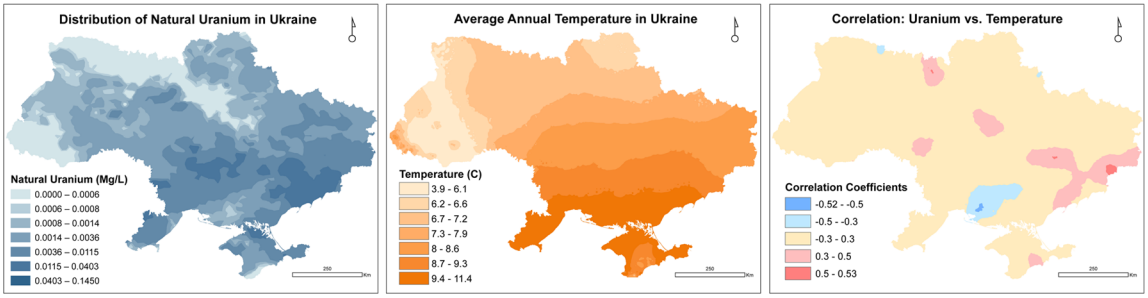


Figure 8. Uranium (left), temperature (center), and distribution of local correlation (right). Global correlation r=0.51



Correlation of uranium with temperature has a clearly distinguishable zonal pattern stretching along the Dnieper River. On the one hand, the Dnieper affects the microclimate in the surrounding regions; on the other, it accumulates uranium from surface and groundwater runoff in the entire river basin.

Significant correlation between air temperature and uranium in the southeastern region corresponds to arrangement of watersheds in the Azov Sea basin. Air temperature and evaporation increases from north to south, while the tendency for average annual rainfall is the opposite. Reduced rainfall with an increased amount of groundwater in areas of elevated concentration of uranium can indicate the "depth" of groundwater.

Precipitation is characterized by a positive correlation in the north and northwest, with the predominance of negative relationships in the center, where associations between the concentration of uranium and geological factors are stronger and the relationships with climate are weaker.

Geomorphological factors have low global correlation coefficients, but could be well used to predict phenomenon at the local level. Local correlation coefficients range from -0.47 to 0.71 for relief (Figure 9), and from -0.71 to 0.42 for isopachs (thickness of sedimentary rocks). Determining factors in this case are the associations of convex landforms in central Ukraine, with granite foundations and folding structures, as well as lower heights in Polesie, where uranium concentrations are minimal. This pattern is not observed for the young mountain systems (the Carpathian and Crimean Mountains). The same problem exists for analysis of the depth of bedrock under sedimentary layers, where the association of uranium with granitic rocks is not always evident.

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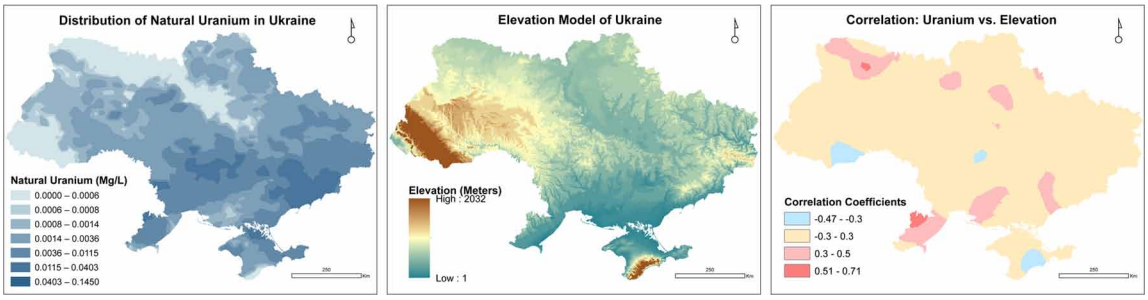
Figure 9. Uranium (left), relief (center), and their local correlation (right). Global correlation r=-0.24



Component 4

The fourth component comprises a group of organic compounds, accompanied by chromium which exhibits the maximum global correlation with uranium in this group (r=-0.39, Figure 10), with the local correlation spanning from r=-0.54 to r=0.45.

The fourth component may reflect processes specific to surface waters, in particular, the oxygen regime. NH_4 is unstable in oxidizing conditions, as the oxygen and bacteria force ammonium to oxidize in nitrite and nitrates as follows:

NH_4 + oxygen + water = nitrites

Nitrite + oxygen = nitrates

Deficiency of oxygen causes a reversible process of denitrification. While NH_4 is the first element in this component group, it shows the lowest global correlation with uranium (r=-0.12). At the same time, the relationships of uranium with NO_2 are stronger with global correlation r=0.29 and local correlation coefficients ranging from r=-0.35 to r=0.57 (Figure 11). Such relations can be explained by the composition of elements in water and geochemical characteristics of migration of metals in water. It has been found that nitrogen oxide bonds stand out from the rest of the environmental variables in this component group. The nitrogen oxide group is also associated with anthropogenic pollutants such as sewage or agricultural fertilization.

Figure 10. Uranium (left), Cr (center), and distribution of local correlation (right). Global correlation r=-0.39

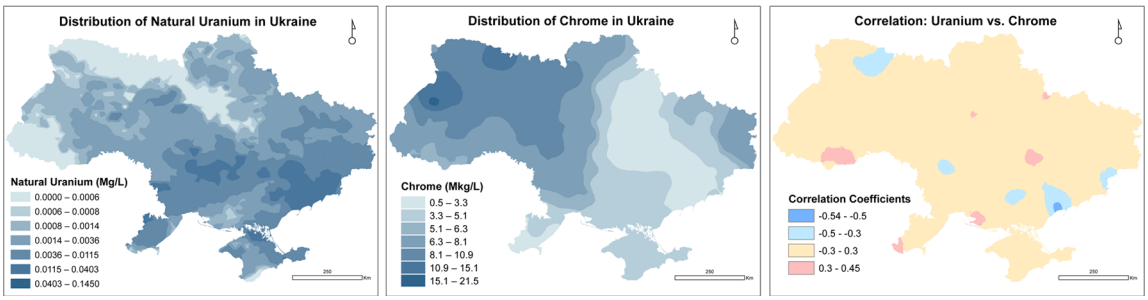


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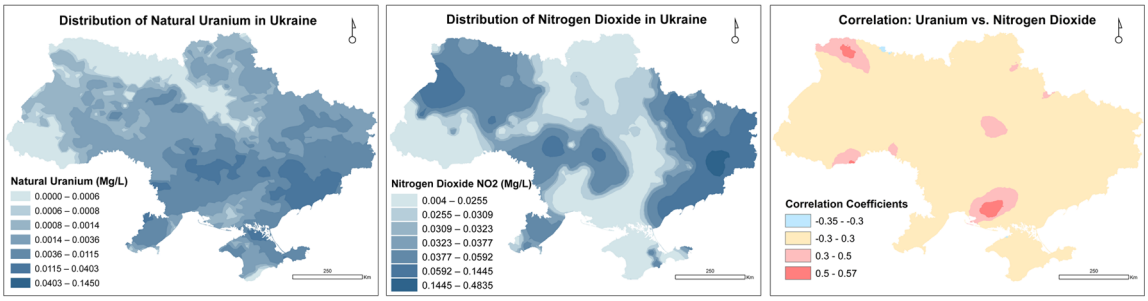
Figure 11. Uranium (left), NO_2 (center), and distribution of local correlation (right). Global correlation r=0.29



Component 5

As discussed above, geomorphological factors can be well used to predict phenomenon at the local level. Global correlation of uranium with isopachs on the global level is weak (r=0.02), but local coefficients of correlation range from -0.71 up to 0.42 indicating very strong associations with uranium (Figure 12).

Humus, a product of climate and biota, creates a specific environment for migration of chemical elements. Concentrations of humus reflect general trends of distribution of uranium and explains some particular characteristics of distribution (Figure 13). Accumulation of humus is associated with absorption of uranium compounds, and a decrease in concentration of humus is observed in areas with high migration of chemical elements.

Component 6

The last component is formed by bicarbonate, fluoride, and arsenic. Bicarbonate is at the top in this group, but has the lowest global correlation with uranium. Fluoride and bicarbonate correlate with uranium with global coefficients r=0.35 and r=0.16 respectively, and show relatively high local correlation with uranium (-0.34…0.72 for fluoride, and -0.22…0.66 for bicarbonate). Geographically, local correlation of uranium with fluoride is clustered in the Crimea and the Poltava region (Figure 14), while bicarbon-

Figure 12. Uranium (left), isopachs (center), and their correlation (right). This is an example of low global correlation (r=0.02) with high values in local variations (r=-0.71, blue, and r=0.42, red)

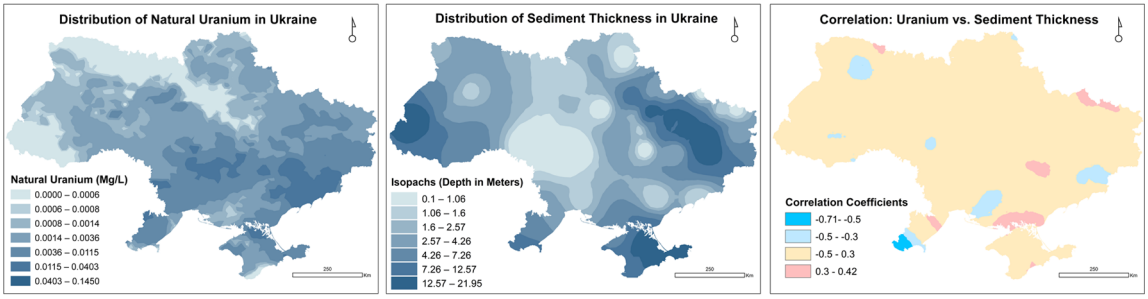


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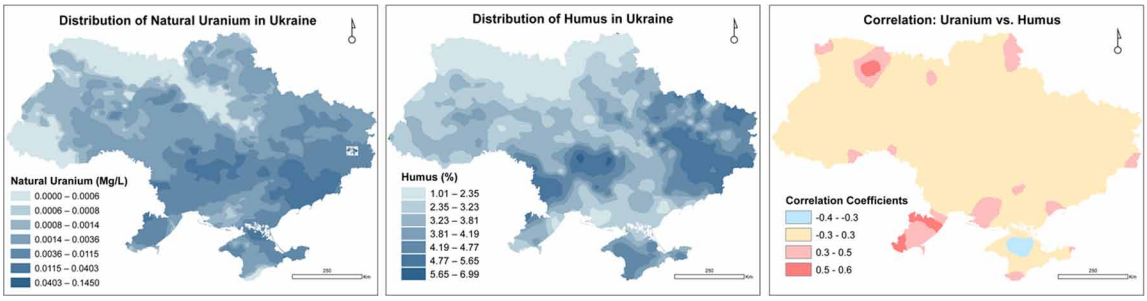
Figure 13. Uranium (left), humus (center), and distribution of local correlation (right). Global correlation r=0.52



ate is highly correlated with uranium in Western Ukraine. Arsenic has relatively low global correlation (r=0.23) and relatively high values of local correlation (from r=-0.28 to r=0.48), which can be explained by geochemical anomalies in relationships between the two elements.

Global and Local Spatial Multiple Regressions and Autoregressive Models

While correlation and factor analyses allowed for identification of significant environmental variables which impact the distribution of uranium in ground waters in Ukraine, contributions of each factor can be better understood by carrying out a multiple regression analysis. The main steps for analysis were: selection of indicators for multiple regression, assessment of their relevance and contribution to the distribution of uranium, and calculation of parameters of regression. Table 3 outlines environmental variables chosen as predictors for building several multiple linear regression models. A summary of multiple regression models is provided in Table 4 and graphically illustrated in Figure 15.

Regression residuals of global multiple regression were tested for spatial autocorrelation. A Moran's I index = 0.4182 on the residuals indicates significant autocorrelation. Spatial autocorrelation among residuals could imply the presence of nonlinear relations between the dependent and independent variables, the omission of one or more regressors, and/or that the regression model should have an autoregressive structure (Cliff & Ord, 1973). Action needs to be taken, e.g., use of spatial local multiple regression or autoregressive models, etc.

Figure 14. Uranium (left), fluoride (center), and distribution of local correlation (right). Global correlation r=0.35

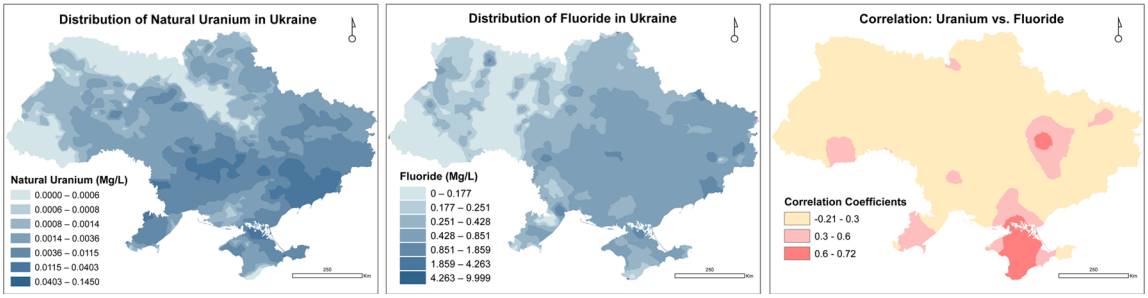


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Table 3. Environmental indicators (predictors), selected for multiple regression analysis

Component	Natural Variables	Group	Predictors
1	Mineralization and hardness of water	Mineralogical	Hardness of water, mineralization of water
2	Metals dissolved in water	Geochemical	Cu, Fe, Cl, Zn
3	Climatic conditions of territory and formation of ground water	Climatic	Precipitation, temperature, humus
4	Organic compounds in water	Mineralogical	NO_3, NH_4, PO_4
5	Geomorphological characteristics	Geological structure and geomorphology	Relief, isopach
6	Mineral compounds and satellite elements of uranium	Geochemical	Bicarbonate, fluoride, arsenic

Table 4. Multiple regression model summary

Model	Predictors	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	precipitation	0.510	0.260	0.260	1.1611
2	1 + humus	0.595	0.354	0.354	1.0849
3	2 + water hardness	0.623	0.388	0.387	1.0564
4	3 + F	0.629	0.396	0.395	1.0496
5	4 + Fe	0.634	0.402	0.402	1.0438
6	5 + As	0.637	0.405	0.405	1.0414
7	6 + SO_4	0.638	0.407	0.407	1.0395
8	7 + isopach	0.641	0.411	0.410	1.0368
9	8 + NH_4	0.642	0.413	0.412	1.0351
10	9 + Cl	0.644	0.415	0.414	1.0332
11	10 + temperature	0.645	0.416	0.415	1.0325
12	11 + NO_3	0.645	0.417	0.416	1.0317
13	12 + HCO_3	0.646	0.418	0.416	1.0310
14	13 + Zn	0.647	0.418	0.417	1.0305
15	14 + Cu	0.647	0.419	0.418	1.0300
16	15 + PO_4	0.648	0.419	0.418	1.0296
17	16 + mineralization	0.648	0.420	0.419	1.0288

A global linear regression model has been used to describe the contributions of several environmental variables on spatial distribution of uranium in ground waters. Calculation of global regression was followed by spatial local multiple regression or GWR.

Fifteen multiple regression models were built incrementally using predictors outlined in Table 4. The first five most significant predictors (precipitation, humus, water hardness, F, and Fe) contribute 40.2% to the overall model. Examination of individual and cumulative contributions of environmental variables is provided below.

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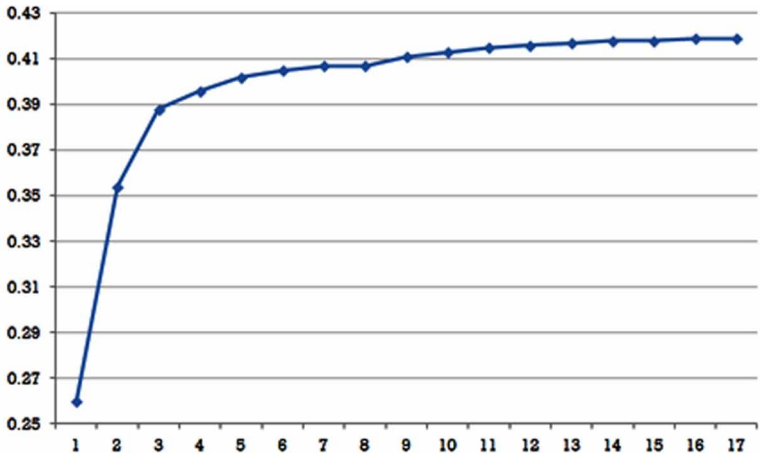
Figure 15. Global multiple regression model summary, R-square vs. model



Analysis of environmental relationships indicates that the most significant environmental variable is precipitation. The second most significant predicting variable is humus content in the top soil. Although this indicator is not a major factor in determining the distribution of uranium, it has a high degree of association to conditions of the geochemical migration of uranium. Soil is a product of interaction of all components of the environment, and has a direct relationship with underlying rocks, mineral composition, climate, and biota. As a result, the humus content in the soil reflects climate and geochemical characteristics of the migration of chemical elements, including uranium. Local r-square coefficients for multiple regression model, built only on the precipitation variable, are shown in Figure 16, left. Adding the humus component and then hardness of water improves the model (Figure 16, center and right correspondingly).

Fluorine (F), iron (Fe), and arsenic (As) add only 1.7% to the variability of the data, but still contribute to the cumulative regression model (Figure 17). None of the rest of environmental variables contributed more than 0.2% in the final model, which indicates their very low impact on the total distribution of uranium. This can be partially explained by the fact that many of these variables depend on each other, and thus, are highly correlated.

Figure 16. Local R^2-square coefficients for geographically weighted regression models: precipitation (left), precipitation + humus (center), precipitation + humus + water hardness (right)

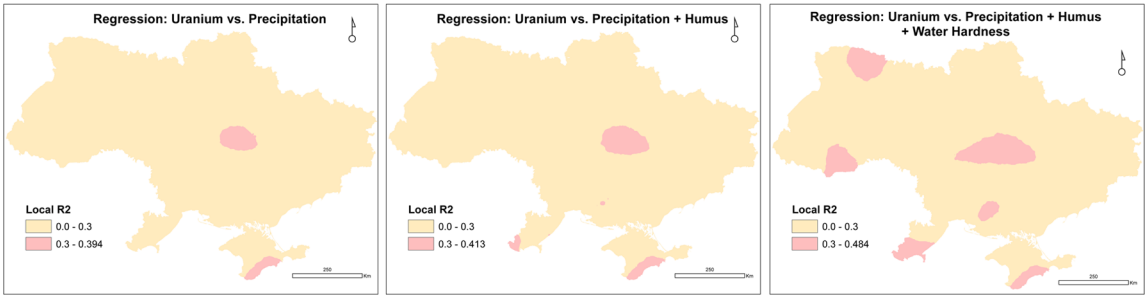


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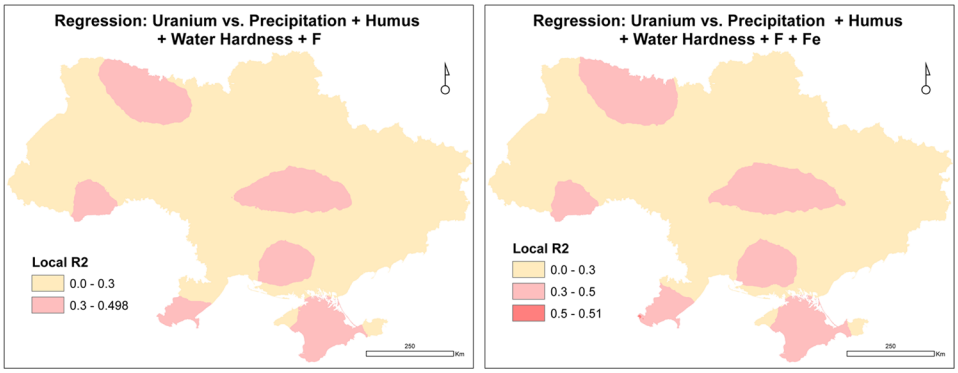
Figure 17. Local R^2-square coefficients for geographically weighted regression models: precipitation + humus + water hardness + F (left); precipitation + humus + water hardness + F + Fe (right)



Overall R^2-square of the six explanatory variables from the GWR model reaches 0.5997. The improved performance of GWR over the global regression models was demonstrated by significantly higher values of R^2-square.

Geographical analysis of the results of local multiple regression indicate that the impact of precipitation and humus on distribution of uranium is mostly noticeable in the southern areas of Ukraine. Inclusion of hardness of water in the model spreads the relationship in the center and northwest. Adding one more variable (F) improves the model and extends it to the central part of the Ukrainian Crystalline Shield and in the southwest. Multiple regression with all six factors strengthens the model, especially in the south and northwest. The local correlation achieved r=0.51, which confirms that the inclusion of all six indicators in the model was sensible. It is also worth mentioning that several variables have shown high local correlation in the spatial multiple regression model. In particular, fluoride and magnesium have a high degree of correlation with uranium in the south of Ukraine.

Results from the models which include both the spatial lag and error term reveal that the spatial lag coefficients are significantly different from zero. The spatial lag model with maximum likelihood estimation produces R-squared of 0.6079, and the spatial error model with maximum likelihood estimation produces R-squared of 0.6054. These results provide strong evidence that spatial correlation exists in uranium distribution. Based on the AIC and R-squared, all of the autoregressive models are preferred to the OLS specification. The spatial lag model that utilizes the distance weights matrix provides the best fit of the data (see Figure 18). Spatial correlation in uranium distribution may be best modeled using a spatial lag. Moran's I index on the residuals from the autoregressive models still indicates significant autocorrelation. However, Moran's I index on the residuals is lower compared to the OLS residuals and equals 0.2013 for the lag model.

Combining geological, geochemical, and climatic factors allows for creation of spatial distribution models which describe associations with uranium as well as identify areas with potentially problematic groundwater quality. The model indicates a high level of uranium in groundwater in central and southeast areas of Ukraine, where historically, there is a high density of population and low supply of drinking water.

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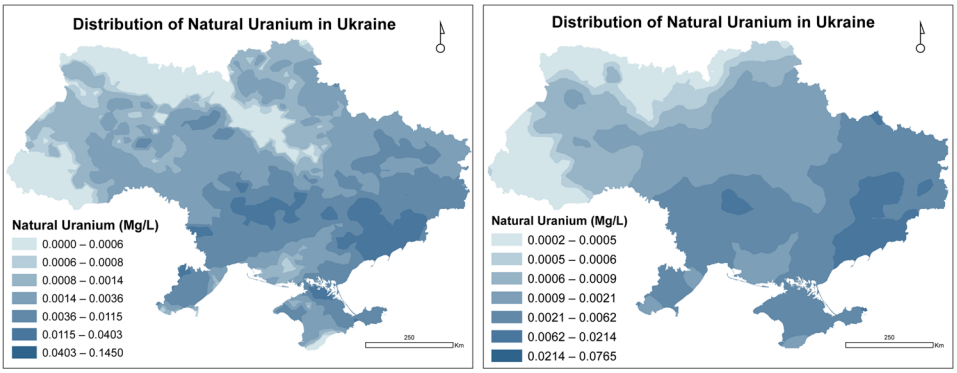
Figure 18. Distribution of natural uranium in Ukraine: source data (left) and prediction map from the lag model (right)



Multiple Regressions Based on Principal Components

Multiple regression analysis in the previous section was based on selection of the most significant environmental variables (predictors), and consecutively adding those individual predictors to incrementally improve the model. An alternative approach is to build the models using principal components. In this approach, all variables constituting the first group of principle components (Component 1, Table 1) are used to create the first multiple regression model. The model is further improved by adding all elements forming the second groups (Component 2). The final regression model will constitute all six principal components (Figure 19). Figure 20 illustrates successive steps in building the multiple regression models using principal components.

Overall R^2-square of the six factors used as explanatory variables from the GWR model reaches 0.5683. Comparison of two multiple regression models based on six principal components and six individual environmental indicators shows that, in general, both models indicate similar associations with the distribution of uranium in groundwater. However, the maximum coefficient of local correlation for the model, based on the principal components, is only 0.48, while the same correlation for the latter model is 0.51. This indicates that the zones of high regression are identified objectively, and the model of the five environmental variables shows stronger local associations compared to the component model which takes into account all studied indicators.

SOLUTIONS AND RECOMMENDATIONS

Several spatial statistics and cartographic visualization methods were used in this study to explore spatial distribution of uranium in groundwater in Ukraine. There is a general trend toward an increase in the concentration of uranium from the northwest to the southeast. Factor analysis reveals six principal components and several environmental variables which describe major factors influencing the distribution of uranium in Ukraine. These components, which often accompany uranium, include total mineralization of water, climatic conditions, metals, anions nitrate and phosphate, geomorphology of terrain, and chemical elements. The model explains nearly 72.5% of the variability in the original 23 independent variables.

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Figure 19. Uranium (top), and maps of six local principal components

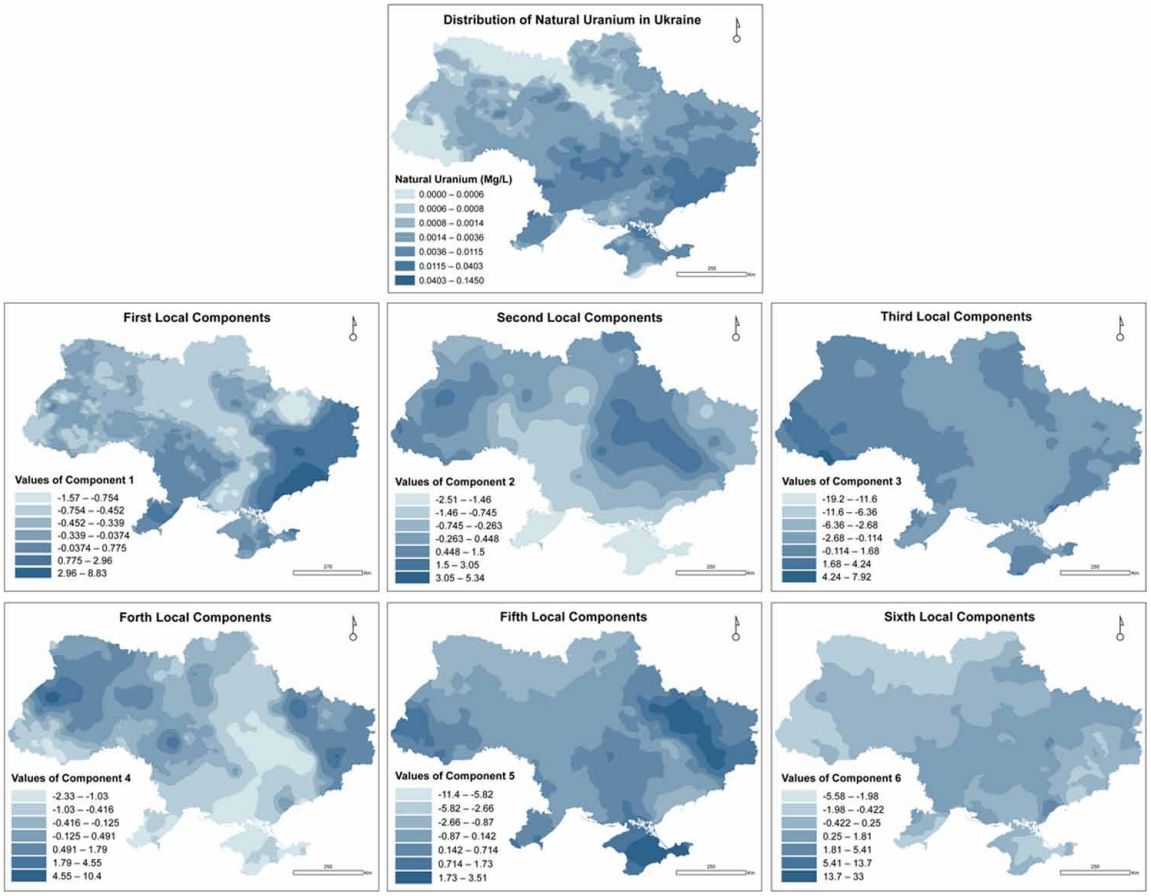
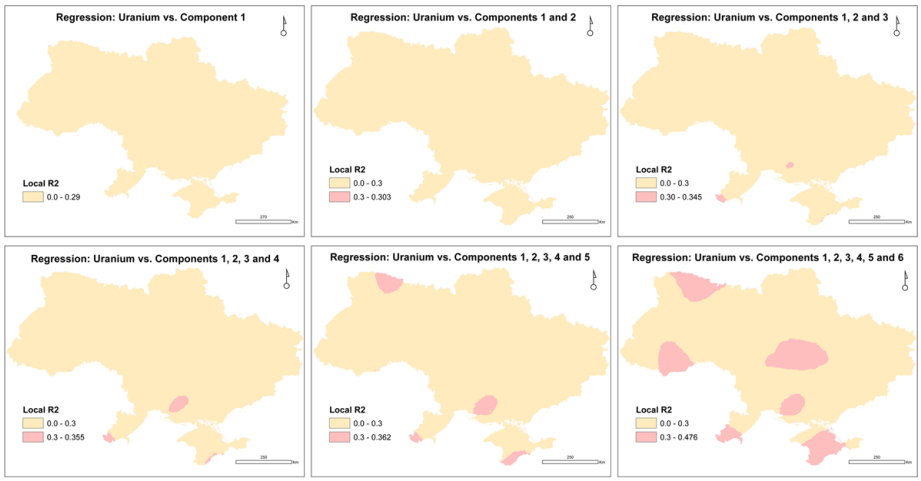


Figure 20. Building consecutive multiple regression models using principal components. First map demonstrates correlation of uranium with component 1, and the last map illustrates correlation with all six principal components, incorporated in one regression model



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The multiple global regression model defines eighteen environmental variables that describe 42% of the variability of the data. The first six most significant predictors (precipitation, humus, water hardness, F, Fe, and As) contribute 40.5% to the overall model. Local spatial correlation and multiple regression analyses show significant spatial differentiation of factors influencing distribution of uranium.

The use of local correlation improves assessment of relationships between environmental variables. Local multiple regression was used to estimate the contribution of individual environmental variables in the resulting concentrations of uranium. The GWR model with six explanatory variables explained 59.97% of variability in the data, and GWR model with six factors used as explanatory variables described 56.83% of variability in the data. However, an autoregressive model yielded better results, with the spatial lag model explaining nearly 60.79% of the variability in the main six independent variables.

The study reconfirms a strong association between climate and distribution of uranium in groundwater. Local correlation reaches 0.55 in the central and southeastern part of Ukraine. Over the past century, there has been a clear tendency of change in the climate conditions in Ukraine. The average annual temperature in the central and northeastern part has increased by 1°C, and precipitation exhibits 110% of the climatological norm in the southeast territories. This may trigger certain alterations in geochemical processes in the landscape, which may have an impact on the concentration of uranium in groundwater. The main consequences can be an increase in the number of uranium-containing compounds in the forest-steppe zone and expansion of the areas of high concentration of uranium in the southeastern part of Ukraine.

CONCLUSION AND FUTURE RESEARCH

The chapter demonstrates the use of a combination of different modeling techniques to better understand large-scale distributions of environmental indicators (such as uranium) by exploring spatial associations and patterns of associated natural variables and predictors. The methods presented in this study (global vs. local for regression and factor analysis) do not always provide overly objective ground for making conclusive inferences, and outcomes from different models sometimes do not match. For example, some explanatory variables have low correlation with the dependent variable, but at the same time have a high percentage of explained variance in factor analysis. Global regression modeling in a large-scale spatial analysis can be unsuitable for the local inference.

Spatial autoregressive modeling and local multiple regression can be successfully used for prediction of uranium concentration in different scenarios for changing climatic conditions in different parts of Ukraine and other territories. One intriguing association discovered from the modeling is the relationship between uranium and climatic variables. Concentration of uranium has strong local correlation with precipitation, temperature, and humus. Precipitation and humus are the first two variables in the regression models for uranium. At the same time, precipitation has very high correlation with temperature ($r=-0.825$). Variation in temperature and precipitation due to global climate change can alter their contributions to the uranium content. Those scenarios can be explored using the proposed spatial regression models. It is necessary to emphasize that the modeling results presented in this chapter, including their cartographic representations, remain mainly descriptive and require detailed analysis and interpretation by experts from various environmental disciplines.

Further research is envisioned to refine relationships among environmental indicators and improve numerical forecasts by expanding the range of applied spatial statistical methods. Study is planned to explore spatial-clustering techniques to improve the robustness of the developed statistical model.

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KEY TERMS AND DEFINITIONS

Environmental Mapping: Field of cartographic sciences dedicated to mapping environmental processes and phenomena.

Exploratory Spatial Data Analysis (ESDA): Statistical techniques used for initial data analysis, such those used for checking statistical distribution, linearity, multicollinearity, etc. Based on results of an ESDA, initial hypotheses and further statistical data exploration can be developed, for example, by carrying out correlation, regression, and factor analyses.

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Factor Analysis: Statistical methods which reduce a set of source variables to a smaller number of new variables, where each new variable is a function of one or more of the original variables.

Geographically Weighted Analysis: Statistical methods used when geographic location of an observed characteristic is one of the key factors; often used to define local spatial variation in relationships between data.

Geographically Weighted Factor Analysis: Spatial statistical method that uses factor analysis (for example, PCA) to estimate principal local factors in location of each observation.

Geographically Weighted Regression (GWR) Analysis: Spatial statistical method used as a regression technique to estimate a local regression in the location of each observation.

Geovisualization: Computer-based methods for mapping and visual presentation of geographical and social phenomena; evolved from classical cartography and can be used to visualize static two- and three-dimensional phenomena, as well as dynamically changing processes.

Multivariate Regression: A statistical method where a set of independent variables is used to explain a single dependent variable; offers a logical extension to the simple, two-variable regression procedure.

Principal Component Analysis (PCA): Mathematical method which transforms a number of variables (possible correlated) into a number of uncorrelated variables called principal components.

Spatial Autocorrelation: Correlation between observations of a variable separated in space; takes into account distances (and/or directions) between sample points. Spatial autocorrelation can be described by "the first law of geography," which states that "everything is related to everything else, but near things are more related than distant things" (Tobler, 1970).

Spatial Correlation: Correlation of geographically distributed data; used to find relationships and dependencies between various geographical objects or environmental characteristics. For example, correlation of certain species of vegetation with a particular type of soil, or the relationship of temperature and relief (elevation).

Spatial Dependence: Spatial phenomenon that occurs when the value of a variable at a point in space is related to its value at nearby points; knowing the value of these points allows us to predict (with some degree of certainty) the value at the chosen point.

Spatial Econometrics: Spatial econometrics is a subfield of econometrics which deals with spatial autocorrelation and spatial structure (spatial heterogeneity) in regression models.

Spatial Heterogeneity: A property of a spatial phenomenon which describes uniformity of characteristics or relationships between geographically distributed variables. Relates to spatial dependence.

Spatial Regression Analysis: Statistical method which, taking into consideration the location of each observation, measures the strength and direction of relationships between a dependent spatial variable and independent spatial variables.

Spatial Statistics: Statistical methods applied to geographically distributed phenomena.

Spatial Structure: The nature of the spatial relationship between points, i.e., how far and in which direction, is the spatial dependence? How does the spatial dependence vary with distance and direction between points?

Uranium in Groundwater: The naturally-distributed concentration of a radioactive element (Uranium) in ground waters, lakes and rivers; one of the key elements defining drinking water quality.

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Chapter 50
Supercritical Fluids as a Tool for Green Energy and Chemicals

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ABSTRACT

Hydrothermal conversion of biomass is a promising technology for the conversion of biomass into biofuels and biobased chemicals. This chapter is focused on the waste biomass conversion for production of biofuels and chemicals by applying sub- and supercritical fluids. One of the biggest disadvantages in biomass conversion by SCF is the extremely high energy requirement for heating the media above the water critical point (374 °C, 221 bar). The idea behind the recent research is to reduce the operating temperature and energy requirements by processing biomass with water at much higher pressures. The importance of knowledge on behavior of multicomponent systems at elevated pressures and temperatures is underlined. Methods, developed by the authors of this chapter for determination of thermodynamic and transport properties for multicomponent systems of different solid compounds and supercritical fluid under extreme conditions are described. Future perspective of hydrothermal technology as a tool to obtain advanced materials and the possible scope for future research is also discussed.

INTRODUCTION

Large amounts of waste biomass produced offer a great opportunity to convert this volume of plant material and animal waste to a huge amount of energy. The conversion of biomass to biofuels and biobased chemicals has attracted a lot of attention recently, largely due to the environmental and socio-economic problems associated with the use of fossil fuels. In recent time, many novel technologies have been

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introduced for conversion of biomass to energy and chemicals. Biomass can be converted to energy by biochemical and thermochemical processes. The two main thermochemical conversion processes to produce biofuel from biomass are the pyrolysis process and the hydrothermal process as promising technologies for the conversion of biomass into biofuels and biobased chemicals. In recent years, hydrothermal energy was accepted as a possible energy resource with a high potential already in the beginning of the previous century. Hydrothermal conversion of biomass has consequently attracted considerable attention. This chapter will therefore focus on the waste biomass conversion for production of biofuels (liquid or gaseous) and biochemicals (furfurals, organic acids, aldehydes, ketones) by applying sub- and supercritical fluids at pressures up to 1000 bar. Operating at high pressures may result in processes that require much lower amounts of energy and maybe also in new processes which are capable of performing new types of reactions that produce completely new bio-based products.

The production of value-added products from waste biomass, such as waste from agriculture, food or forestry industry, will be mostly considered. A topic of the intense research is to reduce the operating temperature and energy requirements by processing biomass with water at much higher pressures or adding supercritical CO_2 to the reaction mixture. Nevertheless, biomass conversion processes at high-temperature and pressures exceeding 300 bar are, for now, a completely new aspect of high-pressure technology for biomass conversion and literature regarding the reactions taking place in such systems practically does not exist. There are also several advantages of supercritical fluid processing under "real" high pressure like new product formulations and economic production of high value products due to the fact that the solubility of several dense gases in low soluble substances increases with increasing pressure and temperature. Most of the commercial supercritical water processes today are limited to pressures, where the complete solubility of water and CO_2 is not achievable. By elevating pressure, the total miscibility of water and CO_2 is already achieved at considerably lower temperatures. Another possibility is lowering the energy barrier by the addition of catalysts. Such treatment of biomass would be a completely new process. However, the data on the mechanisms and kinetics of reactions are scarce. Additionally, the total yields of the final products are practically unknown for these unconventionally high-pressures and temperatures for the multi-component systems.

Considering the above mentioned facts, it is highly important to investigate how of water and CO_2 in such a system would affect the biomass conversion reactions and what products would form, how different ratios and conditions affect the conversion and if it is possible to perform the reactions that normally occur above critical point at milder conditions. This knowledge will open completely new possibilities in biomass conversion, which could also lead to new types of reactions and products. Fundamental data obtained from such research could therefore revolutionize the concept of biomass conversion facilities or could open routes to completely new types of process intensification. Limitations of processes operating at the mentioned high temperatures and unconventionally high pressures are their investment costs that are significantly higher compared to ambient pressure technologies. Nevertheless, many recent studies have suggested that classical large-scale reactors needed for biomass conversion are maybe not necessary for processes involving supercritical water as reaction medium. It has been proven, that reaction kinetics of near-critical water and supercritical water with organic compounds are extremely fast and that long contact times should therefore be avoided.

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BACKGROUND

The ability to produce solvent-free products and handle high viscous materials makes the SCFs technologies unique. Such novel technologies are emerging, for instance for particle design, sterilization, and separation of enantiomers (Brunner, 2005). Particulate products with the desired characteristics can be obtained (Kiran, 1994). The development of a process technology comprises the application of fundamentals to processes and has been a topic of an intense research in the past decades (Brennecke & Eckert, 1989; de Swaan Arons & Diepen, 1963).

Phase equilibria and reaction kinetics, the verification of process steps, as for example in specific reactors, and the design of process sequences to produce a product (energy) from raw materials are the main hindrances concerning the SCF applications. Some important bioconversions have decreased interest today, but other conversions gain interest or will gain interest, so that the fundamentals will somehow have to find its way. Detailed investigations on the basic thermodynamical and transport data like phase equilibria, density, viscosity, dielectric constant and diffusion coefficient have to be carried out to obtain the data fundamental for the design of a process in order to fulfil consumer and economic requirements (Brunner, 2015). Supercritical fluids have been widely applied in several processes developed to the commercial scale; – from pharmacy, food sciences to the textile industry, but however, pilot plant and industrial scale applications in the field of energy are still in its infancy. Solubility of the substance in SC or SubC fluid is the main parameter controlling the feasibility of the process. Determination of solubility of several compounds in SCFs is already reported in scientific literature. However, contributions reporting phase equilibria of systems with CO_2 are offered in particular (Fonseca, Dohrn, & Peper, 2011). Knowledge about phase equilibria and thermodynamic data is essential to design a process with a well-considered union between economic feasibility and safety.

A wide literature review showed that different authors suggest various, mainly well-established methods, to investigate thermodynamic data of binary systems of substances in presence of SCF (Aionicesei, Škerget, & Knez, 2008; Corma, García, & Leyva, 2005; Dindar & Kiran, 2002; Gourgouillon, Avelino, Fareleira, & Da Ponte, 1998; Gutiérrez, Rodríguez, Gracia, De Lucas, & García, 2013; Markočič, Škerget, & Knez, 2011; Mukherjee, Bhattacharyya, & Bagchi, 2002; Pantoula & Panayiotou, 2006). Those methods are either time consuming or require expensive, advanced equipment. Additionally, most of the methods may only be used for pure compounds, and may not be adopted to the diversity of the systems occurring in industry that include materials of a complex composition like biomass, bio oils, etc. There are only few articles dealing with the development of new methods (Calvignac, Rodier, Letourneau, Almeida dos Santos, & Fages, 2010; Calvignac, et al., 2010; Elvassore, Vezzù, & Bertucco, 2005; Knez Hrnčič, Markočič, Trupej, Škerget, & Knez, 2014). Solubility data, density, viscosity, dielectric constant, diffusion coefficient and interfacial tension certainly play a key role in a design of an efficient fractionation process of components of pyrolysis oil that are a product of fast pyrolysis or liquefaction of biomass and are dark brown organic liquids, which are chemically a complex mixture and/or emulsion of water and degradation products of lignin. and also open the innovative routes to completely new types of process intensification.

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MAIN FOCUS OF THE CHAPTER

Issues, Controversies, Problems: Environmental Issues Relating Energy Consumption

The importance of the problem regrading environmental issues reflects also in the field of science popularization. Several conferences are organized worldwide. United Nations Conference on Climate Change was organized in France in the beginning of December 2015. Energy demand is still increasing and the use of fossil fuels still remains the principle energy source which may lead to uncontrolled net global warming and to an increased number of extreme climate events (Paris COP21, 2015).

In the past SCFs were used mainly as solvents in extraction processes such as decaffeination of coffee and tea, spices extraction, extraction of antioxidants from (Knez, Škerget, & Knez Hrňič, 2010), oil from seeds etc..., however in recent time technologies using SCFs as a processing media received new challenges. SCFs present a promising new alternative as a media for biomass conversion to green chemicals and energy. Currently over 80% of energy demand is still met by fossil fuels (oil, gas and coal) but these resources are finite. Beside the impact on the environment, the price of crude oil is fluctuating. However, fossil fuels are still the main source of energy and chemicals. Research on alternative sources of chemicals and fuel and production technologies has therefore attracted a great deal of attention (Barnes, 2015). Several investigations are recently performed in the field of supercritical fluids as a tool for energy production (Brunner, 2015). Biomass conversion processes applying sub- critical water and supercritical water are promising basis for processing of various intermediates to be used for energy and chemical purposes. Water as a reaction media opens new possibilities compared to "dry processes", allowing lower reaction temperatures.

From Sustainable Energy Resources to Energy and Fuel

Nowadays, there is a growing interest in the development of alternative technological processes with minimized environmental impact, such as reduced energy consumption, less toxic residues, better use of by-products and also better quality and safety of the final products (Knez et al., 2014). Currently, chemicals and energy are mainly derived from fossil fuels, what is challenged by the rapidly declined reserves, fluctuating price of crude oil and impact on the environment. Research on alternative sources of chemicals and fuel and production technologies has therefore attracted a great deal of attention Feng, Cheng, Yuan, Leitch, & Xu, 2013). Biomass energy is derived from distinct organic matter that can re-grow over a relatively short period of time compared with the hundreds of millions of years that it took for fossil fuels to form (Kullaiah Byrappa & Masahiro Yoshimura, 2013). Much effort is therefore oriented to the utilization of waste biomass for production of energy and chemicals. Figure 1 presents hierarchy of waste management as advised by the European Union (Wasteshipment, 2016). Residues produced by the agricultural and food industries contain valuable functionalized molecules such as flavonoids, waxes, biopolymers or fatty acids. Food supply chain waste has a high potential to be utilized as a feedstock for electricity generation (i.e. through anaerobic digestion), fuel generation (i.e. conversion of cellulosic biomass to bioethanol) or the production of animal feed (Pfaltzgraff, Cooper, Budarin, & Clark, 2013). Waste biomass and biomass of nature and agricultural cultivation are valuable organic reservoirs of raw materials and must be used in accordance with their organic composition (Kamm, Gruber, & Kamm, 2007).

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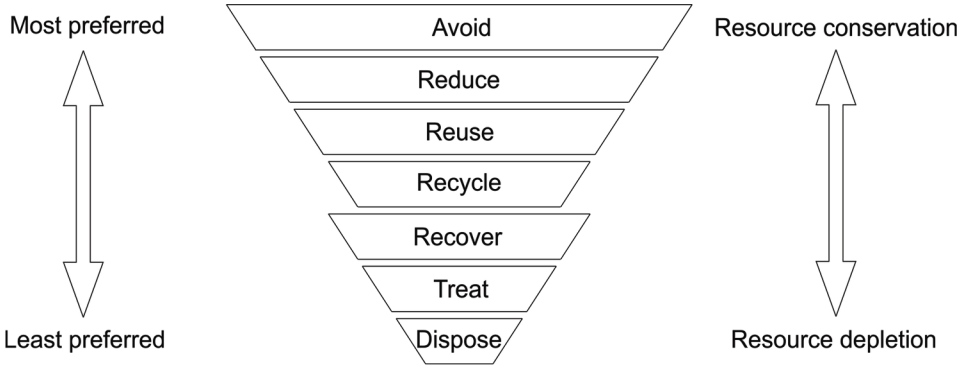
Figure 1. Hierarchy of waste management as advised by the European Union
Wasteshipment, 2016.



Anyhow, harvesting biomass to produce energy may result in reduced soil productivity by depletion of carbon and nutrients and may therefore not be sustainable (Woolf, Amonette, Street-Perrott, Lehmann, & Joseph, 2010). By biomass pyrolysis waste products may be utilized (Woolf et al., 2010).

The vital difference between biomass and fossil fuels as energy sources is the time scale. If it is managed on a sustainable basis, biomass is harvested as part of constantly replenished plants or crops in which the new growth in the re-plantation takes up CO_2 from the atmosphere at the same time as it is released by an energy conversion process (e.g. combustion) of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels, in contrast to that of fossil fuels, and therefore biomass is considered as a renewable energy resource. The large amounts of waste biomass, which is a renewable resource, cause serious problems when not being processed, which is a severe problem facing especially the countries of the third world that do not have strong regulatory instruments to control the environmental challenges.

Biofuels are liquid or gaseous fuels that are predominantly produced from biomass for transport sector applications. As biofuels are renewable, sustainable, carbon neutral and environmentally benign, they have been proposed as promising alternative fuels for gasoline and diesel engines (Hoogwijk et al., 2003). For different biomass types as a renewable resource there are a number of conversion technologies available (Cartmell et al., 2006). Primarily, the options are divided into two groups, namely thermal and chemical conversion. In general, the conversion technologies may release the energy directly, in the form of heat or electricity, or may be converted to another form, such as liquid biofuel (bioethanol, biodiesel), combustible biogas (H_2, CH_4) or charcoal-like solids (biochar). While for some classes of biomass resources there may be a number of usage options, for others there may only be one appropriate technology (Cabeza et al., 2015). Optimization of biomass supply chains could help in commercializing this sustainable energy source by reducing costs (Shabani, Akhtari, & Sowlati, 2013).

Conversion of Waste Biomass to Energy

Nevertheless, biomass derived energents have several pros and cons. Besides, several obstacles that have to be overcome to convert waste biomass to biomass fuels. Finding new methods to convert biomass energy resources to usable energy resources is inevitable (Mazaheri, Lee, Bhatia, & Mohamed, 2010; Van Bennekom et al., 2009) since there are several issues, such as some technical challenges, facing

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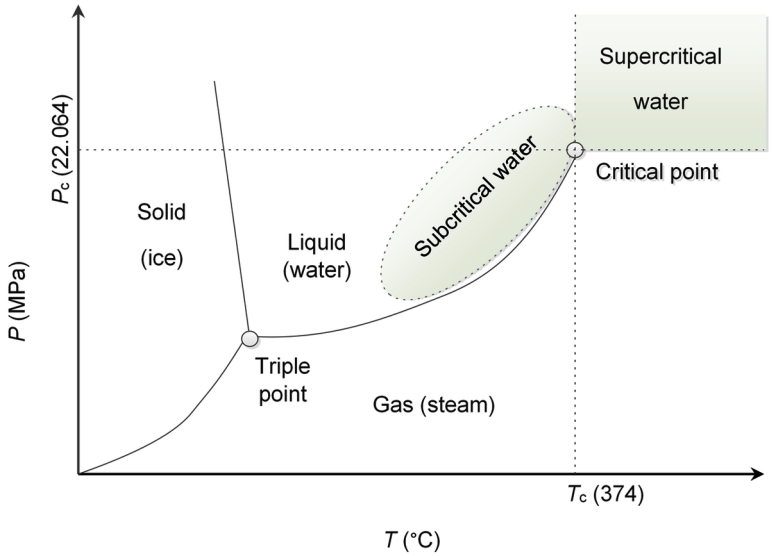
biodiesel production via transesterification, which include long residence times, high operating costs and energy consumption and on the other hand low production efficiency. Problems facing biodiesel production have to be solved in order to make the process more efficient and economical. Many efforts are proposed to convert biomass to bio fuel (Kruse, 2011). Green revolution focuses on the development of biodiesel production based on the use of non-catalytic esterification under high pressure and temperature, or with supercritical methanol (Glisic & Skala, 2009; Kesić et al., 2012; Qiu, Liu, & Riffat, 2011). General approach is to process the biomass in an aqueous phase. The specific implementation of this approach of interest is supercritical water gasification (SCWG), which involves the conversion of organic compounds to gaseous products (H_2, CO, CO_2, and CH_4) via reactions in and with water at a temperature and pressure exceeding the thermodynamic critical point ($T_c = 374$ ∘C and $P_c = 221$ bar) and therefore knowledge about the behavior of these gases with liquid products, obtained by fast pyrolysis of biomass under different conditions of temperature and pressure is essential in designing the separation processes following the conversion reactions. Figure 2 presents phase diagram of water with area of application for hydrothermal treatment. HT pretreatment could not only improve the mechanical dewatering of parent materials, but also the fuel quality, such as the carbon content and energy density (Zhao, Shen, Ge, Chen, & Yoshikawa, 2014). Anyhow, heating value of biomass depends on its composition. For instance, dry woody biomass consists of cellulose, hemicelluloses, lignin and ash. Its heating value can therefore be estimated from the heating value and weight fraction of each constituent.

Overview of High Pressure Processes for Biomass Treatment

Several applications have been proposed in the past years using hot compressed water as a reaction media, e.g. destruction of hazardous materials, synthesis of inorganic and organic materials, recovery of valuables from wastes recycling of polymers and energy recovery of biomass (Cabeza et al., 2015; Jain, Balasubramanian, & Srinivasan, 2016). There are certain drawbacks regarding utilization of waste bio-

Figure 2. Phase diagram of water with area of application for hydrothermal treatment
T_c - critical temerature, P_c - critical pressure.



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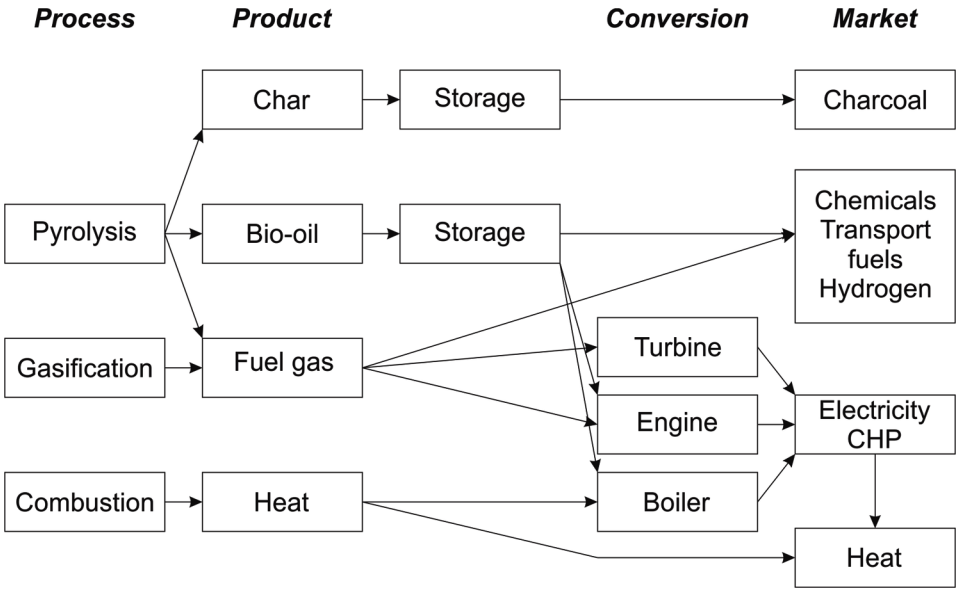
mass materials and forestry residues as sources of energy due to their uneven and troublesome properties and characteristics. Several beneficiation technologies which basically improve the physical and thermal characteristics of the original biomass materials by changing shape, size, size, distribution, density, water content, etc. Amongst these processes, the most important are: sizing and shaping, separation, drying, dewatering, densification (Baling, Pelletization and Briquetting) and torrefaction (Sugathapala, 2013). In many situations, more than one of the above types is required.

Generally, HT processes could be divided into four main processes, as demonstrated in Figure 3: carbonization (HTC), aqueous phase reforming (APR), liquefaction (HTL), and gasification (HTG).

An ancillary advantage of the uncongenially high processing conditions is that product streams are completely sterilized with respect to any possible pathogens including biotoxins, bacteria or viruses (Peterson et al., 2008). Hydrothermal carbonization is normally carried out at moderate conditions (250°C and 20 bar) "Hydro char" as the main product can be generated at even higher temperatures (250-800°C) based on wet pyrolysis. Reaction was tested with several types of biomass (Kruse, Funke, & Titirici, 2013; Liu, Quek, Kent Hoekman, & Balasubramanian, 2013; Titirici, Thomas, & Antonietti, 2007). When performing the process under moderate temperature, reaction rate is lower, normally it takes some hours. However, when applying high temperature, the reactive gasses are produced parallel with other pyrolysis products (bio-oils) resulting in interesting carbon structures like: nanotubes, films, microspheres, advance carbon materials.

The most widely investigated hydrothermal reaction over the past decade has been hydrothermal liquefaction involving conversion of waste biomass into chemicals and biofuels under medium temperature and high pressure (280-370°C, 100-250 bar). Water should be kept in a liquid state. The main product is water-insoluble bio-oil (called also bio-crude) with small quantities of water soluble products like char (solid residue) and light gases (e.g. H_2, CO, CO_2, CH_4). Both, liquefaction and gasification can be minimized at a comparably low temperatures ranging from 160 to 250 °C in order to increase the yield

Figure 3. Applications of biomass thermochemical conversion processes
Kamm et al., 2007.



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of solid biofuel (Huber, Iborra, & Corma, 2006). Produced fuel has a high C/H ratio beside a higher stability and energy content. Various types of biomass have been subjected to the conversion concept, e.g., agricultural residues (Toor, Rosendahl, & Rudolf, 2011), forest residues as well as sewage sludge (Akizuki, Fujii, Hayashi, & Oshima, 2014). Three main types of supercritical water gasification are reported, depending on the temperature range: catalyzed near-critical gasification to methane and aqueous phase reforming (Pavlovič, Knez, & Škerget, 2013).Catalyzed near-critical gasification is conducted under lower near critical temperature range at 300-500°C with addition of heterogeneous catalysts, which is increase selectivity to CH_4-rich gas product and carbon dioxide (Devi, Ptasinski, & Janssen, 2003; Yoshida, Oshima, & Matsumura, 2004). The reaction mechanisms are intensively investigated for different catalysts. Pt-based catalysts exhibit high H_2 selectivity but low conversion of the alcohols. Ni-based catalysts exhibit high activity and conversion but low H_2 selectivity and yield (Chen, Li, Chen & Yan, 2015). The reaction takes place at relatively mild reaction conditions within temperature 220-250°C and pressures typical of 15-50 bar. One of the most important factors of an economic analysis is the expected cost of the end product or products and the total energy efficiency of waste biomass conversion process with SCFs.

SOLUTIONS AND RECOMMENDATIONS

Techniques, applying supercritical fluids as a processing media certainly have a high potentiality for future large-scale biofuel production, especially for biodiesel production from waste oil and waste fat due to a number of advantages that include fast kinetics, high fuel production rate, ease of continuous operation and in some cases even elimination of the necessity of catalysts. The sub-chapter presents high pressure processes for treatment of biomass as a perspective concept for production of energy and chemicals as well as emphasizes the importance of fundamental studies of phase equilibria of substances in the presence of supercritical fluids. Main product of hydrothermal liquefaction, which is one of the most investigated process for converting waste biomass into chemicals and biofuels, is water-insoluble bio-oil (called also bio-crude) with small quantities of water soluble products like char (solid residue) and light gases (e.g H_2, CO, CO_2, CH_4). Bio oil, commonly termed as pyrolysis oil, chemically consist of a complex mixture and/or emulsion of water and degradation products of lignin (e.g. guaiacols, catechols, syringols. vanillins), cellulose (such as levoglucosan, dehydrated sugars, di-sugars, furancarboxaldehydes), and hemicellulose (such as acetic acid, formic acid). Their composition varies depending on the type of biomass feedstock and conditions of pyrolysis process. As these free-flowing organic liquids are composed of numerous highly oxygenated components, which are reactive, a suitable way to stabilize the oil (and allowing production of hydrocarbons) should be considered. A possible solution may be in hydrotreating (Venderbosch, Ardiyanti, Wildschut, Oasmaa, & Heeres, 2010). Hydrogenation of bio oil yield products less prone to produce carbon during oxidation process. Water content of the bio-oil may differ considerably. Organic acids form esters with olefins and esters and water with alcohols, aldehydes form oligomers and resins. With water, aldehydes form hydrates. Combination of aldehydes and alcohols is suitable to form hemiacetals, or acetals and water. Products in thermodynamic equilibrium with the reactants are formed, which means that a change in temperature or relative amounts of water and other reactive compounds will upset the equilibrium and initiate compositional changes. Some reactions may form resins or polyolefins and may be irreversible under likely bio-oil storage conditions. Another important issue is air oxidation that tends to form more acids and reactive peroxides that catalyse the

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polymerization of unsaturated compounds. In a complex, real bio-oil, the number of possible chemical reactions is very high, especially considering the large number of complex oligomers. The reactions between the oligomers are responsible for nearly all the viscosity increases observed during aging of bio-oil (Diebold, 2000).

Several research groups performed experiments and obtained mixtures of gaseous and liquid products. Phase equilibrium data for ternary system bio oil/ diesel/CO_2 and bio oil/tail water/ CO_2 was determined in the frame of our previous research (Knez Hrnčič, Venderbosch, Škerget, & Knez, 2013a). Data for the system H_2/pyrolysis oil and H_2/hydrogenated pyrolysis oil was reported by Knez Hrnčič and co-authors (Knez Hrnčič, Venderbosch, Škerget, Ilić, & Knez, 2013b).

Hydrogen is expected to become an important fuel in the long-term since in combination with fuel cells it offers the opportunity of an intrinsically clean energy supply. Compared with the conventional methods, SCWG process is characterized by its high reaction efficiency and H_2 selectivity. Water plays a role of reaction medium. A high moisture content material can be applied (Wang, Wang, Zhao, Guo, & Guo, 2016). Compared with conventional biomass gasification technologies, supercritical water gasification possesses a number of advantages which are derived from the unique thermodynamic and fluid dynamic properties of water in supercritical state. Dielectric constant of water is besides being a function of temperature, a strong function of pressure. At normal temperature and pressure, dielectric constant of water is relatively large, approximately 80. The main reason the strong effect of hydrogen bond in water. With increasing temperature and pressure, dielectric constant of water decreases and is around 5 at critical point. Several benefits compared to conventional gasification procedures include high thermochemical conversion rate, high pressure products that are easy for future transportation and usage, opportunities for carbon capture, sequestration and storage, as well as to further pure hydrogen production via a further steam-methane reforming process.

During the past two decades, over 100 journal papers have been published regarding different aspects of heterogeneous catalysis in the SCWG process. These studies include both commercial as well as catalysts tailored for gasification in SCW (Wang et al., 2016). A variety of real biomasses including lignocellulosic biomass from different sources, sewage sludge, chicken manure, food wastes, algae, and fermentation residue have been successfully gasified in SCW (Azadi & Farnood, 2011; Matsumura et al., 2005). Performance of a gasification process is generally influenced by operating pressure and temperature, different catalysts and feedstock type and concentration, catalyst and loading, and the contact time between the catalyst and the feed.

Several obstacles are present on the way of scaling-up of a biomass gasification process. High energy requirements are present already in the first step of the process. Water must be heated from ambient to supercritical conditions and above. Another drawback is the highly aggressive nature of water, which is even more evident in combination with an oxidant, leading to corrosion related issues. In addition to the above mentioned drawbacks, salt deposition on the reactor walls as a result of very low solubility of inorganic compounds at supercritical conditions should be considered (Vadillo, Sánchez-Oneto, Portela, & Martínez de la Ossa, 2013). These are the main hindrances that should be removed to enable a wider exploitation of biomass conversion processes applying water in supercritical state on industrial (Kamm et al., 2007). In continuous processes, pumpability of the biomass slurry is a problem. As the dry matter content of the biomass slurry exceeds the pumpability limits, several clogging problems may appear. On the other hand, a high dry matter content contributes to a higher gas production which increases the energy efficiency and the profitability of the plant (Yakaboylu, Harinck, Smit, & de Jong, 2015). A detailed investigation of phase equilibrium for the systems gas/water and gas mixtures/water was carried

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out to provide the fundamental data for the design and operation of the pilot plant and dissemination of the concept to the industrial scale (Knez Hrnčič, Markočič, Kramberger, & Knez, 2011; Knez Hrnčič et al., 2013b; Kramberger, Markočič, & Knez, 2013; Markočič, Kramberger, van Bennekom, Heeres, Vos, & Knez, 2013). In the frame of the past research on reforming in supercritical water, a unit for the conversion of organic compounds to gaseous products was constructed (Figure 4). The main goal of the research was to increase the content of H_2 and CO and to reduce the hydrocarbon concentration, application of catalysts was proposed. Experimental conditions presented here covered a wide range of reaction temperature and types of catalysts. Reactions were performed at high pressure in the range of temperatures between 100°C and 600°C. Results were interpreted on a common basis in terms of carbon conversion and hydrogen and methane yields. No significant change in the composition of the substrate over the entire range of the investigated conditions has been observed. The possible explanation may be that all the catalyst reacted already with the surface of the reactor even before the reaction took place. There were only small changes in the concentration of the gases, which depended on the working pressure, during the experiments performed at a constant temperature of 750°C.

In Table 1, some applications of gasification as pilot scale and semi-industrial scale processes are summarized. Comparison between hydrothermal liquefaction (HTL), hydrothermal carbonization (HTC) and hydrothermal gasification (HTG) processes in last 5 years is presented in the Table 2.

Reaction mechanisms and kinetics of the process are another issues that have to be addressed. Due to the sufficient heat energy all of the biomass feed, including char, is normally converted to gasification products in a single pass through a gasifier system (Sugathapala, 2013). The overall combustion reaction is taking place in the combustion zone. The air introduced contains, besides oxygen, water vapor and inert gases such as nitrogen and argon. The inert gases are normally assumed to be non-reactive with the fuel constituents. However, the water vapor reacts with the hot carbon according to the heterogeneous water gas reaction ($CO + H_2O \Leftrightarrow CO_2 + H_2$). In the subsequent reaction, CO_2 is reduced to CO according to the Boudouard reaction. Salts, usually in the biomass, act as catalyst/promoter for the water-gas shift reaction, producing up to half of the hydrogen (Kruse, Bernolle, Dahmen, Dinjus, & Maniam, 2010). Another important reaction taking place in the reduction zone is the water shift reaction (Sugathapala, 2013). Instead of a deeper understanding of the reaction paths occurring during gasification, thermody-

Figure 4. High pressure - high temperature reactor for catalytic reforming of methane

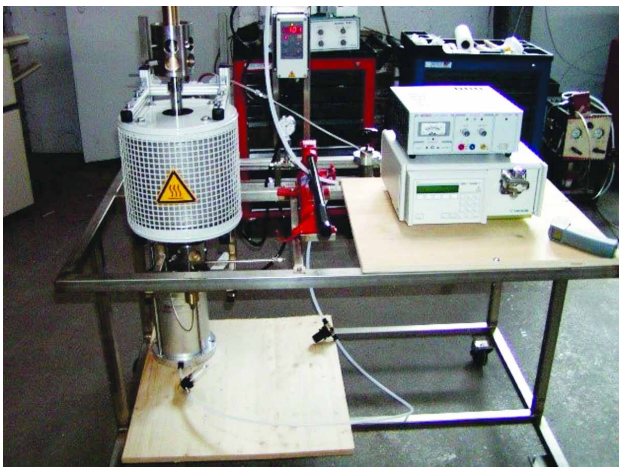

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Table 1. Applications of the concept as pilot scale and semi-industrial scale processes in the last years

Plant	Brief Description	Reaction Conditions	Presence of Catalyst	Process Type	
woody biomass gasification	A high temperature air-blown gasification scale-up model for woody biomass gasification. The down-flow gasifier was used. In large-scale units, the cold gas has ability to achieve 80% efficiency in the air-blown gasification. The cold gas efficiency was over 80%, and the heating value of the produced gas was 6.6 MJ/ m_N^3 .	Feeding rate 1000 kg/h, input air temperature 427 °C. (Maximum achievable temperature is over 1100 °C the O/C is from 1.26 to 1.84).	-	Continuous	(Kobayashi et al., 2009)
CHP Agnion Biomasse Heizkraftwerk Pfaffenhofen	TRL 4-5 - Laboratory Component Testing - Component Prototype Development Pilot CHP - Combinate heat and power technology The Heatpipe-Reformer developed by agnion is an innovative plant for production of renewable energy. Production of high-quality syngas.	Input: Waste Wood (80,000.000 t/y) Output: syngas (32.500 MWth) power (electricity) (6.100 MWel) at temperatures around 800°C – to form a gas mixture made up of hydrogen and carbon monoxide	-	Continuous	(Bioenergy, 2015)
Skive CHP plant	TRL 9 - Full scale commercial deployment A bubbling fluidized bed (BFB) gasifier is used to produce gas from wood-based biomass. This gas is then used in of reciprocating engines in a combined heat and power (CHP) application.	wood pellets (100.000 t/d) power (electricity) (6.000 MWel) heat (20.000 MWth) pressurized, bubbling fluidized bed, bed material dolomite, operated 850°C	monolith catalysts	Continuous fully automated	(Bioenergy, 2015)
Urbas Calvello	A combustible gas, wood gas, is drawn from wood through a thermochemical processes. The raw gas is then separated of dust and tars through a filtering system. Such cleaned gas is afterward used to produce combined heat and power through a gas engine and generator.	Input: wood output: chips power (electricity) (0.199 MWel)	-	-	(Bioenergy, 2015)
Vaskiluodon Voima Biomass Gasification Plant	The biomass feedstock is dried in a belt dryer and gasified in a large CFB-gasifier. Produces biogas from wood, comprising mainly of forest residue, to generate electricity and provide district heating to the local community.	Input: biomass substituting coal Output: power (electricity) (140.000 MW)	-	Continuous Fully automated	(Bioenergy, 2015)
Synthesis Tembec Chemical Quebec	TRL 6-7 Component Prototype Demonstration-Pilot Plant	Input: spent sulphite liquor feedstock Output: ethanol (13,000.000 t/y)	-	Continuous	(Bioenergy, 2015)
FICFB Oberwart	TRL-9 Full-Scale Commercial Deployment High electrical efficiency (almost 30% with combined gas engine and ORC process) No problematic solid residues (only ash, carbon content) Length of District Heating System ca. 5200 m Temperature District Heating System VL 95°C / RL 65°C	Input: wood chips (8.700 MW) Output: - power (electricity) (2.800 MWel) - heat (4.100 MWth)	-	Continuous	(Bioenergy, 2015)
Synthesis Enerkem Sherbrooke	Pilot plant TRL 4-5 Gasification based process technology that transforms sorted municipal solid waste (MSW) and residues from the forest and agricultural industries into transportation fuels, high value chemicals and electricity. Steps: 1.feedstock pre-treatmant, 2. Gasification, 3. Synthetic gas conditioning, 4. Conversion into liquid fuel	Input: municipal solid waste, wood chips, treated wood, sludge, petroleum coke, spent plastics and wheat straw Output: ethanol (375.000 t/y), methanol (475.000 m^3/y), syngas	-	Continuous	(Bioenergy, 2015)

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Table 1. Continued

Plant	Brief Description	Reaction Conditions	Presence of Catalyst	Process Type	
Synthesis Demonstration Plant, Westbury	TRL 6-7 Demonstration Pilot Plant	Input: waste wood, clean wood, saw mill residues (12,000.000 t/y) Output: FT liquids (0.568 m^3/h)	-	Continuous	(Bioenergy, 2015)
CHP Urbas Eberndorf	TRL 9 Full Scale Commercial Power / CHP technology A combustible gas, wood gas, is drawn from wood through thermochemical processes. The raw gas is then separated of dust and tars through a filtering system. Advantage: wood gas cogeneration requires no intermediate medium thus resulting in a higher electrical efficiency throughout the entire system.	Input: waste wood Output: power (electricity) (0.300 MWel)	-	Continuous	(Bioenergy, 2015)
GoBiGas	TRL 6-7 Demonstration Fuel synthesis The gasification technology is based on indirect gasification, which is supllemented by gas upgrading and SNG synthesis.	Input: Wood pellets (6.500 t/h), Forest residues (6.500 t/h) Output: SNG (20.000 MW), heat (5.000 MWth)	-	Continuous	(Bioenergy, 2015)
Holzgasanlage 2 Kaeser Gasel	TRL 9 Full-scale plant commercial Power / CHP technology; CHP gasifier unit with connection to heating device and power.	Input: wood chips (133.000 kg/h) Output: power (electricity) (0.140 MWel), heat (0.240 MWth)	-	Continuous	(Bioenergy, 2015)
BioSynergi CHP demonstration plant	TRL 6-7 Demonstration Pilot Plant Staged Open Core gasifier fuelled with forest wood chips (45-50% moisture on wet basis), as a part of a Internal combustion engine based CHP plant. The annual generation at the plant is expected to be 2,000 MWh electricity and 5,000 MWh heat.	Input: Wood chips Output: power (electricity) (0.300 MWel), heat (0.750 MWth)	-	Continuous	(Bioenergy, 2015)
Holzverstromungsanlage Bucher Escholzmatt	Full-scale Plant includes: feedstock and handling devices with heat and power gasifier unit, connection to district heating and power.	Input: wood chips (4,700.000 m3/y) Output: power (electricity) (0.130 MWel), heat (0.260 MWth)	-	Continuous	(Bioenergy, 2015)
Gasification plant fuelled with olive industry wastes	The energy recovery from olive industry wastes. The pilot plant contains a downdraft gasifier, gas cooling-cleaning stage and spark ignition engine with an adjusted carburettor. Cold gas efficiencies in the range of 70.7–75.5% were reached. The calorific value of the producer gas was 4.8 and 5.4 MJ kg^{-1}. The electric and CHP efficiency: 15% and almost 50%. Phases and main chemical reactions in a downdraft gasifier: Olive oil industry wastes, drying, pyrolysis, combustion, reduction, producer gas.	Operating temperature: 1050–1100 °C Outlet temperature: 400–500 °C Gas caloric value: > 4.5 MJ Nm^{-3}	-	Continuous	(Vera, Jurado, Margaritis, & Grammelis, 2014)
A two stage fluid bed plasma gasification plant	RDF-refused derived fuel from urban solid waste can be converted to clean syngas using conventional Fiber Bragg Grating system (FBG) tied with a plasma converter. Simultaneously converting ash-type components in the RDF into a stable vitrified product. The results show that the slag from the plasma converter unit can be assumed as fully recyclable. 90% of ash-type constituents in RDF are recuperated as a stable vitrified product.	Feed rate of the solids at rates of up to 50–60 kg/h plasma converter: 950–1150 °C FBG: 700–800 °C	-	Continuous	(Materazzi, Lettieri, Mazzei, Taylor, & Chapman, 2015)
Gasification of dried sewage sludge	Special rotary dryer produce particles, which differ significantly in size, geometry, porosity and weight. Three lines were planned to process the entire mass of 5.4 t/a ds6 with a water content of around 3–8%. Gas is blended with biogas from sludge fermentation and utilized in a gas engine or combustion chamber to produce heat.	Gasification temperature: 850–900 °C Installed power: 2.2 MW_{th} Type of dryer: Rotary dryer Electrical consumption: 75 kW Cold gas efficiency:70%	-	Continuous	(Judex, Gaiffi, & Burgbacher, 2012)

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Table 1. Continued

Plant	Brief Description	Reaction Conditions	Presence of Catalyst	Process Type	
Japanese cedar wood (up-draft gasifier)	Gasification of cedar wood in a bench-scale externally heated updraft gasifier. Around 30-50 vol.% of H_2 can be produced from cedar wood gasification.	Feedstock: particle size of 1–2 mm Operating temperature: 650 °C – 950 °C Lower heating value of gas: 1–33.2 $mJNm^{-3}$	-	-	(Aljbour & Kawamoto, 2013)
Rice straw gasification (up-draft gasifier)	Rice straw gasification in an atmospheric fluidized-bed gasifier. A high quality syngas (10% H_2, 18% CO and 4% CH_4) with low tar content was produced.	Operating temperature: 700 °C – 850 °C higher heating value (HHV) of the produced gas: 5.1 $MJ(Nm)^{-3}$ cold gas efficiency: 52%	-	-	(Calvo, Gil, Otero, Morán, & García, 2012)
Willow and other agriculture residue-dry grains (up-draft gasifier)	The gasification has been performed using circulating fluidized bed (CFB) gasifier. The averaged concentration of H_2 obtained from willow and dry grains was around 28 vol. % and 20 vol. % respectively.	Feed rate: max. 20 kg/h Operating temperature: 800 °C–820 °C cold gas efficiency: 50 -70% power range: 60 kW	-	-	(Meng, de Jong, Fu, & Verkooijen, 2011)
gasification of pine woodchips (up-draft gasifier)	Gasification in bench-scale circulating fluidized-bed (CFB) gasifier. Steam was used as a fluidized and gasifying agent. Gas composition CO (27–40 vol.%), H_2 (22–27 vol.%), CH_4 (7–9 vol.%), CO_2 (39–42 vol.%)	Feed rate: 5 kg/h Operating temperature: 700-900 °C Power range: 15 kW higher heating value (HHV) of the produced gas: 17 $MJ(Nm)^{-3}$	-	-	(Ngo et al., 2011)
Bagasse gasification	Gasification was carried out in an intensified auto-thermal air-blown downdraft gasifier and at atmospheric pressure. The system consists of a gasifier, an air blower, a gas clean up system with two cyclones, a water scrubber and an ash collector. Very low tar content between 0.376–0.40 g Nm^{-3} in the gas.	Operating temperature: 1040 °C Power range: 50 kW	-	-	(Jordan & Akay, 2012)
Hazelnut shells gasification	Cracked hazelnut shells size between 5 and 10 mm. The gasifier consists of an ignition unit, a cyclone, a gas cleaning system, a measurement/control system and data recording units. Gas which is produced by the gasifier enters the cyclone and then it is divided into two streams. Gas composition: H_2(13 vol.%), CO (23 vol.%), CO_2 (11 vol.%), CH_4 (4 vol.%) with low tar content.	10 kg feeding capacity Operating temperature: 1000 °C Lower heating value of gas (LHV): 1 MJ/Nm^3 - 5 MJ/Nm^3 Power range: 45 kW	-	batch	(Olgun, Ozdogan, & Yinesor, 2011)
Biomass gasification	Pine wood blocks gasification unit consists of The gasification system consists of air intake equipment, a downdraft gasifier, ash chamber, gas cleaning system, roots blower, flow meters and off-gas burner. First the catalyst is uniformly distributed on the grate. Then the biomass is placed on charcoal. A specified (Lv et al., 2007) quantity of hot water is added into steam generating room. Afterwards feedstock in the gasifier is ignited. The gas contain around 70 vol.% of H_2 and CO. Biomass oxygen/steam gasification has its advantage for improving the hydrogen yield in less energy consumption.	Lower heating value (LHV) of fuel gas: 11.11 MJ/Nm^3 Hydrogen yield: 45.16 g H_2/kg	charcoal	batch	(Kirkels & Verbong, 2011)

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Table 1. Continued

Plant	Brief Description	Reaction Conditions	Presence of Catalyst	Process Type	
Biomass gasification technology using integrated catalytic hot gas cleaning	A lab-scale pilot gasification facility of advanced gasification technology for production of high quality gas using innovative hot gas cleaning catalyst. In this process the tar content in the product gas could be reduced and the large amount of the aromatic ring systems in tar have been reformed and/or cracked. The increase contents of H_2 and CO and decrease of CH_4 and CO_2 was noticed. Gas composition: H_2 (54.2.%), CO (20 vol.%), CO_2 (6.7 vol.%), CH_4 (18.8 vol.%) with low tar content.	Feed rate: 4.4 kg/h gasifier reactor temperasture: 880 °C catalytic reactor temperature: 800°C tar content: below 83 $mgNm^{-3}$	Char-supported catalysts (woody chips soaked in 0.2 M $FeCl_3$ and dried)	batch	(Dong et al., 2013)
Plant of coal and supercritical water gasification system driven by concentrated solar energy	Gasification plant using concentrated solar energy system consists of: nitrogen bottle, feedstock tank, feeder, solar receiver/reactor, heat exchanger, cooler, filter; regulator, separator, pump, tanks, toroidal surface heliostat with the two axis spinning-elevation sun tracking, concentrator. Biomass glucose, corn meal and wheat stalk were gasified in the system for the production of hydrogen-rich gas.	Feedstock:1.03 t/h Maximal temperature and pressure:800 °C and 400 bar, respectively. Maximal concentrated solar power:163 kW. The maximal hydrogen production molar fraction: 55%	-	Continuous	(L. Guo, Jin, & Lu, 2015)
Solar receiver/reactor for hydrogen production	Hydrogen production with biomass gasification in supercritical water by using original solar hydrogen reactor. Gasification of glucose and corncob mixed with carboxymethyl cellulose mixture (CMC) was carried out to generate hydrogen-rich fuel gas. System consists of: feedstocks tank, pre-heater, high-pressure feeder, SCW reactor, heat exchanger, cooler, regulators, separators, pumps, valves, tanks, flow meter, multi-dishes concentrator.	The maximal throughput capacity was 16 kg/h. Feedstock temperature: 200–250 °C The maximal hydrogen production volume fraction: 55% Pressure: 240 bar Temperature: 543°C-676°C Feedstock: - Glucose concentration: 0.1 M, 0.2 M, 0.3 M, 0.4 M 2 wt% CMC + 1.5 wt% corncob, 2 wt% CMC + 3 wt% corncob, 2 wt% CMC + 3 wt% corncob + 0.5 wt% KOH, 2 wt% CMC + 5 wt% corncob	without or KOH	-	(Liao, Guo, Lu, & Zhang, 2013)
A transpiring-wall supercritical water oxidation reactor	SCWO pilot plant with a transpiring wall reactor including five streams (feed, oxygen, air, transpiring water and cooling water) are introduced into the reactor. Reactor is used to treat organic and recover energy. A total organic carbon (TOC) removal above 99% is reached even at a feed temperature of 369 °C.	Feed rate: 8–17 kg/h Reaction temperature: 476-725 °C	-	Continuous	(Zhang et al., 2012)
Hydrogen production from glycerol	Glycerol was used for hydrogen production using continuous flow tubular reactor which consists of: reactor, water tanks, pumps, cooler, preheater, mixer, reactor, regulators measuring equipment. The feedstock (glycerol solution) was first mixed with preheated water for avoiding side reactions. Hydrogen yield in relation to catalysts was in the following order: $NaOH > Na_2CO_3 > KOH > K_2CO_3$ Hydrogen-rich gas products - hydrogen molar fraction was 52.0–68.9%.	Reaction temperature: 445-600 °C Pressure: 250 bar residence time: 3.9-9.0 s.	alkali catalysts	Continuous	(Guo et al., 2012)

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Table 2. Comparison between hydrothermal liquefaction (HTL), hydrothermal carbonization (HTC) and hydrothermal gasification (HTG) processes in last 5 years

Type of Biomass Conversion	Material	Temperature (°C)	Yield (%)	HHV - High Heating Value (MJ/kg)	Energy Recovery (%)	Ref.
HTL	microalgae	350	38–64[a]	25–30	60-78	(Biller & Ross, 2011)
HTL	microalgae	300-350	27-47[a]	32-37.5	-	(Biller et al., 2012)
HTL	microalgae	300	66[a]	33-37	-	(Faeth, Valdez, & Savage, 2013)
HTL	sewage sludge	300	-	14	-	(Fonts, Gea, Azuara, Ábrego, & Arauzo, 2012)
HTL	manures	300	-	10–20	-	(Derek R Vardon et al., 2011)
HTL	lignocellulosics	300	35[a]	12-20	64	(Umeki, Yamamoto, Namioka, & Yoshikawa, 2010; L. Wang, Shahbazi, & Hanna, 2011; Zeton et al., 2014)
HTL	barley straw	280-400	35[a]	17	55	(Zhu, Toor, Rosendahl, & Chen, 2014)
HTL	cellulose	275-320	5.8 – 34[a]	-	-	(Yin & Tan, 2012)
HTL	algae	350	38-63.6[a]	-	-	(Elliott et al., 2013)
HTL	algae	300	24–45[a]	35–37	-	(Derek R. Vardon, Sharma, Blazina, Rajagopalan, & Strathmann, 2012)
HTL	brown macro-algae	350	9.8-17.8[a]	32-34	-	(Anastasakis & Ross, 2015)
HTL	cornelian cherry stones	250-300	28[a]	28.35	-	(Akalın, Tekin, & Karagöz, 2012)
HTL	*Litsea cubeba* seed	250–350	56.9[a]	40.8	-	(Wang et al., 2013)
HTL	microbial yeast biomass	300	56.4[a]	37	83.05	(Jena et al., 2015)
HTL	microalgae	200-300	50-70[a]	36.9	101.8	(Zhang, Chen, Zhang, Luo, & Zhang, 2013)
HTL	wastewater culture algae	300	49[a]	33.3	-	(Chen et al., 2014)
HTC	lignocellulosic biomass	250	35-38[a]	28.4-29.2	-	(Xiao, Shi, Xu, & Sun, 2012)
HTC	woody and herbaceous biomass	175-295	10-12[a]	28–30	60-70	(Hoekman, Broch, Robbins, Zielinska, & Felix, 2013)
HTC	corn Stover	200-260	-	15.6-24.1	-	(Reza, Lynam, Uddin, & Coronella, 2013)
	miscanthus			20.6-22		
	switch grass			19-21		
	rice hull			20.3-24.6		
HTC	coconut fiber	150-375	35[b]	-	-	(Liu & Balasubramanian, 2012)
HTC	eucalyptus leaves		28[b]			
HTC	coconut fibers	250	45.3[b]	28.4	67.0	(Liu & Balasubramanian, 2014)
HTC	eucalyptus leaves		46.4[b]	25.8	63.3	

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Table 2. Continued

Type of Biomass Conversion	Material	Temperature (°C)	Yield (%)	HHV - High Heating Value (MJ/kg)	Energy Recovery (%)	Ref.
HTC	slash pine	235-275	53.6-69.7[c]	22.8-28.56	-	(Hoekman et al., 2014)
HTC	air dried sludge	200	-	14.37-15.09	-	(He, Giannis, & Wang, 2013)
HTC	palm oil empty fruit bunch	150-350	49-76[b]	>27	68-78	(Parshetti, Kent Hoekman, & Balasubramanian, 2013)
HTC	sugar	180-250	47.5-55.7[b]	25.4-25.5	-	(Fiori, Bassoa, Castelloa, & Baratierib, 2014)
	grape seeds	180-250	62.3-80.3[b]	26.4-29.8		
HTC	walnut shell	190–230	36.3-48.6[b]	23.2-29.3	50.2-57.5	(Román, Nabais, Laginhas, Ledesma, & González, 2012)
	sunflower stem		29.2-39.7[b]	24.5-28.9	50.4-58.9	
HTC	lignocellulosic biomass	190-260	47-8-83,5[c]	20.2-25.9	-	(Kambo & Dutta, 2014)
HTC	agricultural residues	180-220	34.1-81.7[b]	21.5-28.3	36.6-102.7	(Oliveira, Blöhse, & Ramke, 2013)
HTC	lignocellulosic biomass	180–260	37–95[b]	20–31	54–98	(Mäkelä, Benavente, & Fullana, 2015)
HTC	different biomasses	200-280	16.5-35.7[c]	21.11-26.15	24.7-58.23	(Gao et al., 2016)
HTC	lignocellulosic biomass	200-275	42-86[c]	-	61.9-95.5	(Lynam, Reza, Yan, Vásquez, & Coronella, 2015)
HTC	pulp and paper waste	180–260	-	-	69-95	(Mäkelä, Benavente, & Fullana, 2016)
HTC	coniferous biomass	180-250	50-72[c]	21.95-28.36	72.5-79	(Sermyagina, Saari, Kaikko, & Vakkilainen, 2015)
HTC	olive mill waste	200-250	-	26.4-32.5	-	(Benavente, Calabuig, & Fullana, 2015)
	canned artichoke waste	200-250		16.8-30.26		
	orange juice waste	200-250		18.2-30.3		
HTC	miscanthus biomass	190-260	42.8-83.5	26–30	66–74	(Kambo & Dutta, 2015)
HTG	lignin alkali	300–600	12.0-54.9[d] 18.0-61.4[e]	-	-	(Güngören Madenoğlu, Sağlam, Yüksel, & Ballice, 2016)
	cellulose		21.1-66.2[d] 29.9-81.2[e]			
HTG	marine biomass	300–600	21-80[d] 62.51[f]	-	-	(Deniz et al., 2015)

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Table 2. Continued

Type of Biomass Conversion	Material	Temperature (°C)	Yield (%)	HHV - High Heating Value (MJ/kg)	Energy Recovery (%)	Ref.
HTG	xylose	400-600	24.4-65.9[d] 30-80.9[e]	-	-	(Gökkaya, Saglam, Yuksel, & Ballice, 2016)
HTG	wood residue	500-600	45-60[e] 20-26[f]	-	-	(Üremek Cengiz, Eren, Sağlam, Yüksel, & Ballice, 2016)
HTG	phenol	400-600	62-75[d] 76-80[e]	-	-	(Selvi Gökkaya, Saglam, Yüksel, & Ballice, 2015)
HTG	biodisel	300-600	8-60[f]	-	-	(Cengiz et al., 2015)
HTG	microalgae	600-650	57-98[d]	-	-	(Patzelt et al., 2015)
HTG	biomass	400-650	10-70[f]			(Castello & Fiori, 2015)
HTG	microalgae	650	-	32.4-33.5	-	(Möbius, Boukis, Hindersin, & Kerner, 2015)

[a]– oil yield dry basis
[b]– hydrochar yield ($kg_{hydrochar}/kg_{dry\ feed}$)
[c]– mass yield
[d]– gas yield without catalyst
[e]– gas yield with catalyst
[f]– hydrogen yield
HTL – hydrothermal liquefaction
HTC – hydrothermal carbonization
HTG – hydrothermal gasification

namic calculations were employed (Schmieder et al., 2000). Thermodynamic equilibrium calculations indicate that methane is preferably formed at lower temperatures, whereas at higher temperatures, hydrogen is the main product, besides CO_2 (Waldner & Vogel, 2005). Lower heating rates usually promote the formation of refractory compounds, resulting in more methane (rather than hydrogen) production. A possible solution to lower the high energy demand characteristic for the process could be the application of pressures exceeding conventional ones, up to 1000 bar. After exceeding the critical temperature (374 °C) at a pressure of 250 bar C_p of water decreases with further increase of temperature. The subsequent conclusion is that heating water at higher pressures to near critical conditions would result in a less energy intensive process.

Numerous non- conventional working fluids have been suggested for application in energy production processes due to their unique thermal and transport properties. The thermo-physical property change of the fluids is significant, in the high temperature and /or high pressure region (Yu, Chen, Zhao, Li, & Zhang, 2015). There are many advantages when using CO_2 supercritical cycles instead of classical systems: the compression ratio is low, so compressor efficiency is relatively high; volumetric refrigeration capacity is high, which helps reducing the size of the systems. Namely, in the proximity of critical point, the CO_2 fluid is very much expandable/compressible, the density and thermal conductivity change to be near one order of magnitude lower as temperature approaches the critical point. At the same time the Prandtl number and specific heat also form high peaks (Chen, Zhang, Okajima, Komiya, & Maruyama, 2016). When in a certain reaction system SCFs are applied as a reaction media, the particular thermodynamic

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and transport data have to be considered. Investigations of basic thermodynamic and transport data like phase equilibria, density, viscosity, dielectric constant and diffusion coefficients are of fundamental importance to overcome many uncertainties associated with the parameters of the extreme supercritical systems, the methods for incorporating risk and uncertainty into process design and optimization.

In the frame of our past research, several gravimetric methods have been developed or modified to carry out the measurements at elevated pressures and temperatures:

- **Determination of Density of the Binary Systems:** Density of some gases increases significantly at certain conditions and thus the buoyancy effect when applying the magnetic suspension balance method can be well expected. Consequently, the sample is lifted and the measurement cannot be performed. For these systems, the external balance method presents an alternative to the Magnetic Suspension Balance (Figure 5).
- **Determination of the Viscosity of Binary Systems:** Experimental viscosity data at high pressure and high temperature was measured for multi-component mixtures. The measurements were conducted in a HPHT reactor (Figure 6).
- **Investigation of Interfacial Tension of Binary Systems:** A novel technique for predicting the interfacial tension based on the capillary rise phenomenon for the gas saturated compounds has been proposed for performing interfacial tension tests at high pressure and high temperature conditions (Figure 7).

Figure 5. Magnetic suspension balance

Figure 6. a) NWA view cell with variable volume b) modification of system allowing viscosity measurements c) a sample of Polyethylene glycol (PEG) 1500 after addition of CO_2

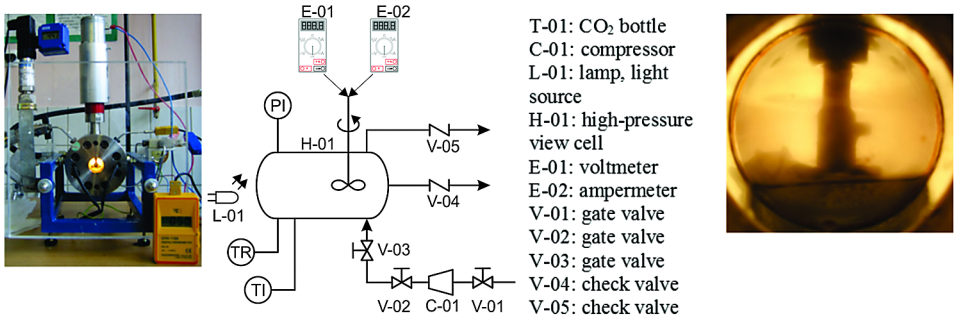

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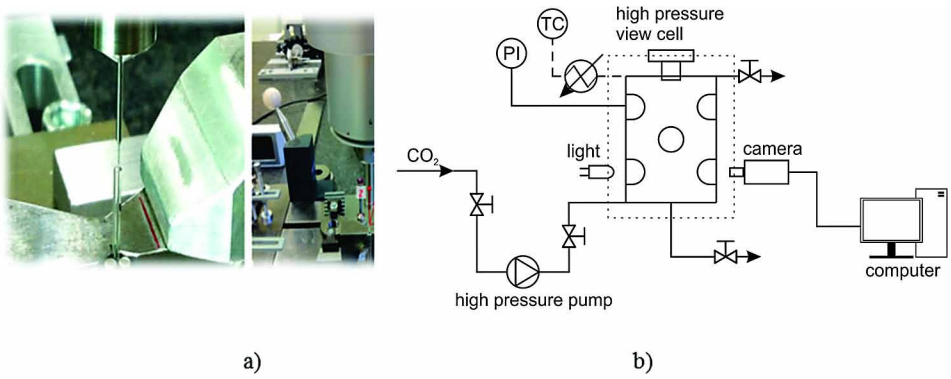
Figure 7. a) A coordinate measuring Machine Zeiss UMC 850 for determination of the radius of capillaries b) a scheme of the measuring system for determination of the interfacial tension



To reduce hydrocarbon concentration and to increase the content of H2 and CO in the product, catalysts are introduced to the reaction mixture. If the aim of the reaction was the efficient gasification of biomass, alkali and metal catalysts were used. The alkali catalysts (NaOH, KOH, Na_2CO_3, $KHCO_3$, $K2CO_3$) (Cantero, Álvarez, Bermejo, & Cocero, 2015) significantly increased the H_2 and CO_2 yields and decreases CO yield by promoting the water-gas shift reaction (Guo et al., 2010). As heterogeneous catalysts, transition metals (Ru, Pd, Ni, Cu, Co) on different supports (TiO_2, Al_2O_3, ZrO_2, $CeZrO_2$, SiO_2) were used to increase biomass conversion and the yield of gas formation (Guan et al., 2014; Mehrani, Barati, Tavasoli, & Karimi, 2015). For the SCW reforming of biomass metals are much more attractive than alkalis. Their catalytic activity and stability of is influenced by the type of the support. Promoters such as Na, K, Mg or Cs may be also added to further improve catalyst activity and stability, and to favor the water-gas shift reaction. Activated carbon was also proposed as heterogeneous catalyst for enhancing biomass gasification in SCF (Ding, Azargohar, Dalai, & Kozinski, 2014). It was found that carbon gasification, the water-gas shift reaction and methanation reaction are favored by the presence of activated carbons. The main drawback is that activated carbon is prone to chemisorption of the intermediates which decreases the surface area, thus affecting its activity.

Corrosion is another issue that should be solved before considering construction materials. Unfortunately, it is almost impossible to prevent corrosion, however it is possible to control it. selection and the amount of corrosion inhibitor used depend on the acid type and its strength, the steel type, the desired protection time, and the expected temperature (Brondel et al., 1994). The main drawback considering corrosion inhibitors is that they are effective only for a particular metallic material in a certain environment (Finšgar & Merl, 2014). Already a very small change in the composition of a solution or alloy can significantly change the inhibition efficiency. Because the mechanism of how corrosion inhibitors work is usually not known and in spite of some proposed models for forecasting corrosion inhibition effectiveness, empirical experimental testing is still unavoidable (Brondel et al., 1994; Finšgar & Jackson, 2014). Inhibitors must be chosen after taking into account the nature and combinations of metals present, the nature of the corrosive environment, and the operating conditions: flow, temperature, and heat transfer. Recent studies have attempt to find a green (environmentally acceptable) corrosion inhibitor/inhibitor formulations such as plant extracts, essential oils and purified compounds (Znini et al., 2012).

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FUTURE PERSPECTIVES

Applications of supercritical fluids certainly have a bright future. Particularly for the products for use in medicine, tissue engineering and nutrition from the point of the high value added products and treatment of excessive wastes generated by a wide range of processes, such as domestic and industrial wastewater treatment, wastes from oil and biodiesel industry, wastes from food, biomass processing and chemical industry. Combination of hydrolytic and bio-catalytic processes has proved to be a suitable method to convert very wet biomass and liquid streams to gases or other bio-based chemicals.

Integration of advanced processing concepts enable further application of residues from different industries with the principle goal to obtain value added products, avoiding the problems related to waste disposal. Limited supply of petroleum resources together with the ever-increasing demand for petroleum-based products has fueled the emergence of the bio economy. Global trends highlight the growth in fuel, energy, materials, chemicals and other products based on renewable feedstocks as economically viable alternatives to petroleum-based products. Therefore, there is no uncertainty that research needs and challenges that support the biorefinery concept, which is analogous to petroleum refinery, where instead of nonrenewable fossil fuels; renewable feedstocks are converted into chemicals, fuel, materials and other products. Thus, a biorefinery would integrate a variety of separation and conversion processes to produce multiple product streams from renewable feedstocks with little or no waste. Such developments in biorefinery approaches force us to consider integrated approaches to utilization of supercritical technology in biorefining where new approaches, such as energy recovery have key relevance. Namely, high temperatures involved in the process and the high energetic consumptions of these processes have been studied many times without an appropriate heat integration scheme. In design, knowledge of the reactions kinetics at different pressures and temperatures is of utmost importance and represents the fundamentals in the design of such process. The choice of biomass applied will dictate the operational conditions aiming to achieve a rapid conversion of polysaccharides with high saccharide production and low degradation products. The composition of biomass available varies considerably. Some natural materials contain relatively high amounts of complex substances that increase the resistance of the material to hydrolysis processes and require that conditions that are more aggressive. Lignocellulosic materials such as corn stover and sugar cane bagasse are some of them. Lignin is present in a complex structure with cellulose and hemicellulose that require high pressures and temperatures to carry out the complete hydrolysis. Thus the composition of the raw material is of fundamental importance in SubWH and SupWH processes, since it will determine (Brunner, 2015).

To overcome the obstacles between the research and application of the sustainable processing concepts in practice, more research is needed in order to understand the reaction mechanisms. Beside biomass treatment, hydrothermal technology has a great perspective for industrial scale production of materials, as they are part of the green chemistry. Particularly supercritical CO_2 and H_2O will have an important role in production of nano-particles and of nano-material owing to the multi-faceted advantages. The obtained products may be used as insulating materials or as catalysts. In such a process, initial material is dissolved in supercritical water in the first step. Then it is mixed with cold solutions to reduce the solvent power of the supercritical water and to achieve precipitation of the nano-materials. These are swept out with another flow of cold water and then separated from the water. Operation cost of such processes are relatively low due to the lower energy consumption and above all, the approach is less time consuming than the traditional processing methods (Brunner, 2015). Besides, the properties of the obtained products such as structure of electronic energy levels and transitions, electron affinity,

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conductivity, phase transition temperature, magnetic properties, melting points, etc. may be "tailored" since they depend on the nanoparticle size and shape, which is relatively easily controlled by varying the process conditions (Byrappa, 1991).

CONCLUSION

The chapter discussed hydrothermal processing of biomass to obtain bio-oil, bio-gases and bio-carbon with a highlight on current research trends that tend towards growth and implementation of new technologies which enable transition to "green" chemistry without further use of environmentally and health hazardous organic solvents as a basic step towards sustainable development. Such processing concepts comprise reuse of residues according to a basic concept of biorefineries. After extraction of source material, further conversion of residues (biomass) to a wide range of useful products, including second-generation biofuels, base chemicals, biospecial chemicals and bioefficient materials, is suggested. The main impetus for this conversion is on one way driven by a concern to the environment to reduce the usage of conventional solvents and energy. By the assessment of sustainable biomass potential and the evaluation of benefits of different bioenergy options, favorable conditions to set up a second-generation biofuel industry will be established. Several benefits are derived from the economic point of view; countries that are currently not able to produce second-generation biofuels could profit from new technology and market opportunities once the technology is commercially available.

"Process intensification" as a part of necessary sustainable development and "green" revolution uses also high pressure as a processing tool which enables production of goods with completely new specifications. Since higher pressures allow economically feasible processing, the future research will most probably lead towards investigation of the fundamental thermodynamic data pertaining to the conditions such processes.

Hydrothermal technique offers a great perspective of the future as an excellent possibility for processing of various product options from biomass degradation in hot compressed water. Hydrothermal processes are also a promising basis for the production of a variety of different intermediates to be used for energy and chemical purposes. As a reaction media water opens new perspectives compared to "dry processes", needing lower reaction temperatures. The polar character of water and the high reactivity of biomass with its many polar bonds in water offers an opportunity of processing at lower temperatures. Selectivity of water can be easily fine-tuned by slight changes in operating conditions – therefore different products with special properties can be obtained and by variation of pressure and temperature, production yields may be increased considerably. The advantages of hydrothermal technology are several and the waste biomass conversion for production of energy carriers are performed by applying supercritical water and supercritical water by the introduction of supercritical CO_2 to the binary systems supercritical water/biomass or supercritical water/biomass. The benefit of such processing reflects in lower energy consumption and production of specific products of a benefit. Current trends in hydrothermal materials processing are presented in relation to the concept of soft solution processing and above all, low energy consuming fabrication technique. Dissemination of the new approaches to the industrial scale processes, with the emphasis on waste biomass conversion for production of biofuels and bio-chemicals by applying supercritical fluids to improve the economic, environmental and energy efficiencies will play a significant role in the upstream and downstream processing in the oilfield industry. The challenge is not in the conversion of the feed to the product, but to achieve the product efficiently by understanding process

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backgrounds in terms of mass transfer, thermodynamic system characteristics, process optimization and scale up, which is still the main obstacle for a wider application of these technologies.

It is thus about the development of advanced technologies involving sub- and supercritical fluids which can provide efficient products, have low or even zero impact to the environment and do not require much energy.

Undoubtedly, much research is still needed and a close collaboration between scientists, industry and governmental agencies is required to make the large-scale application of such advances technologies for production of energy possible.

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KEY TERMS AND DEFINITIONS

Bio Based Chemicals: Sustainable, cost-advantaged, drop-in replacements and substitutes for petroleum-based chemicals that are used in variety of industrial applications.

Bio Oils: Dark brown organic liquids, which are chemically complex mixtures and/or emulsions of water and degradation products of lignin.

Biofuel: A fuel, such as biogas or biodiesel that is produced from renewable resources, especially plant biomass, vegetable oils, or treated municipal and industrial wastes.

High Pressure Phase Equilibrium: Equilibrium relations between phases at high pressure.

High Pressure View Cell: A reactor that allows both, observation through the windows and quick and precise thermodynamic measurements during experiments, carried out at elevated pressures by a precise volume control with measurement of the piston position in the cell. Pressure and temperature are maintained constant during entire measurement.

Hydrothermal Carbonization: Thermochemical conversion process, which usually takes place at moderate conditions (523 K and 2 MPa) where carbonaceous bio solid product named "hydro char" is obtained.

Hydrothermal Gasification: A process in which biomass waste without pre-drying reacts with water that acts not only as a solvent, but also as a reactant under subcritical and supercritical conditions to produce gaseous products, mainly CH_4, H_2, CO_2 and C_1-C_4 carbon gases.

Hydrothermal Liquefaction: A process for converting waste biomass into chemicals and biofuels, where the reaction is performed under medium temperature and high pressure (553-643 K, 10-25 MPa), sufficient to keep the water in a liquid state.

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Chapter 51
Life Cycle Costing for Sustainability

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ABSTRACT

Life cycle costing supports sustainability by stressing the costs not only in the production and selling phases but also considering the costs which are incurred after the sale of the products. This chapter reveals main characteristics of life cycle costing as follows: Life cycle costing also includes production costs which are; (a) research and development costs, (b) marketing, selling, distribution and design costs, (c) and also user costs. User costs have three dimensions: transaction costs, maintenance costs, and disposal costs. Therefore one can simply assert that life cycle costing has a broader approach in the calculation of the costs compared to other conventional costing systems. After introducing the main characteristics and basic definitions of life cycle costing, this chapter will discuss the implementation of life cycle costing in comparison with other conventional costing systems. Following this, we will analyze the link between life cycle costing, waste management and sustainability. Overall review will be done in the conclusion.

INTRODUCTION

The businesses are the catalyst in the development of globalization and some problematic impacts of their operations on the environment become an international issue. The largest corporate initiative in the world, the United Nations Global Compact determined ten principles for the companies that setting core values in the four different basic areas affect the human life. These principles ask the companies to substantially respect human rights, labor standards, the environment and anti- corruption. The principles 7-9 are related to environment area and call the companies; to be precautionary against the environmental challenges, undertaking initiatives to promote greater environmental responsibility and to be supportive

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in the development and diffusion of environment friendly technologies (Rasche & Kell, 2010). Existence of the Global Compact acknowledges that environmental problems arose from the businesses' operations have rising importance and cannot be left local regulations and regulators or initiatives in the solution of the problems which affect the humanity. The businesses are the economic units to produce and sell their products to meet the needs of the society and to survive in future by earning profit. While the environmental problems, particularly pollution, may occur in the production phases, inefficient use of products by consumers or dispose of products may cause some other environmental problems too.

Especially to prevent side effects in product disposals, some businesses have begun to undertake more responsibility within the corporate sustainability and/or corporate social responsibility approaches. Besides estimating the cost of production, they started considering the cost of disposal before the sale of the products. This contemporary costing system, which is named life cycle costing (LLC) is used to achieve this objective. There, LCC includes disposal cost in the determination of total product costs. Life cycle costing considers both production costs and user costs. User costs are also known as transaction, maintenance, and disposal costs which they are closely involve in sustainability and waste management. Therefore, one can simply assert that LCC has a broader approach providing full cost in the calculation of the costs, compared to other conventional costing systems.

This study primarily focuses on revealing the fundamentals of the LCC and its relations with waste management, considering the sustainability perspective. In order to fulfill these objectives, the organization of the paper is as follows. The main characteristics and basic definitions relating to life cycle costing are presented in the background. After the background of LCC, the implementation of life cycle costing and the comparison of LCC with other conventional costing systems are discussed. In following, the links among life cycle costing, waste management, and sustainability will be analyzed. An overall review will be done in the conclusion.

BACKGROUND

The Basics of Life Cycle Costing

LCC varies from other traditional costing systems by considering the total cost of products throughout the life cycle of products. To enhance a clear comprehension of the LCC, explanation on the term of 'product life cycle' is vital. The graph below demonstrates the stages of the product life cycle. A product moves four major stages through its life cycle; introduction, growth, maturity, and decline.

Introduction is the first stage of the life cycle of product. Launching a new product incurs development costs, in addition to some other important period expenses, which incur during promotion and distribution. This situation results with low revenue and zero profit in the earliest phase of introduction stage. As time passes, sales start to increase and earn profit. Second stage is 'growth' and during the growth stage sales rise rapidly, and profits reach a peak. This stage is the most significant stage for the battle with competitors in order to gain consumers' acceptance and create loyal customers. Therefore, companies increase their promotion expenses. The third stage is 'maturity'. As it is seen on the figure above, sales curve peaks and it starts to decline parallel with profit curve. There is still a severe competition with the competitors and improvements and differences are required to promote the products. The last stage is 'decline'. During the decline stage, sales fall rapidly due to launch of the new products developed or updated with new technologies. As one product is declining, other products of a company

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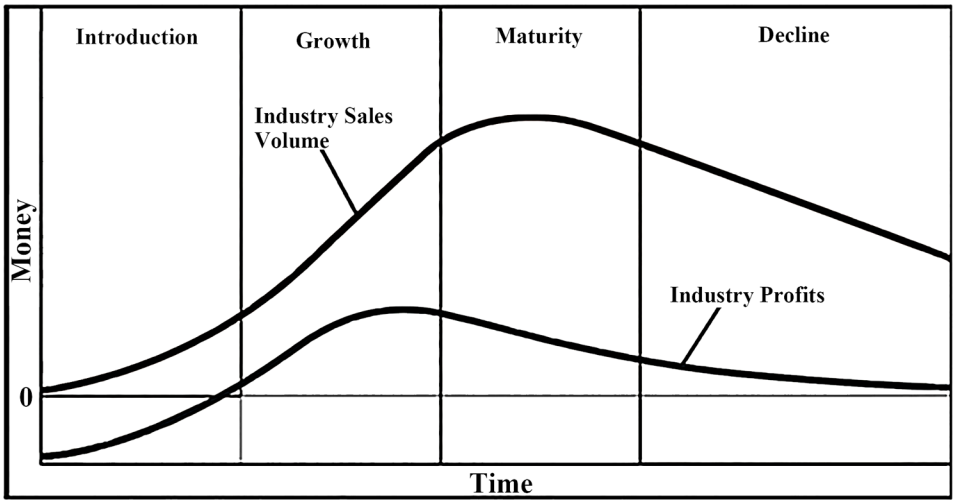
Figure 1. The four stages of the product life cycle
Source: Pride, Hughes, & Kapoor, 2014



are in the introduction, growth or maturity stages. Thus, when companies understand and ensure that the product has completed full life cycle, they deal with new products and do not promote the existing product anymore. Moreover, sales volume and profitability are very low though costs are high in the decline stage of a product life cycle (Pride, Hughes, & Kapoor, 2014).

The use of LCC was the first in US Department of Defense, in order to provide an effective cost management on the procurement of weapon systems dating from1960s. It took a notable place in construction management literature owing building industry that needed a more holistic approach (considering the environmental costs such as; demolition of buildings at the end) in the calculation of full cost. For example, the initial costs start in the designing project, then surveying, construction of the buildings, after finishing the construction, other operational costs incur such as maintenance of the buildings. In some cases, demolition of the buildings completes the life cycle in this industry. Especially, calculation of the full cycle's cost at the beginning, starting from the cost of project design phase to the demolition of the building in the end; this process requires advanced technical skills.

In this context, one of the main advantages of LCC over the traditional cost systems is that, it estimates future costs, which were not addressed very well (Emblemsvag, 2003; Gluch & Baumann, 2004). Jan Emblemsvag who is one of the prominent scholar studies on LCC, reviews on the comparison of the traditional systems' past oriented and LCC's future oriented (estimated) time perspectives by reminding with the concept of 'cost management' with following sentences: *"Even worse, we try to control costs after they are incurred instead of eliminating them before they are committed. The result is a massively wasteful economy"*(Emblemsvag, 2003). The cost is sacrifice, measured by the money and there are many cost classifications according to different criteria in the cost and managerial accounting theory. A cost classification refers the 'according to calculation of the costs as full or partial (direct) cost will be taken' full cost is the most appropriate cost insight for the LCC(Davidson, Maher, Clyde, & Weil, 1981; Altug, 1996). In other words -and in a more practical sense- the full cost is referencing to LCC.

There are many LCC definitions found in the extant literature. Here, some of the basic definitions are presented:

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The life cycle cost of an item is the sum of all funds expended in support of the item from its conception and fabrication through its operation to the end of its useful life. Thus, the LCC of a physical asset begins when its acquisition is first considered, and ends when it is finally taken out of service for disposal. (Woodward, 1997)

The total costs that are incurred, or may be incurred, in all the stages of the product life cycle. (Emblemsvag, 2003)

LCC is a system that tracks and accumulates business function costs of the value chain attributable to each product from initial R&D to final customer service and support. (Horngren, Datar, Foster, Rajan, & Ittner, 2009)

As it was mentioned above; first implementations of LCC were in public procurements. In this context, another LCC definition from public administration point view, which defines the LCC with regard to public purchase process, is following:

LCC is purchasing process which considers the total cost of ownership of a commodity. In contrast to the traditional purchasing approach which relies on the initial acquisition cost, LCC also takes into account the cost of the using and disposing of particular commodities. (Coe, 1981)

As the definitions given above, LCC includes production costs which are; (a) research and development costs, (b) marketing, selling, distribution, and design costs, (c) and user costs. User costs have three dimensions: transaction costs, maintenance costs, and disposal costs respectively and they are much related to sustainability and waste management. Thus three dimensions of the user costs will be explained elaborately. Production costs, which mentioned here, are also considered by the conventional costing systems and they are very well known cost types in existing literature.

Transaction Costs

"Transactions costs are those costs associated with consummating a trade, over and above the trade itself. A simple example is the commission paid to an agent to sell a house" (Kolstad, 2000). In addition to the commissions payments, the property tax payments and expenses incurring when someone buys a house such as notary and registration for transferring of title deed can be assessed in transaction cost terms. This cost is the first cost component appears in user costs because when a person starts to buy something, transaction costs incur before acquiring it fully. Thus, transaction costs can be pointed as a prerequisite for having ownership of the goods.

Maintenance Costs

This cost is necessary to keep the product ready for useable and/or using it in an efficient way. Maintenance costs include direct labor, materials, fuel power, and equipment and purchased services. Maintenance costs can normally be broken down into smaller classifications such as:

- Regular planned maintenance;

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- Unplanned maintenance (responding to faults);
- Intermittent maintenance (for major life refurbishment).

A regular, planned, preventive maintenance policy reduces the downtime costs but resources are used in the form of maintenance expenditure. The 'run it until it breaks' approach, on the other hand, reduces the maintenance expenditures but increases the downtime loss (Woodward, 1997).

Disposal Costs

This cost type is incurred at the end of an asset's working life in disposing of asset/product. The disposal cost may occur in following forms: demolition, scrapping or selling the asset/product. This user cost component has crucial importance on protecting environment and sustainability.

Lastly, it should be also specified that user costs are subject to effects of changing economical conditions and technical developments, for example a technological development may require making some updates in a product which it incurs maintenance cost (Ross, 1960). Though acquisition cost term includes and recognizes the transaction costs in external financial reporting, it is evident that, the other two user costs have never been taking place in the external financial reporting or traditional costing approaches.

THE COMPARISON OF LIFE CYCLE COSTING WITH TRADITIONAL COSTING METHODS

While traditional costing systems emphasizes the calculation of costs that incurring during the production, however, the LCC has a broader perspective. Firstly, it takes into account the costs incurred after the production and secondly it does not only take into account the production costs but also sales, marketing, administrative, and user costs in terms of variety. The main differences between traditional costing systems and LCC are evaluated in Table 1.

As it is seen from the table there are significant differences between traditional costing methods and LCC. These differences may affect the unit product cost computations. Although, recognition of product development costs as period expenses does not bring serious difference from the point view of external financial reporting, it is important for a more precise determination in the matching of the product's total income and cost throughout its entire life.

Table 1. The comparison of life cycle costing with traditional costing methods. Source: Acar, 2005.

Traditional Costing Methods	Life Cycle Costing
The development costs of the product are recognized as period expenses.	The development costs of the product are recognized as component of product costs and capitalized.
In the computation of the unit product cost only production costs are considered.	In the computation of the unit product cost all the costs items linking to product are considered.
Time perspective of reporting is in periodical basis.	Time perspective of reporting is theentire life of product (life cycle).

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THE INTERRELATIONS OF LCC WITH WASTE MANAGEMENT AND SUSTAINABILITY

The sustainable development means business activity that produces the goods and services needed in the present without limiting the ability of future generations to meet their needs (Hilton, 2009). The green accounting, environmental and societal accounting, accounting for carbon emissions and LCC are the concepts that very related to sustainability and they can be merged in a broader term 'accounting for sustainability'.

The accounting for sustainability or sustainable development has emerged as a new accounting area concerning with environmental accounting and social accounting concepts, which sometimes this three terms are used interchangeable. In other words, the environmental and social accounting can be pointed out as initial attempts or movements towards the rising of broader term 'accounting for sustainable development'. The emerging of environmental accounting as an identifiable research area in the accounting discipline occurred in 1980s (Bebbington & Larrinaga, 2014).

In this section, the relationships of LCC among waste management and sustainability will be reviewed with the major previous studies in the literature. Reich (2005) examined the economic assessment of municipal waste management system using the combination of LCA and LCC through a case study. The study's results showed that economic methods (LCC financial and LCC environmental approaches) can provide useful tools to an evaluation of waste management systems.

Gluch & Baumann, (2004) assessed the usefulness of LCC oriented tools for environmental decision-making in building industry. They conclude the study with pros and cons of usefulness of LCC in environmental decision making as folow.

Kumaran, Ong, Tan, & Nee, (2001) studied the environmental life cycle cost analysis of products. They included the eco-costs into the total cost of the products. Eco-costs are defined as both the direct and indirect costs of the environmental impacts caused by the product in its entire life cycle and these

Table 2. Pros and Cons of LCC of Usefulness of LCC in Environmental decision making in building industry. Source: Gluch & Baumann, 2004.

Pros of LCC	Cons of LCC
Uses a familiar unit, money	Fails to handle decisions under uncertainty
Gives an indication on which aspects to consider	Fails to handle irreversible decisions
Limits the information flow by simplifying multi-attributed alternatives.	Neglects items without owner, such as the environment
May entail learning by participating in the calculation process	Over-simplifies environmental problems into a monetary dimension
Has a life cycleperspective	Underrates future environmental costs
	Suffers from poor availability and reliability of data
	Relies on many estimated variables due to the complexity of the building and building process
	Results are biased towards the decisionmaker's personal values
	May restrain learning if too mechanically used
	Is beset with conceptual confusion due to many similar LCC-oriented tools and inconsistent life cycles.

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costs can be also accepted in user cost definition. The aim of the research to design a hypothetical conceptual model including to a new category of costs which named eco-costs in addition to traditional product costs. They determined elements of eco-costs as follow:

- Cost of effluent control;
- Cost of effluent/waste treatment;
- Cost of waste disposal;
- Cost of implementation of EMS;
- Costs of eco-taxes;
- Costs of rehabilitation (in case of environmental accidents);
- Costs of energy; and
- Cost savings of recycling and reuse strategies.

LCC is costing system developed to compute product cost, and it was found very useful decision-making tool for the companies stressing the sustainability and environmental issues. The academic studies on sustainability and environment are interested in LCC as a useful tool. On the other hand, a pure or traditional LCC approach has been also criticized by some academics, because of taking mostly economical aspects into account and paying less attention to environmental aspects. Therefore, a differentiation appears about the LCC approach in the environmental context (Ristimaki, Saynajoki, Heinonen, & Junnila, 2013).There are three types of LCC implementations taking place in the existing waste management and sustainability literature in the environmental context, which uses the LCC together with Life Cycle Assessment (LAC). The types of LCC may vary from each other in terms of convergence and appropriateness of life cycle assessment. The first LCC is "conventional" and its relation with LAC only recognizes internal costs. The second LCC is "environmental" and its relation with LCA is very parallel besides internal costs, including external costs as well. The third LCC is "societal". It internalized the LAC thus, it can be asserted as the most appropriate LCC with LAC (Sanchez, Kromann, & Astrup, 2015).

This section ends with showing a theoretical design of product life cycle proposed by Emblemsvag (2003). In figure 2, each activity is in the manufacture and demanufacture process, considered precisely in the cost calculation LCC approach.

As it is seen from the figure, reuse or recycling starts from product take back at early stage to the material demanufacture stage. First factor of production is land and raw materials are taken from it. After they were processed, they are finally disposed again to land. But the figure elaborately shows that, before the products dispose, there are four opportunities to recycle or reuse them. By the way the resources will be consumed efficiently in terms of the needs of the humanity. LCC considers the every type of cost item incurring in this figure to calculate product cost in its lifespan.

CONCLUSION

This chapter aimed to reveal the foundations of life cycle costing and its relationship with sustainability. The future oriented time perspective of LCC prevents using more resources to fulfill the organizational objectives and provides efficiency and sustainability. Traditional costing systems are past or present oriented and they try to control the costs after committed. Eventually, this situation can result in waste

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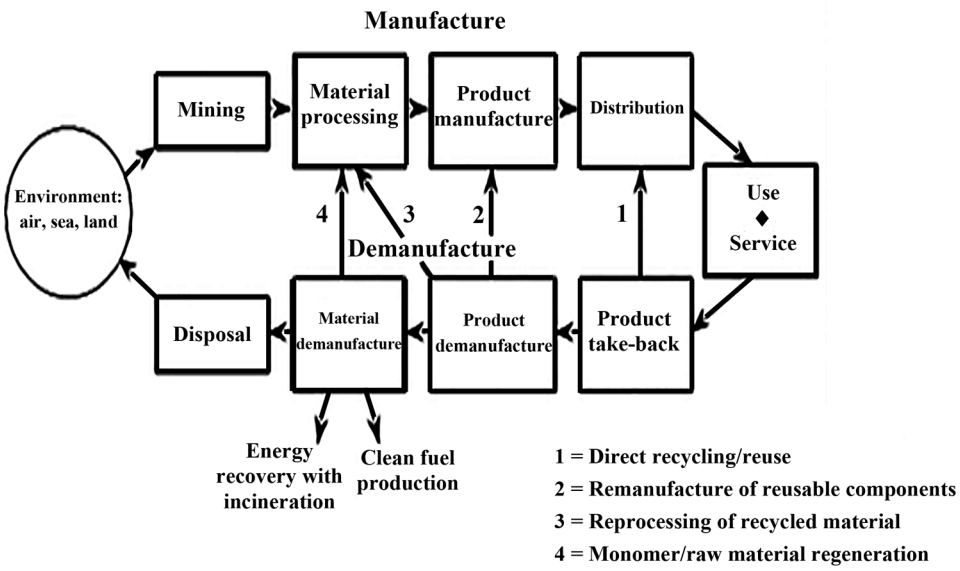
Figure 2. Product life cycle with activities
Source: Emblesvag, 2003



of the resources. LCC considers not only manufacturing costs but also user costs which incur after the sale of product. The aspect of LCC which considers the user costs is linked to sustainability, and among the user costs; maintenance and disposal costs have particular importance on sustainability. Current paradigm in businesses is not taking into account disposal costs unless a regulation requires. Therefore, they do not involve and take responsibility for negative impacts of the disposal of products on the environment. LCC recognizes the disposal costs within the total production cost and this aspect makes the LCC a very environmental costing system. With regard to using LCC by more businesses, we can draw a conclusion that widespread adoption and use of LCC will increase the awareness of the businesses about the disposal costs and potential impacts of the disposal of products on the environment.

Coe (1981) defines the rationale behind LCC as follows. While the initial acquisition cost of a product may be greater than a *competing product*, the total cost of ownership may be less because over its useful life it is less expensive to operate. With respect to Coe's definition on the rationale behind LCC, we can revise it by adding the sustainability perspective with replacing 'competing product' with 'ability and opportunity of the future generations to acquire and benefit from the similar products' in his definition. Because in his times, LCC was understood as a only superior cost management technique to compare two different products, therefore the definition of rationale emphasizing competing product. But when we adapt it into the conditions of the present time, we are altering the term of 'competing product' with 'sustainability'. In terms of the sustainability, both in purchases of products and in the manufacturing, the companies take maintenance and disposal costs into considerations. If a product's maintenance cost is very high and its dispose causes some environmental problems though it has very low acquisition cost and has benefit for its present users, that product must not be produced for providing the sustainability. The use of LCC in the product purchase processes and in the manufacturing will be helpful to protect the environment for future generations.

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KEY TERMS AND DEFINITIONS

Life Cycle Assessment (LCA): Life cycle assessment (LCA) is an established way of measuring total environmental effects of products and services. It considers the impact of a product or service on the environment.

Life Cycle Costing (LCC): The total costs incurred or may be incurred in the all the stages of product life cycle. The main difference between LCC and traditional cost systems is LCC also considers user costs in the cost calculations.

Production Costs: It is also known as manufacturing costs. They are direct material cost, direct labor cost, indirect material and indirect labor costs which the combination of these two indirect costs is called as overhead cost.

Sustainability: Business activity that produces the goods and services needed in the present without limiting the ability of future generations to meet their needs.

Traditional Costing: It is also referred as conventional costing and basically consists of two main systems, which they are job-order costing and process costing. In job-order costing; costs are collected for each unit produced and in process costing system; costs are accumulated in a department or production process. Both systems' ultimate objective is to find out total and unit production cost and they do not consider user costs.

User Costs: The term 'user costs' is used for the costs which are incurred after sale such as; transaction, maintenance and disposal costs. Life cycle costing considers the user costs in the cost calculations and especially disposal cost is much related to sustainability.

Waste Management: A set of activities that include collection, treatment and disposal of waste. It provides sustainability in environment and economy.

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Chapter 52
Advancement in Bioremediation of Pharmaceutical and Personal Care Products

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ABSTRACT

Pharmaceutical and personal care products (PPCPs) are regularly used by human being for their day to day life. These products contains various chemical compounds which are regularly added in our surface and ground water sources either through untreated or partially treated domestic and industrial wastes or through agricultural runoffs etc. These are present at the concentration of µg liter-1, and at such low concentration also these have shown harmful affect to living being. A lot of studies have been carried out for studying their effects on animal biodiversity, which can directly or indirectly affect human being also. So their removal from waste water is essential. Various technologies are being tested for removing these compounds from polluted water; bioremediation is also one of them. Present chapter will briefly give the description of various PPCPs present in waste water, their impact and removal technologies available for their removal with special emphasis on bio remediation.

INTRODUCTION

Water is one of the prime element and necessary for every living being on earth. Two third of the earth is covered by water and major fraction of our body is also made up of water. Further in the body, it regulates the activities of fluids, tissues, cells, lymph, blood and glandular secretions. So its contamination can easily affect our metabolism as well as that of all the living creatures. Fresh water present in the earth's surface is put to multifarious uses. It is used for drinking, domestic and municipal uses, agricultural irrigation, industries, navigation, recreation, etc. The used water becomes contaminated and is called waste water. Water passing through industries, agricultural lands and the urban settlements gets spoiled up and is rendered harmful to plants, animals and human being. This water gets loaded

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with organic and inorganic chemicals, pathogenic and non- pathogenic organisms including viruses and cysts. Usually these waters do not remain fit for human consumption and for life of plants and animals as well. There are different types of pollutants polluting the water e.g. Sewage and fertilizers, chlorinated hydrocarbons and pesticides, heavy metals, oil and petroleum products, radioactive substances, plastics, pharmaceutical and personal care products (PPCPs) etc. Role of PPCPs as environmental pollutant is recent in comparison to other pollutants.

Now the question is what are pharmaceutical and personal care products? Different types of medications both for human as well as for livestock, cosmetic products, and antibiotics for agriculture etc are being used. Excess of these flush out through domestic effluents and become a part of water or sediments/ soil if not treated properly, known as PPCPs. Places where the waste water from hospitals, residential areas and industries are directly released into surface water without pretreatment, chances of presence of PPCPs becomes more prominent. As these group of compounds are still emerging therefore also known as a subgroup of "contaminants of emerging concern," as well as "emerging contaminants" or "trace organic compounds" (Sedlak et. al., 2000). Contaminants of emerging concern as a whole are compounds that are not commonly monitored due to their "emerging" nature. A wide range of PPCPs may be present in wastewater and the environment receiving it (Daughton & Ternes, 1999; Kolpin et. al., 2002). These compounds are mostly less biodegradable, high persistent in the environment, poorly removed in wastewater treatment plants (WWTPs), and often detected in the micro to nano grams per liter concentrations. Leaching of these compounds in groundwater is the potential risk as due to its usage for drinking purposes in most o the areas. The present chapter is providing different aspects of PPCPs such as type of PPCPs present in environment, their impacts on environment and available removal technologies for PPCPs from waste water with the emphasis on bioremediation.

BACKGROUND

Bioremediation was first used by the Romans, at around 600 BC, to clean their waste water. This process was officially invented in the 1960's by George Robinson. He had experimented with microbes inside of polluted glass jars. In the 1970s, Ananda Chakrabarty and his colleagues at General Electric discovered a strain of bacteria that is able to degrade some components in crude oil. He obtained this strain by isolating a Pseudomonas from a soil filled with. First commercial in situ bioremediation system was installed in 1972 to cleanup a Sun Oil pipeline spill in Ambler, Pennsylvania. The Exxon Valdez oil spill in 1989 in Prince William Sound, Alaska, was the genesis of global attention to this process. Importance of bioremediation is that it can completely destroy contaminants, converting them to carbon dioxide, water, and new cell mass. So this can be a good technique for removal of PPCPs from waste water.

Now days many PPCPs are detected at wide concentration ranges in a variety of environmental samples (Halling-Sørensen et al., 1998, Snyder et al., 2003) and in animal tissues, human blood, and breast milk samples (Rimkus et al., 1999; Adolfsson-Erici et al., 2002). Study was conducted by researchers at the U.S. Geological Survey in 1999 and 2000 to provide baseline information on the occurrences of pharmaceuticals, hormones and other wastewater contaminants in water resources. Researchers found organic wastewater contaminants (OWCs) in 80% of the streams e.g. coprostanol (a fecal steroid), cholesterol (a plant and animal steroid), tridosan (an antimicrobial disinfectant), 4-nonylphenol (a non-ionic detergent metabolite) and caffeine as the most frequently detected compounds (Nakada, 2007). The highest concentration reported was 40 ng/l for meprobamate (Benotti et al., 2009). Several pharmaceuticals were

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found in tap water at different concentrations ranging from nanograms to low micrograms per litre in several countries in Europe, including Germany, the Netherlands and Italy (Huerta-Fontela et al, 2011). 20 different drugs were found in rivers and streams of Germany having water coming out of sewage treatment plants (STP). Some of them were lipid regulator bezafibrate, antiphlogistics diclofenac, ibuprofen, naproxen, metabolites like clofibric acid, salicylic acid, betablocker metroprolol, propranolol, antiepileptic carbamazepine etc (Ternes, 1998). Two separate studies in Germany (Reddersen et al., 2002; Zühlke et al., 2004) found phenazone and propylphenazone (an analgesic and an antipyretic drug, respectively) in Berlin drinking-water, with the highest concentration being 400 ng/l for phenazone. This high value was largely attributed to groundwater, used as a drinking-water source, contaminated with sewage (Jones et al., 2005).

In the Netherlands, traces of antibiotics, antiepileptic and beta blockers were detected in the drinking-water supply at concentrations below 100 ng/l, with most concentrations below 50 ng/l (Mons et al., 2003). Pain reliever ibuprofen was detected in the influents of several Switzerland WWTPs at concentration levels of 1 to 3.3 μg L^{-1} (Buser et al., 1999). As medical substances are developed with the intention of performing some sort of biological function, they have a tendency to bioaccumulate and induce effects in aquatic and terrestrial ecosystems (Halling-Sorensen et al., 1998). These compounds can easily come out from water treatment plants in original or modified forms, so their removal techniques from waste or drinking water need to be modified.

PPCP: SOURCES IN WASTE WATER, IMPACT ON ENVIRONMENT AND APPROACHES FOR REMOVAL

Sources of PPCPs in Waste Water

Millions of dollars are spent each year on PPCPs, many of these products are never used or only partially used and end up thrown out in the trash or dumped down the drain (Daughton & Ternes, 1999; Meador et al., 2016). The pervasive use of biocides in consumer products to improve hygiene and destroy bacteria creates another set of chemical contaminants that pass readily into water supplies as they are usually associated with cleaning and are dumped directly into household or industrial drains. These can affect human health due to their potential biomagnifications through the food chain in aquatic organisms (Crane et al., 2006). Generally the water is examined in terms of conventional physico-chemical parameters i.e., major nutrients, bulk organic matter in terms of BOD, COD, TOC etc. But with development, problems related to PPCPs have increased as these are harmful even at ng/L levels. The tendency for these compounds to persist or be only partially degraded during treatment or to bypass treatment altogether via sewage overflows will, therefore, contribute to their load in receiving waters, many of which serve as recreational and drinking water sources. These include PAHs, PCBs, pesticides, detergent residues (alkylphenols), plasticisers (DEHP), linear alkylbenzene sulfonates (LASs), natural and synthetic estrogens, poly brominated diphenyl ethers (PBDEs), disinfection by-products and others (Figure 1, Figure 2, and Figure 3). High percentages of many pharmaceuticals can be excreted from the body unmetabolized and enter wastewater as biologically active substances (Buhner, 2002) e.g. 90% of the drug, propofol found in anesthesia, is excreted un-metabolized (Kummerer, 2001). Aquaculture wastes are also the source of antibiotics in the waste water as it contains fish feed, dead fish, faecal matter, egg shells and chemicals used for treatment of fishes (Antibiotic overflow. Down to Earth, 1-15 August, 2016).

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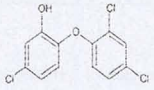
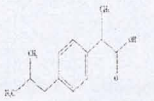
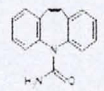
Figure 1. Some important PPCPs reported in waste water throughout the world

S.No.	PPCPs	Structural formula	Log K_{ow}	Nature of solubility	Usage	Adverse affects on bioaccumulation in water or sediments	References
1	Triclosan		2.39 - 4.54	hydrophobic	bactericide in personal care products such as toothpaste, shampoos, and soaps as a stabilizing agent in a multitude of detergents and cosmetics	skin irritation, allergy susceptibility, ecological toxicity to the aquatic and terrestrial environment (effect on earth worms (Eisenia fetida) and on Japanese medaka fish	Adolfsson-Erici et al., 2012 Coogan et al., 2007 Lin et al., 2010 Nassef et al., 2010 Chen et al, 2012 Bhargava & Leonard, 1996
2	Ibuprofen		0.82 - 3.40	hydrophobic	Analgesic, anti-inflammatory , cyclooxygenase inhibitor	Risk to aquatic environment with chronic toxic effect (such as inhibited polyp regeneration and reduced reproduction)	Stumpf et al. (1999)
3	Carbamazepine		1.51	hydrophobic	anticonvulsant drug, and also as a specific analgesic for trigeminal neuralgia	Immune disorder	Tina et al., 2009 Deniz et al., 2000

Impact of PPCPs on Environment

PPCPs potentially impact both the ecology and environment as these compounds may be active at very low concentrations. These are wide spread and released in large quantities in water bodies through waste water. In an aquatic system, the residence time of a pollutant and its distribution between water, sediments, and biota depends on its capacity to bound to suspended particles and accumulate in sediments. Thus, the affinity of hydrophobic organic compounds for biotic and abiotic phases is an important determinant of both the rate of a detoxification of water system and its response time to changing loadings. Polarity of these compounds determines their fate in potential matrices of environment. Non polar compounds generally more attracted towards soil colloids and sediments as also accumulate in biota (Heberer, 2002), while the polar PPCPs are more labile in the environment.

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Figure 2. Some important PPCPs reported in waste water throughout the world

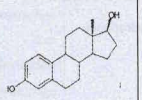
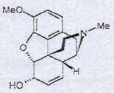
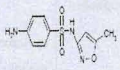
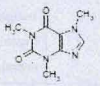
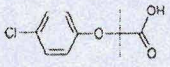
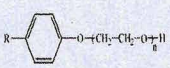
4	Diclofenac		1.12	hydrophobic	anti-inflammatory	Risk to aquatic environment with chronic toxic effect (such as inhibited polyp regeneration and reduced reproduction)	Stumpf et al. (1999), Heberer et al. (2001), Heberer et al. (2002) Buser et al., 1998a
5	Estradiol		2.89	hydrophobic	Hormone	Cancer, endometriosis, birth defects etc.	Baronti et al., 2000, Johnson et al. (2000)
6	Codeine		1.14	hydrophobic	Analgesic		Thai et al., 2016
7	Sulfamethoxazole		0.79	hydrophobic	Antibiotic	alterations to the balance of naturally-occurring microorganisms, the nitrogen cycle, genetic mutations, and aquatic toxicity.	Laville et al., 2004
8	Caffeine		-0.07	hydrophobic	Stimulant	Affect respiration and function of heterotrophic microbial biofilms present in aquatic environment so impact the	Potera, 2012

Figure 3. Some important PPCPs reported in waste water throughout the world

						ecological environment of water sources	
9	Clofibric acid		2.88	hydrophobic	Lipid regulator		Buser, et al., 1998b.
10	Alkylphenol polyethoxylates		>4.5		Surfactant	Nonionic surfactants added in detergents	La Guardia et al., 2001

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These compounds can affect human health due to their potential biomagnifications through the food chain in aquatic organisms (Crane et al, 2006). These are found to be associated with various health hazards as presence of PPCPs in water can potentially leads to carcinogenic, reproductive developmental effects by interfering with various hormonal pathways, disruption in general metabolism, producing acute toxicity, immune system effects (Kotz et al., 2012). These compounds often exert their effects at relatively low concentrations and through specific mode of action. Reduction of vulture population by consuming declofenac contaminated carcasses (Oaks et al., 2004), feminization of fish due to ethinylestradiol contaminated water obtained after sewage treatment are the examples of effect of PPCPs on living creatures (Shanmugam et al., 2014, Desbrow et al., 1998, Larsson et al., 1999, Thorpe et al., 2003, Kidd et al., 2007). Most pharmaceuticals are non-bioaccumulative and eliminated from human or animal body after administration. After passing through body metabolism, hydrophilic functions generally added in the molecule for their successful excretion with urine/ feces (Katzung, 2001). These compounds often exert their effects at relatively low concentrations and through specific mode of action.

PPCPs are used as antibacterial agents, these when released in waterways and sediments allowed bacterial flora to develop antibacterial resistance to those particular agents. The development of resistance to antimicrobial agents makes treatment of infections very difficult to cure; therefore this issue is an important consideration for the treatment of wastewater, especially that which is discharged from hospitals, veterinary clinics, or other locations where large amounts of antibiotics are used. Interplay of bacteria with antibiotics present in waste water make them resistant and increases their populations in waste water. Quaternary ammonium compounds (QACs) are cationic microbial compounds that are important ingredients in disinfectants, which are used in hospitals as well as households. They are known to inhibit the proper functioning of aquatic microorganisms, and they have a low biodegradability. Inhibitory effects have also been found against denitrifying bacteria in very low concentrations of QACs. In India, high resistance is observed in treatment of prevalent infectious diseases like pneumonia, tuberculosis, urinary tract infection, and infection of bloodstream and gut ('Hatching Superbugs', Down to earth, 1-15 August 2014).

The tendency for these compounds to persist or be only partially degraded during treatment or to bypass treatment altogether via sewage overflows will, therefore, contribute to their load in receiving waters, many of which serve as recreational and drinking water sources.

Some Advanced PPCP Removal Technologies

PPCPs include a wide range of compounds with different chemical and physical proprieties that affect their removal. Due to the low PPCP concentrations reported in wastewaters (ppb or ppt) and their complex chemical structure, common technologies used in sewage and drinking water treatment plants may not be efficient enough to accomplish their complete removal. Various bench- scale studies have been conducted for removal of PPCPs from polluted water. Coagulation, lime softening, activated carbon adsorption, biofiltration, chlorination, membrane bioreactor, photocatalytic treatment, ultraviolet photodegradation, ozonationation and advanced oxidation (AOP) are some of the methods tried in batch scale studies for removal of PPCPs from waste water. Information about physico-chemical characteristics such as acidity, lipophilicity, volatility and sorption potential is a useful tool to understand the different removal patterns observed. In the removal efficiency of biological treatment processes for PPCPs is related to hydrophobicity and to consequent adsorption in activated sludge, whereas more polar compounds are

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released in the effluent (Heidler & Halden, 2008). In the conventional physical-chemical processes, surface water conventional treatments (i.e. coagulation, sand filtration, softening) frequently used as tertiary wastewater treatments, and are not efficient for the complete removal of organic micropollutants. Particularly, the use of aluminium sulphate, ferric chloride or lime removes less than 20% of many EDCs and PPCPs (Westerhoff et al., 2005).

Advanced treatments with high removal efficiencies of emerging contaminants are adsorption on activated carbon, nanofiltration (NF) and reverse osmosis (RO) (Snyder et al., 2007). However, the NF/RO processes produce a large amount of concentrate whose treatment and disposal is very expensive, therefore, their application is less suitable in inland areas. The typical doses used in disinfection by UV irradiation (< 40 mJ/cm^2) are unable to remove EDCs and PPCPs (removal efficiencies are often less of 20%) (Rosario-Ortiz et al., 2010). Ozone and chlorine oxidation are selective for the chemical structure and functional groups of PPCPs and EDCs, whose removal range between 90% with a prominent efficiency of ozonation (Westerhoff et al., 2005). However, chlorination and ozonation are known to lead to the formation of by-products that account for largely unidentified compounds to date. This issue raises concerns regarding their potential impact on the environment and human health. The AOPs, including ozonation which produces OH radicals in wastewater application, are able to degrade a wide range of emerging contaminants. Membrane processes are an effective mean to reduce the concentrations of several EDCs and PPCPs from drinking water and wastewater. The removal rate is related to membrane characteristics and to molecular properties of particular contaminant.

The performance of activated carbon depends on the properties of the activated carbon sorbent (surface area, pore size distribution, surface charge, oxygen content) and on the properties of the solute (shape, size, charge and hydrophobicity). Hydrophobic interactions are the dominant mechanisms of removal for most organic compounds in activated carbon adsorption systems. However, ion exchange interactions can result in removal of polar solutes (Crittenden et al., 1999; Matsumura et al., 1985; Youssef et al., 1982). As a result of the hydrophobic interactions, activated carbon efficiently removes most non-polar organic compounds. The ability of activated carbon to remove most polar compounds will depend upon the strength of the polar interactions. Tanghe & Verstraete (2001) showed that the sorption capacity of crushed granular activated carbon for nonyl phenol (NP) was at least 100 mg/g. Based on the results of their static adsorption tests, they concluded that a full-scale GAC filter unit would be adequate to remove environmentally relevant NP concentrations of 10 µg/L. Many other studies have been carried out for removing organic pollutants from contaminated water (Knappe et al, 1999; Rodriguez et al, 2016).

Biological activated carbon (BAC) consists of a pre-ozonation followed by a GAC filter which supports the growth of bacteria. This technology has been used for drinking water treatment and has proven to be able to significantly remove natural organic matter, ozonation by-products, disinfection by-products precursors as well as odour and taste compounds. Recently, it has been reported that BAC systems are very effective to remove EDCs and PPCPs (Gerrity et al., 2011; Reungoat et al., 2011). However, more studies are needed for a better evaluation of BAC removal efficiencies taking into account several operating conditions through full-scale applications. During IBAC treatment, the process of microorganisms immobilizing is of great complexity, which is not only related to various acting forces, but also involves microorganism growth as well as the ability for producing extracellular and external appendages (Collins et al., 2003). Although there is a relatively high repulsive force during the process when the bacteria approaching to the activated carbon, the bacteria will ultimately contact with the activated carbon under the bridging effect of EPSs (Takeuchi et al., 1996). There are various ways to immobilize microorgan-

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isms, and any method with a limitation for free flowing of microorganisms can be used to produce and immobilize microorganisms, an ideal and universal application way for immobilizing microorganisms is still not available (Jin et al., 2013).

MICROBIAL POTENTIAL IN PPCP BIOREMEDIATION

Bioremediation is the technology of using biological agents particularly microorganisms, to remove toxic pollutants from the environment, particularly from soil and water. In case of bacteria, it can grow in both the aerobic as well as anaerobic conditions. Under aerobic conditions, bacteria use molecular oxygen as their terminal electron acceptor and in anaerobic conditions other compounds such as carbon dioxide is used (Figure 4).

This is a continuous method as it cannot be turned on or off because it is a living system, so constant source of nutrients are required for microbes. Aerobic bacteria is suitable for degrading organic compounds for the range of 50 to 4000 mg/l with some exception up to lower range while anaerobic bacteria can work in the range of 4000 to 50000 mg/l concentration (Nyer, 1992). It was also found that organic contaminants are mineralized and recycled more efficiently when a diverse microbial population is present (Torsvik & Øvreås, 2002). However the relationship between microbial diversity and biodegradation is not linear as many metabolic processes are carried out by a consortium rather than individual microbial species (Jjemba, 2004). Mixed microbial communities have the most powerful biodegradable potential because the genetic information of more than one organism is necessary to degrade the complex mixture of organic compounds present in contaminated sites.

Pollutants are decomposed to non-toxic substances through microbial metabolism (Pelczar, et al., 1993). In-general biodegradation process is based on two processes: growth and co-metabolism (Figure 5).

Microbes use naturally occurring as well as synthetic chemicals for growth by using these molecules as source of carbon, nitrogen, phosphorus, sulfur, energy and any other elements needed by the cells (Riser-Roberts, 1998). For all these processes, optimum conditions of pH, temperature, nutrient concentrations and target organic concentration below toxic limit for microbes should be maintained (Figure 6). The target organic pollutant should be compatible with microbes. Initial intracellular attack of PPCPs is an enzymatic reaction. These are oxidation reactions catalyzed by oxygenases and peroxidases. Oxygen

Figure 4. Electron exchange during bioremediation by microbial cell

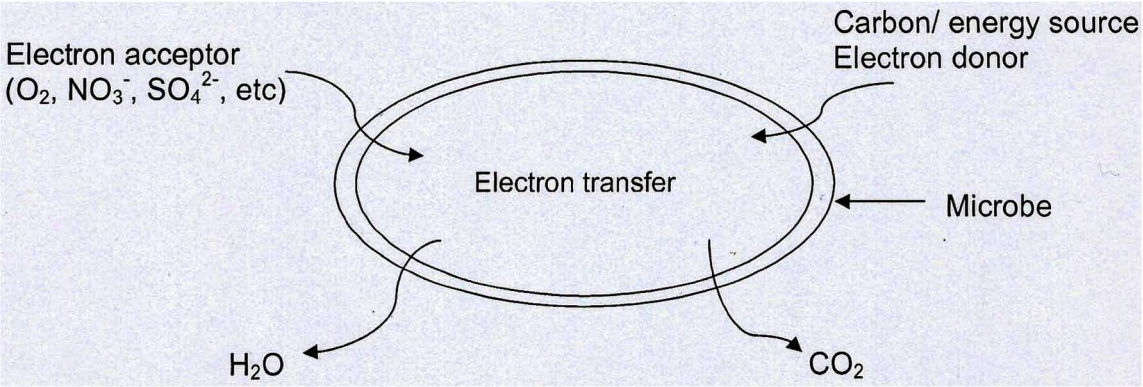

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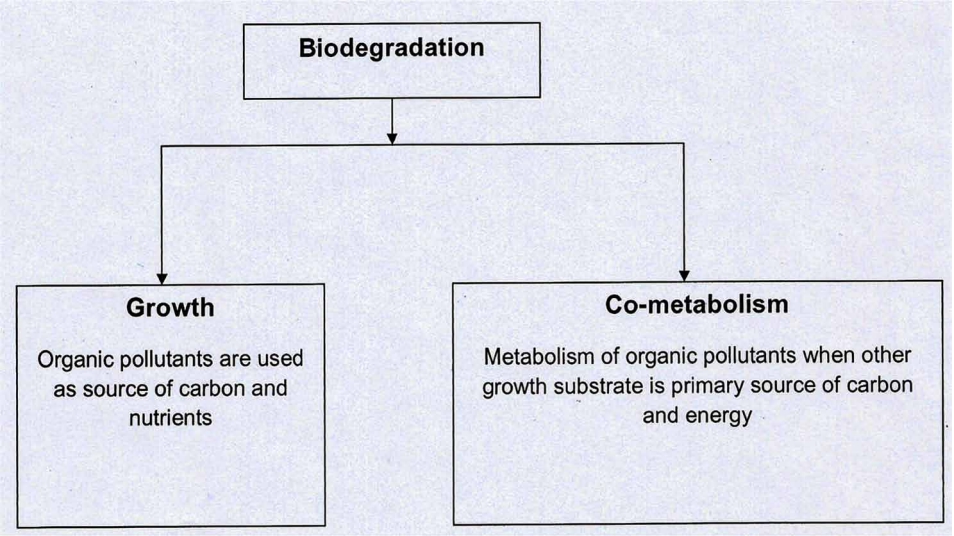
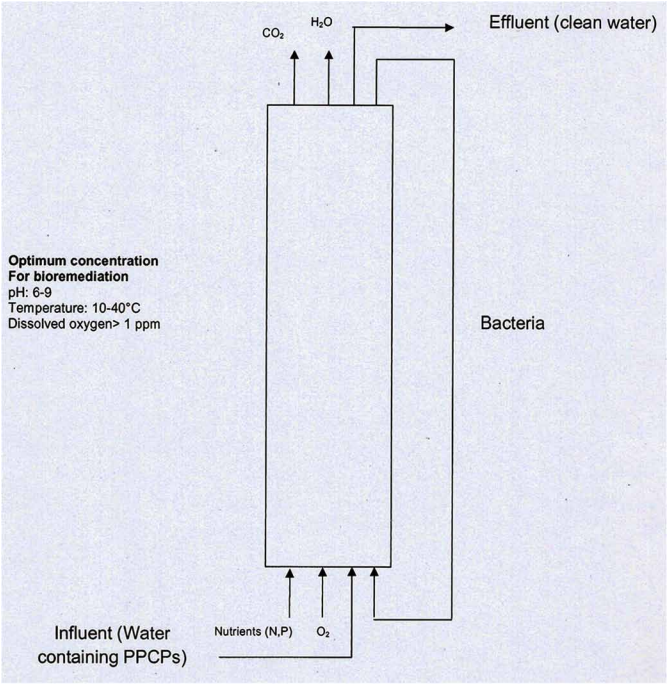
Figure 5. Biodegradation process in case of microbes



molecule is also required for respiration process. Peripheral degradation process converts organic pollutants into the intermediates of converts' organic pollutants into intermediates of tri-carboxylic acid (TCA) cycle, then biosynthesis of cell biomass takes place. In case of cometabolism, organic pollutants are transformed or degraded by microbes but they are unable to use the substrate as a source of energy or of one of its constituent elements.

Figure 6. Bioremediation of PPCPs contaminated water



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In an aquatic system, the residence time of a pollutant and its distribution between water, sediments, and biota depends on its capacity to bound to suspended particles and accumulate in sediments. Thus, the affinity of hydrophobic organic compounds for biotic and abiotic phases is an important determinant of both the rate of a detoxification of water system and its response time to changing loadings. Polarity of these compounds determines their fate in potential matrices of environment. Non polar compounds generally more attracted towards soil colloids and sediments as also accumulate in biota (Heberer, 2002), while the polar PPCPs are more labile in the environment. Microbial degradation of any compound starts with low molecular weight compounds and proceeds to higher molecular weight compounds. Degradation of molecules proceeds through introduction of molecular oxygen into the structure of target molecule. Normal paraffin proceeds via terminal oxidation and subsequently β oxidation to yield C-3 units and carboxylic acid. In case of aromatic hydrocarbons, ring cleavage required de-hydroxylation reaction, introduction of both the oxygen atoms of the molecule in the aromatic ring and subsequent formation of cis- diol. Small molecules generate CO_2 and water after degradation but aromatic hydrocarbon yields phenolics and benzoic acid intermediates, which are then readily metabolized by β-oxidation and incorporated in TCA cycle with the uptake of some ATP (Figure 7) (Fritsche & Holrichter, 2005).

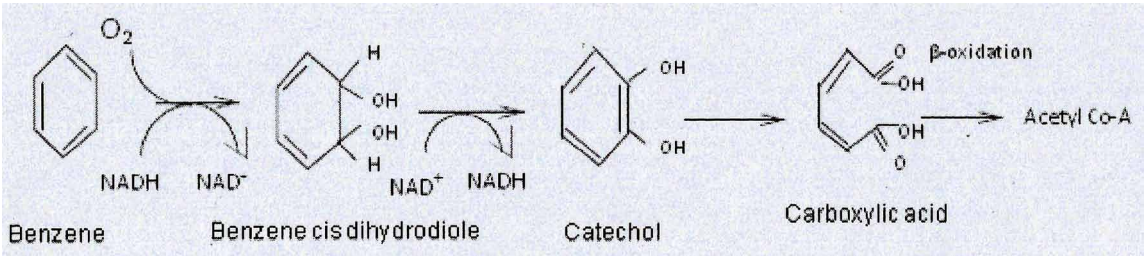
The distribution of non-polar organic compounds between water and natural solids (e.g., soils, sediments and suspended particles) or organisms, can be viewed in many cases as a partitioning process between the aqueous phase and the bulk organic matter present in natural solids or in biota (Schwarzenbach et al., 2004). Fate of their attachment to different environmental matrices can be determined through analyzing log of K_{ow} value of PPCPs. The octanol/water partition coefficient (K_{ow}) is defined as the ratio of a chemical's concentration in the octanol phase (C_o) to its concentration in the aqueous phase (C_{aq}) of a two-phase octanol/water system (Equation 1).

$$K_{aw} = \frac{C_O}{C_{aq}} \tag{1}$$

Values of K_{ow} represent the tendency of the chemical to partition itself between an organic phase (e.g., a fish, a soil) and an aqueous phase. Biological activity of selected organic pollutant can be correlated with log K_{ow} through the equation (2)

$$BR = a + b\log K_{ow} \tag{2}$$

Figure 7. Biodegradation of benzene to carboxylic acid



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BR may be one of the large numbers of reactions of organisms after introduction of organic pollutants, a and b are the constants for particular system. When organic pollutants come in contact with the cell, then partitioning of the compound takes place from aqueous like phase to organic like phase, which is controlled by the partition coefficient of that compound. Hydrophobic compounds tend to accumulate in organisms because they are metabolized slowly and are effectively stores in tissues (Sangster J., 1997).

Compounds which are resistant to microbial attack can be rendered biodegradable by chemical treatment to yield low molecular weight carboxylic acid (Garg et al., 1994). Mode of degradation of compounds by microorganisms depends upon the nature of chain length of hydrocarbons along with its stereochemistry as well as species of microorganisms. Aliphatic organic compounds are more readily attacked than aromatic compounds by microbes. These are potential carbon and energy source for microbes so these are biodegradable (Bartha & Atlas, 1977). *Pseudomonads* (aerobic gram negative rods) were found to have immense potential of degrading organic compounds due to their catabolic enzymes along with their capability of metabolic regulations (Haughtan & Shanley, 1994). *Rhodococci* and *Corynaform* bacteria have also shown degradation capacity of organic compounds. Some bacteria under this group generate mycolic acid at the external surface of the cells which are long chain alcoholic and fatty acids, esterified to peptidoglycans of the cell wall. So these can work against the lipophilic/ hydrophobic organic compounds. Pharmaceutical and Personal care products also occur either as aliphatic or aromatic moieties with either polar or nonpolar nature. But major differences with other general organic compounds are that PPCPs are mainly designed to harm microorganisms responsible for infections. So selections of microbes from nature, which are not harmful, are essential.

Adsorption processes using activated carbons are widely used to remove pollutants from wastewaters and occurrence of large numbers of bacteria on GAC filters is well documented (American Water Works Association. 1981, Eberhardt, 1976). The microorganisms attached to the GAC then convert the biodegradable portion to biomass, carbon dioxide, and waste products before that material can occupy adsorption sites on the GAC. Biological Activated Carbon (BAC) process is developed on the basis of activated carbon technology, which uses the synergistic effect of adsorption on activated carbon and biodegradation to purify raw water. Activated carbon has a high specific surface area and a highly developed pore structure, so it is characterized by its great effect on absorbing dissolved oxygen and organics in raw water. For BAC technology, activated carbon is used as a carrier, by accumulating or artificially immobilizing microorganisms under proper temperature and nutrition conditions. The microorganisms will reproduce on the surface of the activated carbon and finally form BAC, which can exert the adsorption and biodegradable roles simultaneously (Qing & Jihua, 2006). Activated carbon is suited as supporting material by its large adsorptive surface (Andrew & Tien, 1981; Shimp & Pfaender, 1982). Microbes can take part in the degradation of harmful aromatic compounds as these are the growth substrate for microorganisms. The crucial step in their degradation is overcoming the resonance energy that stabilizes the ring structure (Fuchs et al., 2011). Inoculation and maintenance of bacteria with special degradation capabilities resulted in a lower consumption of GAC and thus to extended shelf life (Stucki & Thuer, 1994). Microorganisms which can carry out biodegradation in different environments are identified as active members of microbial consortiums. These microorganisms include: *Acinethobacter, Actinobacter, Acaligenes, Arthrobacter, Bacillins, Berijerinckia, Flavobacterium, Methylosinus, Mycrobacterium, Mycococcus, Nitrosomonas, Nocardia, Penicillium, Phanerochaete, Pseudomonas, Rhizoctomia, Serratio, Trametes* and *Xanthofacter* (Singh et al., 2014). Species of *Candida* and *Pseudomonas* have been used for their immobilization on activated carbon. Phenol adsorbed on carbon surface was 90% degraded by microbes (Ehrhardt & Rehm, 1985).

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The relationship between the activated carbon and contaminants is simply the effect of adsorption on activated carbon, and the reaction depends on the properties of the activated carbon and contaminants. Meanwhile, the activated carbon can absorb dissolved oxygen (DO) and microorganisms which were adsorbed on the surface of activated carbon, feed on DO will biodegrade contaminants. The activated carbon used in BAC process, should be highly developed in the pore structure, especially for the filter pores. The basic principle of immobilization biological activated carbon (IBAC) is screening and acclimation dominant bio-community from nature, followed by immobilizing the community on activated carbon, to enhance the efficiency and rate of degradation. Meanwhile, dominant biocommunity should be nonpathogenic and has strong antioxidant capacity and enzyme activity which enable the growing and reproducing under poor nutrition environment. Therefore, the effect of biodegradation after activated carbon adsorption saturation is highly improved by Immobilization BAC (Scholz & Martin, 1997; Wang & Luo, 2003). Due to large surface area available for degradation of pollutants by microbe (Bancroft et al., 1983), biological activated carbon can be a better approach in combination with other conventional or advanced methods to solve the problem of PPCPs present in different matrices of environment.

FUTURE RESEARCH DIRECTIONS

PPCPs are a group of diverse chemicals consumed as drugs, cosmetics, as well as in agriculture etc. These compounds can easily become a part of fresh water resources either through agricultural runoff or through the addition of untreated or partially treated sewage water containing the waste water of household and industries. Various technologies are available for the treatment of waste water, and a lot of work on removal of PPCPs from waste water is also going on. Still in many areas of the world, even the preliminary screening of PPCPs in water resources is lacking, so the first requirement is to assess the concentration of these compounds in water resources (both the surface and ground water) used for the purpose of drinking. After getting the exact concentration of these compounds, the removal technologies should be used accordingly.

So, future area of research on PPCPs removal may be classified in two parts. First will be their assessment and quantification in existing water resources and their possible point sources and then the development of suitable removal technology for PPCPs based on their concentration in the area. As these compounds are harmful at very low concentration and varies in their physico-chemical properties, so no single removal technologies will be able to solve the problem. Combination of existing removal technologies with bioremediation process will be helpful for removal of these harmful compounds from water. In Bioremediation, microbes use these compounds as source of energy or as secondary substrate. So selection of suitable microbes for biodegradation of PPCP compounds present in waste water will be required. This will be helpful for utilization of microbes for bioremediation directly in the sludge or in the form of biological activated carbon.

CONCLUSION

Chemicals used as PPCPs are being released into the environment in extremely large quantities on a regular basis. Exact effect of these compounds on human system is not yet completely known, still based on some studies their harmful effects cannot be ignored. These compounds are tremendously harmful in

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respect to environmental and human health at very low concentration even at microgram level, therefore, effective and efficient removal technologies need to be developed to treat the contaminated effluents in order solve this dreaded problems. As bioremediation using microbes is based on biodegradation of pollutants and these living cells of microorganisms are able to degrade organic compounds at very low concentration, this could be play important role in this respect as an ecofriendly efficient technology for removing PPCPs from waste water.

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KEY TERMS AND DEFINITIONS

Activated Carbon: It is a highly porous carbonaceous substances composed by carbon atoms having potential adsorption properties.

Biodegradation: Degradation of materials using biological systems e.g. enzymes generated by microbes etc.

Bio-Magnification: Accumulation of any toxic substance in living cells.

Bioremediation: Removal of pollutants using biological materials e.g. microbes, plants etc.

Hydrophilic: Material which attract water.

Hydrophobic: Material which repel water.

Partition Coefficient: Ratio of distribution of any compound between two immiscible mediums.

Water Partition Coefficient: It refers to ratio of concentrations of a compound in a mixture of two immiscible phases at equilibrium.

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Chapter 53
Treatment of Landfill Leachate by Anammox Process

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ABSTRACT

In most cases, the anammox process is used for nitrogen removal from reject water coming from dewatering of digested sludge. However, there are more industrial streams suitable for treatment by partial nitritation/anammox process. The landfill leachate may be a good example of such wastewater. Generally, landfilling is the most used solution for treatment of urban solid wastes. The problem with landfill leachate production and management is one of the most important issues associated with the sanitary landfills. These streams are highly contaminated wastewater with a complex mixture of organic and inorganic compounds and characterized by a high ammonia content and low biodegradable organic fraction matter. The objective of this chapter is the short characteristic of landfill leachate and a short review of its treatment methods with special focus on nitrogen removal by partial nitritation/anammox process.

INTRODUCTION

In Europe, the total amount of landfilled municipal waste has been diminishing, due to European Commission Council Directive (Council Directive 1999/31/EC). Nevertheless, landfilling of the municipal waste is still a common practice in the waste management system in some European countries and the rest of the world because it is the simplest and cheapest method of waste disposal. Even discontinuation of landfilling in the EU will not instantaneously eliminate the problem related to landfill leachates because even closed and capped landfills will produce these wastewater streams. Such waste management option has several negative impacts on the environment. The major potential environmental impact related to landfill leachate generation is pollution of groundwater and surface water (Kjeldsen et al., 2002). The problem with landfill leachate production and management is one of the most important issues associated

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with the sanitary landfills. These streams are highly contaminated wastewater with a complex mixture of organic and inorganic compounds and are characterized by high ammonia concentrations and low biodegradable organic fraction matter content. High loads of refractory compounds, the low value of BOD_5 (five days Biochemical Oxygen Demand) to COD (Chemical Oxygen Demand) ratio and high concentration of nitrogen cause that this kind of wastewater is complicated and expensive for treatment, as well as requires various processes to be effective (Kaczorek & Ledakowicz, 2006). The changes in waste management caused by the EU directives resulted in reduced volume of leachate produced per tonne of waste landfilled and thus increased leachate strength (Brennan et al., 2015).

Both physical/chemical methods and the biological process can be used to treat landfill leachates. In spite of stable treatment effects, and preferable adaptability to the changes of wastewater quantity and quality, physical/chemical methods have several shortcomings: odors, air pollution, high chemical costs and high energy consumption. The main reason for the selection of a biological process for nitrogen removal is the lower cost compared to the physicochemical methods. Conventional biological nitrogen removal with the use of nitrification/denitrification is probably the most efficient process to eliminate nitrogen from leachate; however, the biodegradable carbon to nitrogen ratio necessitates the use of external carbon source for complete denitrification. Additionally, the nitrification process requires high energy input for aeration. For these reasons, it was important to obtain technology that facilitates enhanced nitrogen removal under the conditions of low carbon availability and with low energy requirements for nitrification. During the last two decades, the possibility of treatment of highly loaded streams with low C to N ratio by partial nitritation and the anammox process has been tested and demonstrated. However, up to now, there are still very few studies reporting the use of anammox process to treat landfill leachate.

CHARACTERISTICS OF LANDFILL LEACHATE

Landfill leachate is generated by the rainwater infiltrating through the landfill site, the surface and groundwaters flowing into the site as well as water present in the wastes and generated as a result of organic matter degradation. The quality and the quantity of leachate is mainly related to: chemical and physical properties of waste, volumes of infiltrating water, environmental conditions, the landfill age and also storage and reclamation techniques (Christensen et al., 2001; Kulikowska & Klimiuk 2008; Müller et al., 2015).

Generally, the discharge from landfill depends on rainfall, evaporation losses and redistribution in time of infiltrating water in the soil cover and in the waste deposited. The water infiltrating into the site may be transpired to the atmosphere, evaporated from the surface soil, stored in cover soil or percolate downwards through the cover (Peyton & Schroeder 1993; Bengtsson et al., 1994). The water balance on the landfill site can be summarized as follows (Blakey, 1992):

$$L = P - R - \Delta U_s - ET - \Delta U_W \quad (1)$$

where: L – leachate production, P – precipitation, R – surface run-off, ΔUs – change in soil moisture storage, ET – actual evaporative losses from the bare-soil/evapotranspiration losses from a vegetated surface, ΔUw – change in moisture content of the refuse components.

Leachate is known as wastewater whose treatment is very complicated and expensive as its composition is variable from different landfills and, moreover, its composition is changing with the landfill age.

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For this reason, the treatment methods have not been unified so far (Kaczorek & Ledakowicz 2006; Kulinowska & Klimiuk 2008). The components present in the leachate usually have different origins. However, four main groups of compounds may be distinguished (Alkalay et al., 1998; Christensen et al., 2001; Kjeldsen et al., 2002): dissolved organic matter, inorganic macro-components, heavy metals and xenobiotic organic compounds. Generally, it is stated that low BOD_5/COD ratio, the presence of heavy metals and high concentration of nitrogen compounds are the most important problems associated with landfill leachate treatment (Kaczorek & Ledakowicz 2006; Renou et al., 2008).

As landfill leachate contains numerous categories of contaminants, like organic compounds, ammonia, refractory macro and micropollutants and heavy metals, it may be toxic to the aquatic environment. Additionally, the leachate composition is unstable, and furthermore the toxicity of leachate is a consequence of its composition as well as their synergistic or antagonistic effect and different physical-chemical properties (Alkalay et al., 1998; Bloor & Banks, 2005; Kalka, 2012; Marttinen et al., 2002; Słomczyńska & Słomczynski, 2004; Ribé et al., 2012). Thus, the physicochemical methods of leachate characterization should be accompanied with the toxicity tests to get more specific information about the potential environmental impact (Kalka, 2012; Oliveira et al., 2014). Research conducted by Ribé et al. (2012) showed that even treated landfill leachate may still have an acute toxic effect on aquatic organisms. Kalka (2012) studied the change of toxicity of landfill leachate in the function of landfill age in combined treatment with municipal wastewater. The leachate was mixed with the municipal wastewater in different ratios (1 and 10%) and then treated in a lab-scale A2O system (Anaerobic-Anoxic-Oxic activated sludge system). The toxicity of raw and treated wastewater was determined using toxicity tests with *Daphnia magna, Thamnocephalus platyurus, Vibrio fischeri* and *Raphidocelis subcapitata*. The toxicity of this wastewater declined during treatment, however still it was harmful to all tested organisms. It was stated, that the concentration of landfill should be only 0.05% not to be harmful to aquatic organisms (Kalka, 2012).

It is also very important that the composition of landfill leachate is not stable and undergoes changes with time. These changes in time are related to the seasonal changes and what is even more important with the age of landfill. Generally, the leachate may be characterized with its biodegradability which is decreasing with landfill age (Kulikowska & Klimiuk, 2008, Lo, 1996, Renou et al., 2008, Yao, in press). In young landfills (usually up to 5 years) there is an acidogenic phase and as a consequence, the leachate contains large amounts of readily biodegradable carbon with volatile fatty acids (VFA) as the main product (Renou et al., 2008; Słomczyńska & Słomczyński, 2004; Welander et al., 1997). Generally, young landfills are characterized by the pH in the range of 3.7 – 6.5 (as a result of presents carboxylic acid and bicarbonate) and high biodegradability as the BOD_5/COD ratio ranges from 0.2 to 0.7. The BOD_5/COD ratio of leachates decreases from 0.7 to 0.1 and even less with the aging of landfills, thus becoming less biodegradable. Additionally, the pH for old landfills rises to 8.0-8.5 (Kulikowska & Klimiuk, 2008, Renou et al., 2008; Słomczyńska & Słomczyński, 2004). The landfill leachate may be characterized by the basic standard parameters: COD, BOD, BOD/COD, suspended solids, pH, ammonium nitrogen, total Kjeldahl nitrogen (TKN) and heavy metals (Renou et al., 2008). Table 1 summarizes the composition of landfill leachate in terms of standard wastewater parameters based on different studies.

The landfill leachate contains a high concentration of ammonium nitrogen which can vary from less than 100 mg/l in low-strength leachate to over 5000 mg/l and more for high-strength leachate. The ammonium nitrogen, especially in the form of free ammonia is toxic to the aquatic environment and can also disturb the biological treatment of landfills leachate, so it should be removed from this wastewater stream. However, the BOD_5/N-NH_4 ratio for young leachate is usually larger than 1, conversely, for older

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Table 1. The chemical composition of leachate (all values are in mg/l; pH unitless)

COD	BOD_5	NH_4-N	NO_2-N	NO_3-N	TN	pH	Reference
2200±100	100±20	2000±100	0.4±0.1	0.5±0.1	2030±12	8.0±05	Miao et al., 2014
757	105	362	n.d.	n.d.	397	n.d.	Kulikowska & Klimiuk, 2004
896±36.8	106±5.26	786±15.2	n.d.	n.d.	834±36.8	8.1±0.14	Kulikowska, 2012
2180±252	n.d.	1170±220	1±4	21±2	n.d.	8.58±0.12	Li et al., 2014
2301	461	627	41.17	n.d.	n.d.	7.95	Mojiri et al., 2016
4425-4860	433-588	790-821	n.d.	n.d.	920-977	8.3 – 9.0	Ferraz et al., 2014
4295±520	2086±358	1750±89	n.d.	n.d.	1980±108	7.9±0.2	Huang et al., 2014
1703±393.5	n.d.	1972±408.2	n.d.	n.d.	2117±426	8.5±0.3	Liang & Liu, 2008
3921±1264	123±88.9	5975±213	0.0±0.0	<2	6317±251	8.54±0.12	Gabarró et al., 2012
4357±692	810±278	3772±956	0.2±0.5	1.4±3.2	4058±987	8.11±0.2	Ganigué et al., 2009
9500	4515	2000	n.d.	n.d.	2500	7.5	Lina et al., 2009
3203±1176	2296±872	1000±337.8	n.d.	17.7±23.3	1264±616.4	n.d.	Quant et al., 2009
2766±528	485±141	1895±527	n.d	n.d	2045±489	n.d	Fudala-Książek et al., 2012
1219	n.d.	800.8	0.14	5.7	957.84	n.d.	Białowiec et al., 2012
7511	1436	500	n.d.	n.d.	n.d.	8.22	Li et al., 1999
3006±552	451±105	2189±317	n.d.	n.d	n.d	8.4±0.1	Oulego et al., 2016
6709±1863	2076±619	2813±441	n.d.	n.d.	n.d.	8.5±0.2	Oulego et al., 2016
6560±226	3326±565	1740±83	n.d.	n.d.	2021±97	8.2±0.1	Müller et al., 2015

leachate this ratio is very often lower than 1 (Słomczyńska & Słomczyński, 2004). As a result of high nitrogen concentration and, additionally, unfavorable nitrogen to biodegradable organic carbon ratio the nitrogen removal from landfill leachate is complicated and there is no standard method.

LANDFILL LEACHATE TREATMENT METHODS REVIEW

The landfill leachate treatment technologies can be based on biological, physical-chemical or integrated methods (Wiszniowski et al., 2006a). The treatability of landfill leachate depends on its composition and characteristics (Kurniawan et al. 2006). The application of biological processes for the treatment of landfill leachates is a challenging task due to their complex matrix and high toxicity. Consequently, some physical-chemical methods are needed either as a pretreatment step or a polishing step (Wiszniowski et al., 2006a). Renou et al. (2008) proposed that the treatment methods for landfill leachate can be classified into three groups:

1. Leachate transfer including recycling and combined treatment with municipal wastewater,
2. Biodegradation: aerobic and anaerobic processes,
3. Chemical and physical methods:

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a. Chemical oxidation,
b. Adsorption,
c. Chemical precipitation,
d. Coagulation/flocculation,
e. Sedimentation/flotation,
f. Air stripping,
g. Struvite precipitation, and
h. Membrane processes.

Combined Treatment with Municipal Wastewater

Both co-treatment and recycling of landfill leachate were common methods used for the indirect treatment of this waste stream (Renou et al., 2008). The application of these methods was detrimental to the treatment efficiency at the municipal wastewater treatment plants and was found to inhibit methanogenesis in the mound (Renou et al., 2008). Quant et al. (2009) investigated the co-treatment of municipal wastewater with increasing, from 1 to 5% (vol.), quantity of landfill leachate in the A2O system. It was possible to achieve high BOD_5 and COD removal exceeding 90%. However, there was also a significant increase in nitrogen concentration in the effluent. Additionally, the addition of leachate caused a significant drop in phosphorus removal. Çeçen & Çakiroğlu (2001) studied the influence of landfill leachate added to domestic wastewater in a volumetric ratio from 5 to 20%. They observed extensive nitrification, however the nitrite accumulation was also observed. It was as a result of an increase in the initial NH_4-N concentration and the same the increase of free ammonia concentration what caused the nitrite build-up. Ferraz et al. (2014) used pilot-scale submerged aerobic biofilter for co-treatment of leachate (pretreated by air stripping) with domestic wastewater and observed high efficiency of this treatment method with an optimum volumetric ration of the leachate of 2%. However, in other study, Kalka (2012) showed that even 1% (vol.) of leachate addition to municipal wastewater can cause acute toxicity to aquatic organisms. Noteworthy, the accepted maximum volume of leachate to be co-treated at a municipal wastewater treatment plant is based on the annual influent hydraulic loading and is regulated by the respective authorities (e.g. 4% in Ireland) (Brennan et al., 2015). In a recent article, Brennan et al. (2015) pointed out that increasingly stringent wastewater treatment plant discharge limits may disrupt sustainability of co-treatment of landfill leachate with municipal wastewater. This is also because high leachate production coincides with high maximum hydraulic loading at municipal treatment plants as suggested by Brennan et al. (2015).

Biological Treatment

Biological methods for landfill leachate treatment are commonly used for the treatment of leachate containing a high concentration of BOD. This is a reasonable treatment especially for the young leachate (high biodegradable carbon to nitrogen content). In the case of stabilized leachate, problems with achieving permitted COD levels due to recalcitrant characteristics of organic carbon in the leachate may be encountered. Another problem is related to the toxicity of high concentration of ammonia nitrogen. Generally, the biological nitrification and denitrification are probably the most common methods for elimination of nitrogen from leachate mainly because they are well-known processes. Problems associated with nitrification and denitrification of landfill leachate are associated with ammonia toxicity,

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low temperature during the winter time and lack of biodegradable organic carbon, especially in mature leachate. Hoilijoki et al. (1999) studied the nitrification process of landfill leachate at low temperature. They tested three different temperatures: 10, 7 and 5°C in two kinds of activated sludge reactors. One was with the addition of plastic carrier material (ASC) and the second one without (AS). In both reactors complete nitrification was achieved at temperature 10°C, at 7°C the nitrification efficiency was decreased to 93% and finally at 5°C in the ASC reactor the complete nitrification was achieved after reducing the nitrogen load from 0.023 g NH_4-N/g MLVSS to 0.01 g NH_4-N/g MLVSS. At the same time, in the AS reactor the nitrification efficiency was only 61%. Also, Isaka et al. (2007) conducted nitrification at 10°C using nitrifying bacteria immobilized in a polyethylene glycol gel carrier material. The stable ammonium oxidation was maintained for more than one year. However, due to the low affinity of immobilized nitrifying bacteria for ammonium, in the effluent from the reactor, the ammonium nitrogen at low concentration was detected. Moreover, the nitrite oxidizing bacteria were inhibited by the free ammonia present in the reactor. Welander et al. (1997) investigated nitrification and denitrification of landfill leachate at temperature varied from 10 to 26°C. They proved that in such condition it is possible to sustain complete nitrification and denitrification using suspended carrier biofilm reactor. In the case of the denitrification process the carbon to nitrogen ratio is one of the most important issues. Generally, in landfill leachate there is a deficiency of biodegradable carbon, thus the artificial carbon source should be added. Usually acetic acid (Welander et al., 1997), sodium acetate (Kaczorek & Ledakowicz, 2006) or methanol (Kulikowska & Klimiuk, 2004) are used as a carbon source for denitrification.

An interesting and low-cost technology for leachate treatment is the use of constructed wetlands (CWs) (Białowiec et al., 2012; Kadlec & Zmarthie, 2010; Nivala et al., 2007; Yalcuk & Urgulu, 2009; Miksch et al., 2015). CWs have been shown to be very effective in the treatment of landfill leachate and additionally they have low operational and maintenance requirements (Yalcuk & Urgulu, 2009). The main types of CWs that could be used for the on-site treatment of landfill leachate are free water surface systems, and subsurface flow systems with either vertical or horizontal flow (Kadlec &Zmarthie, 2010). Ammonia can be efficiently removed in vertical flow CW due to their elevated oxygen transfer rate. Horizontal flow CWs and free water surface CWs are more effective for denitrification and may follow vertical flow CWs in order to remove nitrates and some poorly biodegradable organic compounds and residual metals via multiple-mechanism pathway including biotic and abiotic processes (Kadlec & Zmarthie, 2010). Due to the carbon deficiency of the wastewater treated in vertical flow CWs it may be necessary to add external carbon source for denitrification in the subsequent treatment steps unless the carbon generated in the CWs is sufficient (Kadlec & Wallace, 2009; Rustige & Nolde, 2007). The combination of several low-energy treatment steps offered a very high mass reduction of ammonia (99.5%) and several other contaminants (including metals and trace organics) in a well-documented system in Saginaw Township, MI, USA (Kadlec & Zmarthie, 2010). This system consists of a sedimentation basin (preceded with cascade aeration), vertical gravel beds and free water surface CWs. Białowiec et al. (2012a) showed that horizontal flow CW with reed and willow can effectively remove ammonium nitrogen. In the research performed by Nivala et al. (2007) it was shown that in spite of seasonal variation in leachate composition, and additionally in temperature, the ammonium nitrogen removal may be stable with very high efficiency exceeding 90% when horizontal flow system with forced aeration is used. Sawaittayothin and Polprasert (2007) showed that using subsurface-flow CW it is possible to remove even over 90% of total nitrogen. Kadlec and Wallace (2009) suggest, however, that multiple cells or multiple units should be used to provide very high removal efficiency. This is because of the constraint of hydraulic efficiency. Leachate quality may be detrimental to some wetland plant species, therefore species that can tolerate

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elevated concentrations of ammonia should be used and additionally recirculation of treated effluent may be needed to protect the plants (Kadlec & Wallace, 2009). The elevated concentrations of Fe and Mn in landfill leachate may reduce hydraulic conductivity of bed medium of subsurface flow CWs and cause clogging. According to Urbanc-Berčič (1996) the application of aerated lagoon and a sedimentation lagoon as a pretreatment step prior to subsurface flow CWs could efficiently reduce the risk of clogging. Interestingly, Sun and Austin (2006) demonstrated through mass-balance analysis that the CANON (Completely Autotrophic Nitrogen Removal Over Nitrite) process took place in a subsurface vertical flow experimental columns treating landfill leachate containing high ammonia concentration but low BOD. The overall removal of total nitrogen in one of the columns was 52% and was partly associated with CANON process. Indeed, Zhi et al. (2015) found that anammox was one of the primary processes responsible for efficient performance (76% removal of ammonia nitrogen and >81% removal of TN) of experimental tidal flow (fill-and-drain operation) CWs treating artificial wastewater (not a landfill leachate). Zhu et al. (2011) presented an integrated approach to sustain high anammox bacteria activity and biodiversity in the microcosm CW. Further studies are needed to evaluate the feasibility of using CW with enriched anammox for long-term treatment of various types of wastewater including landfill leachate.

Physical-Chemical Treatment

The physical-chemical methods for the treatment of landfill leachate are used as a pre-treatment step, polishing step or as a main process for the removal of major contaminant (e.g. air stripping of ammonium) (Renou et al., 2016).

Air stripping is the most common method for the elimination of ammonium from various types of wastewater (Anfruns et al., 2013; Kurniawan et al., 2006; Marttinen et al., 2002; Renou et al. 2008). For this method high pH is required. Ozturk et al. (2003) studied the ammonia stripping from landfill leachate. After 2 hours of aeration at pH equal to 12 the ammonium removal efficiency was 72%, while it was only 20% at pH equal to 10 and 11. Also, Hasar et al. (2009) investigated ammonia air stripping as a pretreatment step before biological treatment. They tested four different pH values 9.0, 10.0, 11.0 and 12.0 at different air flow rates and contact time. The best results were obtained for pH 11.0 and 12.0 and were equal to 91.7% and 93.3% respectively. Guo et al. (2010) showed that at pH 11 and 16 hour contact time it is possible to remove over 96% of the ammonia. However, the drawback of this method is the necessity of pH adjustment and that the contaminated gas phase must be treated (Renou et al., 2008).

The struvite precipitation is another method used for ammonia removal from landfill leachate. Li et al. (1999) showed that ammonium may be effectively reduced as magnesium ammonium phosphate (MAP) within 15 minutes, when $MgCl_2 \bullet 6H_20$ and $Na_2HPO_4 \bullet 12H_2O$ were applied with Mg_2^+:NH_4^+:PO_4^{3-} molar ratio of 1:1:1. As usually there is a lack of the Mg_2^+ and PO_4^{3-} in the landfill leachate, and there is demand for large amounts of these compounds, Huang et al. (2014) proposed the waste phosphoric acid as phosphorus source and low cost of MgO obtained from calcinations of magnesite. The obtained ammonia nitrogen removal was 83% with Mg:N:P ratio of 3:1:1. Using low-cost of phosphate and magnesium source enabled to reduce chemical cost by 68%.

Adsorption can be used to reduce the concentrations of COD and ammonium nitrogen. Activated carbon (granular or powder) is the most commonly used adsorbent and it allows for 50-70% removal of both COD and ammonia nitrogen (Wiszniowski et al., 2006a). The aim of using activated carbon is to:

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1. Remove residual heavy metals and recalcitrant organic pollutants in the final treatment steps, and
2. To provide growth support for microorganism and thus enhance biodegradation.

Other absorbents provided elimination efficiencies comparable with those achieved with activated carbon. These adsorbents are: zeolite, vermiculite, illite, keolinite, activated alumina, municipal waste incinerator bottom ash (Abbas et al., 2009) and clinoptilolite (Wang et al., 2006).

Coagulation-flocculation has been successfully used for the treatment of landfill leachate both as pre- and post-treatment step (Abbas et al., 2009). The coagulation processes served as a pre-treatment step prior to membrane bioreactor and reverse osmosis and it allowed for 36% and 46% removal of COD and suspended solids, respectively (Hasar et al., 2009). The coagulants commonly used in the treatment of landfill leachate are: aluminium sulphate (alum), ferrous sulphate, ferric chloride and ferric chlorosulphate (Wiszniowski et al., 2006a). One of the main drawbacks of coagulation is the production of large volumes of sludge and increased concentration of aluminium or iron (Abbas et al., 2009), and when coagulation is used as a pre-treatment prior to membrane processes, membrane fouling (scaling) may occur mainly due to application of lime or sodium hydroxide to control the pH (Wiszniowski et al., 2006a).

The main membrane processes applied in landfill leachate treatment are: microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Renou et al., 2008). Hasar et al. (2009) stated that reverse osmosis and nanofiltration have been used alone to treat the water, whereas microfiltration and ultrafiltration have been coupled with other processes namely biological treatment and as pre-treatment for other membrane processes (Renou et al., 2008). For nanofiltration, nearly 60-70% removal of COD and 50% removal of ammonia nitrogen were widely reported, whereas reverse osmosis provided at least 98% removal of COD and 99% of heavy metals (Abbas et al., 2009). Wiszniowski et al. (2006a) identified fouling and the need to treat the retentate as the main drawbacks of the membrane processes. Also the combination of membrane processes with activated sludge technology in membrane bioreactors seems a viable technology for the treatment of wastewaters with high organic and nutrient loadings and offered removal of COD and total nitrogen as high as 90% in a single bioreactor at SRT of 30 d (Hasar et al., 2009).

Chemical oxidation (including advanced oxidation processes, which are based on the generation of highly reactive hydroxyl radicals) is widely studied and applied to remove recalcitrant organics from various types of wastewater including landfill leachate and offers high removal efficiencies for a wide range of organic pollutants (Renou et al., 2008; Miksch et al., 2015). Chemical oxidation methods can be used to fully mineralize (as a final treatment step) the target pollutants or to increase biodegradability of contaminants prior to biological treatment. Advanced oxidation processes are recommended for the treatment of industrial wastewater with relatively low COD (<5 g/L), which is due to high energy and reagents consumption (Miksch et al., 2015). Chemical oxidation techniques have been regarded as expensive, but the operation cost can be decreased when hybrid processes are used (e.g. with biological methods) and when sunlight-induced photodegradation (preferably with a catalyst) is used. Indeed, a combination of CWs with sunlight-induced photodegradation is a promising low-cost solution for treating various types of wastewater (Liu et al., 2015). Photocatalytic post-treatment (UVC with TiO_2 catalyst) of biologically treated leachate caused further removal of more than 80% refractory organics remaining in the leachate (Wiszniowski et al., 2006b). In a recent study, a combination of persulfate and hydrogen peroxide was applied to treat landfill leachate and 81% removal of COD and 83% removal of ammonia nitrogen was observed (Hilles et al., 2016). The treatment of landfill leachate in an O_3/H_2O_2-based advanced oxidation system resulted in 48% reduction of COD, enhanced biodegradability of 0.7 (from 0.1) and color removal of 94% (Tizaoui et al., 2007). Deng & Englehardt (2006) reviewed various

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studies related to the application of conventional Fenton process, photo-Fenton, electro-Fenton process to the treatment of landfill leachate to observe that the range of COD removal was 45-85% and that the biodegradability was enhanced up to 0.60 (as BOD_5/COD ratio). Despite high removal efficiency and low operating cost (in comparison to other chemical oxidation methods), Fenton treatment of landfill leachate may be limited as:

1. Some organic compounds are recalcitrant to this method,
2. Significant amount of acid needed to adjust the pH of typical leachate,
3. Slow initial kinetics at temperature less than 18.3°C (Deng & Englehardt, 2006).

Also electrochemical oxidation was proposed as an efficient method for the treatment of landfill leachate as it offered maximum removal efficiencies as high as 90% for COD, almost 100% for ammonia nitrogen and 86% for color (Deng & Englehardt, 2007). The drawbacks of this process that may somewhat limit its application are high energy consumption and potential chlorinated organics formation may limit its application (Deng & Englehardt, 2007).

LEACHATE TREATMENT USING ANAMMOX PROCESSES

Because of requirements for high oxygen input and external carbon source addition, treating nitrogen-rich streams with nitrification/denitrification would become expensive and unsustainable. The least resources consuming pathway for the conversion of ammonium to nitrogen gas is a combination of partial nitritation and anammox processes. The main advantages of this combined processes compared to the conventional nitrification/denitrification are: low sludge production, decrease in the aeration costs by almost 60% (only half of the ammonia is oxidized to nitrite in the nitritation process without further oxidation to nitrate), and no need for external organic carbon source addition (anammox process) (De Clippeleir et al., 2011; Mulder, 2003). Furthermore, anammox bacteria oxidize ammonium under anoxic conditions with nitrite as the electron acceptor, and converse energy for CO_2 fixation, which resulted in 90% reduction of CO_2 emission in comparison to nitrification-denitrification. Additionally, the biomass yield of the anammox process is very low (0.08 kg VSS kg NH_4-N^{-1} in comparison to 1 kg VSS kg NH_4-N^{-1} in conventional nitrification/denitrification process) consequently, little sludge is produced. The low sludge production is another factor that contributes to the substantially lower operation costs compared to conventional denitrification systems. However, the low biomass yield also demands efficient sludge retention (Strous et al., 1997).

Partial Nitritation

As the anammox process requires nitrite nitrogen as electron acceptor, the partial nitritation is needed as a preceding step and for its application in wastewater treatment, different set-ups are used to provide nitrite: in the single reactor systems (Van der Star et al., 2007; Cema, 2009) or in the two-reactor systems (Kartal, 2008; Vázquez-Padín et al., 2009; Cema, 2009). In the two-step process part of the ammonium nitrogen is converted to nitrite in the first reactor which is followed by an anoxic reactor where the anammox process occurs. Separation of nitritation and anammox processes in space allows flexibility and more stable process performance since both steps can be controlled separately (van Hulle et al.,

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2010).The partial nitritation may be achieved in several ways like using high temperature to promote ammonium oxidizing bacteria (AOB) growth over nitrite oxidizing bacteria (NOB) or by changing other parameters like pH or dissolved oxygen. Kulikowska (2012) investigated partial nitritation followed by denitrification in a two-stage SBR system treating mature landfill leachate. The operational temperature of the system was equal to 20±2°C. It was shown that for oxygen concentration between 1.2 and 1.3 mg O_2/l the nitrite accumulation ratio was between 32 and 37%, whereas with the decrease in the oxygen concentration to 0.8 – 0.9 mg O_2/l the nitrite accumulation ratio increased to 96%. Fudala-Książek et al. (2014) showed that during the co-treatment of landfill leachate with municipal landfill leachate, the volumetric addition of leachate up to 10% promoted the partial nitritation if the oxygen concentration was in the range from 0.5 to 1.5 mg O_2/l and free ammonia ranged from 2.01 to 35.86 mg N/l. Li et al. (2013, 2014) achieved stable partial nitritation using endpoint pH control which was necessary to get nitrite-to-ammonium ratio suitable for the anammox process. The high free ammonia and low dissolved oxygen were also necessary to inhibit the nitrite oxidation. The other possibility to achieve partial nitritation was to operate the process at high temperature (over 30°C) and with low sludge retention time to wash out nitrite oxidizers from the system (Akgul et al., 2013; Ganigué et al., 2007; Sri Shalin & Joseph, 2012). Gabarró et al. (2012) showed that for leachate with very high concentration of ammonium nitrogen (around 6000 mg N/l) it was also possible to get stable partial nitritation. At temperature 25°C the free nitrous acid was responsible for inhibition of NOB whereas at temperature equal to 35°C the combination of free ammonia and free nitrous acid was responsible for suppression of NOB.

Anammox

The anammox process is considered as a technology specifically used for nitrogen rich wastewater with deficiency of organic carbon. This process, in combination with partial nitritation, was successfully used for the treatment of landfill leachate. The single-reactor process of partial nitritation/anammox was first observed in a rotating biological contactor (RBC) for the treatment of landfill leachate in Mechernich, Germany (Hippen and Rosenwinkel, 1997), Kölliken, Switzerland (Siegrist et al., 1998) and Pitsea, Great Britain (Schmid et al., 2003). Up to now, there is over 100 full scale applications of the anammox process (Lackner et al., 2014). Most of these installations are used for reject water treatment, however, there has been very intensive research on the application of the anammox process to landfill leachate treatment (Akgul et al. 2012; Cema et al., 2007; Miao et al., 2012; Scaglione et al., 2012; Sri Shalini & Joseph, 2012; Wang et al., 2014). Zhang & Zhou (2006) showed the possibility of nitrogen removal from landfill leachate by the anammox process performed in the Upflow Anaerobic Sludge Blanket Reactor (UASB). The leachate treated in UASB was the leachate mixture blended with leachate and effluent of SBR system. The average removal efficiency of total nitrogen was 79.6%. Cema et al. (2007) used RBC for landfill leachate treatment by the anammox process. They demonstrated that nitrogen removal by anammox process is possible at a temperature below 20°C. Scaglione et al. (2012) demonstrated the use of single-stage partial nitritation/anammox SBR with granular anammox biomass for the treatment of landfill leachate. Akgul et al. (2012) demonstrated the nitrogen removal using anammox process from young landfill. In order to remove high organic content, which can inhibit the anammox bacteria, the biodegradable carbon was removed in UASB reactor and a membrane bioreactor in sequence, and the effluent was given to the SHARON (Single reactor system for high activity Ammonium Removal Over Nitrite) reactor were partial nitrification takes place and then to the anammox reactor. In such system

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the COD and nitrogen removal efficiency exceeded 90%. Miao et al, (2014) demonstrated a three stage SBR comprising: pretreatment of organic matter, nitritation and anammox for nitrogen removal from mature leachate. The nitrogen removal efficiency reached 90%.

Heavy Metals Inhibition

Landfill leachate is characterized by high concentration of COD and ammonium nitrogen and especially in the case of old landfills by low COD to nitrogen ratio. This causes that, generally, landfill leachates are difficult to be treated by biological methods. Additionally, they can contain several heavy metals and high salinity which may lead to process inhibition. In Table 2 heavy metals concentration in landfill leachate and the IC_{50} for the anammox are presented.

Kimura and Isaka (2014) studied the effect of heavy metals (Ni, Cu, Co, Zn and Mo) on anammox bacteria. Molybdenum was the most influential on the anammox activity, and the concentration higher than 0.2 mg/l strongly influences the anammox reaction. Additionally, the inhibition caused by Mo is irreversible. The 50% inhibition concentration (IC_{50}) of Ni, Cu, Co and Zn were 7.9, 6.5, 9.7, and 12.5 mg/l, respectively. Li et al. (2015) studied the inhibitory effect of six metals commonly present in landfill leachate (Cu, Cd, Ni, Zn, Pb and Mo). In short-term studies, Cu, Zn, Cd, and Ni were the most toxic metals with 50% inhibiting soluble concentrations of 4.2, 7.6, 11.2, and 48.6mg/l, respectively. Lead caused only 32% inhibition at the highest tested concentration (6 mg/l of soluble Pb). The IC_{50} values of Cu and Zn were comparable with the results obtained by Kimura and Isaka (2014). In the research performed by Li et al (2015), Mo was not inhibitory at a soluble concentration up to 22.7 mg/l, however in contrast to studies of Kimura and Isaka (2014) this was performed in the batch test without any earlier biomass exposure to the heavy metals. Lotti et al. (2012) investigated the Co and Zn influence on the anammox sludge, and they found the 50% inhibition concentration after 24 hours exposure equal to 1.9 and 3.9 for copper and zinc, respectively. Zhang et al. (2015) studied the short and long-term effect of Zn(II) on the anammox process. The Zn concentration to 5 mg/l was tolerated by the anammox bacteria, and they were suppressed at 8 mg/l. The 50% inhibitory concentration of Zn(II) was 25 mg/l. The inhibitory effect was reversible and after short term of recovery period, the sludge characteristics were remitted to the normal. Zhang et al. (2016) evaluated the long-term effect of Cu and Zn on the anammox activity. Cu and Zn at a concentration of 1 mg/l both, and with a joint loading rate of 0.4 kg/m^{3}d did not affect the process,

Table 2. Heavy metals concentration in landfill leachate and the IC_{50} for the anammox

Heavy Metal	Concentration in Landfill Leachate		IC_{50} for Anammox	
	Value [mg/l]	Reference	Value [mg/l]	Reference
Co	0.005-1.5	Kjeldsen et al., 2002	9.7	Kimura and Isaka 2014
Cu	0.005-10	Kjeldsen et al., 2002	6.5	Kimura and Isaka 2014
Ni	0.015-13	Christensen et al. 2001	7.9	Kimura and Isaka 2014
Pb	0.001-5	Kjeldsen et al., 2002	6*	Li et al. 2015
Zn	0.03-1000	Christensen et al. 2001	12.5	Kimura and Isaka 2014

*32% inhibition at the highest tested concentration

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while the joint loading rate of 0.12 kg/m^{3}d caused it rapid collapse. Generally, the IC_{50} concentrations for anammox process are quite high, however in the case of Cu, Ni, Zn their concentration in landfill leachates may be much higher than IC_{50} concentration. Also, the composite inhibition research is needed.

Influence of Organic Matter

Also, the presence of the organic matter in the landfill leachate could cause some problems as a result of the development of heterotrophic denitrifiers. Generally, partial nitritation/anammox process was mainly applied for wastewater with low COD to N ratio (even below 0.5). The COD requirement for nitrate denitrification is 2.9 g COD/g N-NO_3^-, but for nitrite denitrification COD to N ratio is decreasing to 1.71 g COD/g N-NO_2-. Chamchoi et al. (2008) demonstrated the reduction of anammox activity with an increase in COD to N ratio from 0.9 to 2.0, which was caused by the concurrent denitrification. The reactors were continuously fed with synthetic wastewater and the operational temperature was 35°C. They found that the COD concentration of 300 mg/l could inactivate or even eradicate anammox biomass when the reactor is operated under low nitrogen loading rates (below 0.1 kg/m^{3}d). Similar observations were performed by Molinuevo et al. (2009) using a semi-continuous UASB reactor at 37°C, fed with synthetic wastewater and then with pig manure effluents (after UASB post digestion and after partial oxidation). By contrast, Tang et al. (2010) showed that with a high nitrogen loading rate of 13.92 kg/m^{3}d heterotrophic denitrification prevailed in the UASB (upflow anaerobic sludge blanket) reactor fed with synthetic wastewater in which high influent COD/NO_2 ratio of 2.92 was applied. Generally, the anammox bacteria growth is suppressed due to weaker competition for nitrite and much lower specific growth rate in comparison to heterotrophs. Recently, Janni et al. (2014) showed the application of partial nitritation/anammox with the step wise increasing COD to N ratio to 1.4. They noticed a decrease in sludge retention time (SRT) to the critical value for the anammox bacteria with increased COD loading. However, reduction of biomass loss caused the rise of anammox bacteria activity. What was interesting, the anammox population changed from mixed community to *Candidattus Brocadia fulgida* as the dominant type which is known to oxidize acetate. However, to avoid the heterotrophic bacteria growth in the anammox reactor, the two step process is recommended (Nhat et al., 2014). In such configuration, the organic carbon is oxidized in the first aerobic reactor so the second anammox reactor is protected from high organic influent and the same anammox bacteria overgrowing by heterotrophic bacteria. Nhat et al. (2014) showed the successful combination of partial nitritation in SBR reactor followed by anammox process in anammox hybrid reactor (HAR) treating old landfill leachate. The same principle of operation is in Panammox® technology which consists of two step partial nitritation-anammox process operated in two SBR reactors treating real landfill leachate. The first partial nitritation SBR reactor is operated under high temperature (35°C) with free ammonia (FA) and free nitrous acid (FNA) as key parameters for NOB suppression. The following SBR reactor was operated as anammox reactor with working temperature at 36°C. The obtained results showed that the anammox process is not inactivated by denitrification and moreover nitrates produced by anammox were removed by heterotrophic denitrification. An 85.1% of the nitrogen removal was due to the anammox process whereas the denitrification was responsible for 14.9% of nitrogen removal (Ruscalleda et al. 2008). Further study showed that the suitable influent nitrite-to-ammonium molar ratio is a crucial factor for process stability, and the lower nitrite supply may result in loss of anammox activity due to nitrite competition with denitrifiers

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(Ruscalleda et al., 2010). Miao et al. (2014) demonstrated nitrogen removal from landfill leachate using three stage SBR system, comprising pretreating SBR (SBR_{pre}), nitritation SBR and anammox SBR. The SBR_{pre} was used for pretreating the biodegradable organic substances and at the same time for reducing the adverse effect of organic substances on anammox process. In this system, the overall nitrogen removal efficiency reached 90% with nitrogen loading rate at 0.81 kg/m^3d (Miao et al., 2014 and 2015). Lu et al. (2016) demonstrated the coupling of upflow anaerobic sludge blanked with ANITA™Mox process. The pilot study demonstrated that the combined process was capable of treating high strength leachate with high COD and nitrogen removal. The total nitrogen removal efficiency was about 70%. The system was designed and patented for young landfill leachate treatment with high organic carbon content. The high COD concentration about 45000 mg/l was first removed in UASB reactor with an efficiency about 93% and then before the anammox reactor, there was the C-stage MBBR (Moving Bed Biofilm Reactor) to treat additional 500 to 1000 mg/l of COD to protect the anammox step from high organic carbon inflow.

Salt Inhibition

Another problem associated with the landfill leachate is high salinity considered as an inhibitory factor for biological nitrogen removal processes (Dapena-Mora et al., 2010; Liu et al., 2014). The high concentration of salt in the leachate mostly is chloride (250 – 4500 mg/l), Sodium (70-7700 mg/l) and Potassium (50-3700 mg/l) (Kjeldsen et al., 2002). Kartal et al. (2006) operated two SBRs for one year using seeding sludge consisting of equal amounts of marine and freshwater species. One reactor was operated with the salinity up to 30 g/l. It was shown that *Kuenenia stuttgartiensis* can adapt to high salt concentration. The same observation was later made by Liu et al. (2009). Also, Dapena-Mora et al. (2010) demonstrated that the anammox bacteria can adapt to high salinity and consequently can be used to remove nitrogen from effluents with high salinity.

Physical-chemical treatments have been found to be suitable not only for the removal of refractory substances from stabilized leachate, but also as a refining step for biologically treated leachate. Anfruns et al. (2013) studied the combination of partial nitritation anammox process with two AOP-based technologies (coagulation-flocculation + ozonation and photo-Fenton) in terms of nitrogen removal and carbon. Biological treatment prior to advanced oxidation processes allowed to reduce the amount of reagents. It was possible to achieve total nitrogen removal efficiency in the range from 87 to 89%.

Recently, the full scale application of partial nitritation and anammox treating landfill leachate was reported (Wang et al., 2010). Wang et al. (2010) demonstrated the occurrence of simultaneous partial nitrification, anammox and denitrification process (SNAD) in a single partially aerated full-scale bioreactor. The process was performed in two aeration tanks with 384 m^3 of working volume and 1.26 d of hydraulic resident time, which was located in Taiwan. The DO concentration in the reactor was maintained at 0.3 mg/l which promoted coexistence of anammox microorganism and denitrifiers. The reactor was operated at a temperature ranging from 30°C to 33°C.The removal efficiencies of COD and $N\text{-}NH_4$ were 28% and 80%, respectively, with the total nitrogen removal by partial nitritation/anammox as high as 68% and contribution of heterotrophic denitrification to 5% and 23% of total nitrogen and COD removal, respectively.

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CONCLUSION

The landfill leachate is very difficult to be treated due to its complex composition. So far, there has not been a standard treatment method for this type of wastewater. In last years there has been an increasing interest in using partial nitritation in combination with the anammox process for nitrogen removal from landfill leachate. Due to complex composition of landfill leachate and the presence of inhibitory substances like heavy metals, organic carbon or salts, there is a tendency to use combined treatment methods with some pretreatment – especially for organic carbon removal, and also with some post-treatment methods like constructed wetlands or with AOP-based technologies. The use of partial nitritation with combination of the anammox process gives a cost effective alternative for biological removal of nitrogen from landfill leachate. Although, some full scale applications are single stage technology (first installations used rotating biological contactors), there is rather tendency to use two-step partial nitritation/anammox technology instead of a one-step process, for example the Panammox® technology. It is mainly because the first partial nitritation reactor protects the following anammox reactor from organic carbon and some potentially toxic substances. However, further research is needed to determine the influence of very low temperatures especially with combination of some toxic substances which may be present in leachate. Also, further research is required on combined methods coupling partial nitritation/anammox process with other techniques.

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KEY TERMS AND DEFINITIONS

Ammonia Air Stripping: The process in which the ammonia in high concentration is stripped by aeration or air flow.

Anammox: Anaerobic Ammonium Oxidation is a microbial process performed by Anammox bacteria belonging to planctomycetes group. In this process the ammonium nitrogen is anaerobicallu oxidized to dinitrogen with nitrites as electron acceptor.

Denitrification: The reduction of nitrate nitrogen to nitrogen gas performed by heterotrophic bacteria.

Landfill Leachate: A liquid that passing the waste deposited in a landfill. Once in contact with solid wastes, the perocating water becomes polluted.

Nitrification: The microbial process performed by chemolitotrophic bacteria in which the ammonium nitrogen is oxidized to nitrate nitrogen.

Nitritation: In this process the nitrification process is limited to its first step – ammonium oxidation to nitrite nitrogen.

Struvite: Magnesium ammonium phosphate is a white crystalline substance with formula $NH_4Mg-PO_46H_2O$.

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Chapter 54
Application of Potential Biological Agents in Green Bioremediation Technology: Case Studies

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ABSTRACT

Upgradation and advancement in every field related to mankind leads to the origin of a contaminated environment. Development in science and technology enabled humans to combat the rate of contaminants by using biological agents, commonly known as bioremediation. The chapter deals with the different species of bioremediation agents viz. bacteria, fungi, algae, plants, animals and organic wastes to treat diverse environmental pollution. The extent of environmental bioremediation encompasses inorganic viz. arsenic, chromium, mercury, cyanide etc. and organics viz. Hydrocarbons, petroleum, pesticides etc. Thus, the reasons for the control of water and soil by considering bioremediation are concern on public health, protection of environment, and cost reduction of decontamination. Different case studies have been demonstrated herein to understand the enigmatic process and evaluate practical efficacy of the environment to decontaminate itself by the presence of various biological organisms.

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INTRODUCTION

Expeditious growth of population and their anthropogenic activities in industry, agriculture and domestic sectors leads to the generation of huge hazardous toxic materials. These toxic elements can persist in the environment for a long time. Thus, continuous generation along with long persistence make a favorable condition for pollutants to accumulate in different matrices (air, water and soil). This filthy condition is gradually capturing our world with its adverse effect on the human health. Hence there is an utmost requirement to combat with the pollution load for our better health and environment. There are several processes to deal with the contaminants, among them biological process is recently gaining popularity for its eco-friendly nature. Nature teaches us different remedies to manage any type of condition. Development in scientific research, scientists are able to develop efficient and economic processes for remediation of contaminants (Elekwachi et al., 2014). Use of biological agents like plants, animals, algae, fungi, microbes, etc. in pollution abatement is commonly known as bioremediation. Some species of plants, animals, algae, fungi, microbes, etc. also increases in certain places so as to make them highlighted by being polluted.

The principle of bioremediation involves the biological organisms to wipe out the contaminants or convert them into less harmful variety by formation of porous fence, intra and extracellular confiscation, active transport, enzyme mediated detoxification, chelation of metals, precipitation through the production of organic harmless substances and biotransformation reactions (methylation, oxidation, reduction and volatilization). They multiply themselves by generating energy and nutrients from the atmosphere. In very few cases, the nature provides all the essential materials for cleaning up the contaminated sites, known as intrinsic bioremediation. But in most of the cases, essential materials are regularly supplied from an outer source to the organisms, this process is known as engineered bioremediation. These two types can further be classified under different techniques viz. biostimulation i.e., by stimulating viable native microbial population; bioaugmentation i.e., artificially introducing viable population; bioaccumulation i.e., applying live cells; biosorption i.e., using dead microbial biomass; phytoremediation i.e., by using various species of plants and rhizoremediation i.e., by using plant and microbes at the same time (Chowdhury et al, 2012). Different species of these agents are used to identify pollution as well as treat diverse environmental pollution. Inorganic, organic as well as air pollutants can be treated through bioremediation. Aquatic plants also act as biosensor and help in the remediation of polluted water. It is an interesting fact that besides plants and microbes, soil animals like protozoans, nematodes, earthworms, mites, insect larvae, arachnids, millipedes and centipedes are also involved in bioremediation. They usually play a very regulative role in the decomposition rate of the contaminants. The process of bioremediation is very simple and very cost effective usually driven by the solar energy (Prasad, 2011). The only part for effective bioremediation includes the proper selection of biological species for a definite problem of contamination in polluted sites may it be land or water. Progress in various paths for the destruction and degradation of pollutants and contaminants has been developed for ensuring a sustainable bioremediation strategy. Following proper techniques of bioremediation can result in productive and non-deleterious quality of the environment. Till now several researches are going on to find the best agent for providing best green remediation. This chapter explains the causes, processes and mechanisms used in bioremediation emphasizing efficiency of different living organisms (tools) and case studies to cleanup the environmental contaminants.

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A BRIEF HISTORICAL OVERVIEW

In bioremediation, different microorganisms, fungi, algae and plant species has been extensively used to decrease, degrade, transform and detoxify the pollutants from the contaminated sites. Potential living organisms present in the contaminated sites spontaneously may involve in the remediation process, mimicking this natural process, researchers are trying to make the process more efficient.

The concept of bioremediation is not new; Romanian in 600 B.C established a sewer system for biological wastewater treatment. Before the 1940s, scientists hypothesized the degradation of petroleum hydrocarbons by microbes but their mechanism and limitation was unknown. However, in 1960 George M Robinson has invented a bioremediation process during experiments with polluted containers. His pioneer concept for commercial utilization of dried microbes gained acceptance throughout the 1960s (Sonawdekar, 2012). In 1970 Dr. Ananda Mohan Chakrabarty discovered crude oil degrading bacterial strain. First commercially, bioremediation techniques were used in 1972 to clean up the Sun oil pipeline spill in Ambler, Pennsylvania. In this meantime, research had progressed in the field of genetic modification of microbes to enhance its stability, substrate specificity and efficiency and therefore, in 1975 Dr. Chakrabarty once again brought revolution by discovering oil-eating superbug (*Pseudomonas putida*) using genetic cross linking. Burning, mechanical cleanup and chemical dispersants methods were used to remediate the contaminated shoreline after Exxon Valdez oil spills in 1989. By 1990s, bioremediation got its significance through the commercial application of this process for the treatment of contaminated soils and groundwater. According to the Environment Protection Agency (EPA) survey report in 1992, 240 bioremediation cases were identified. In the year of 2005, UK researchers identified uranium degrading bacteria from a decomposed state in an insoluble forms (Evan, 2005). In 2014, Norwegian researchers in Trondheim have gotten remarkable results of nature's ability in oil spills clean up (Doan, & Domingo, 2015; Pal et al., 2010).

MECHANISM OF BIOREMEDIATION

For the bioremediation purpose environmental factors and the properties of the biological agent involved in this process plays a crucial role. A proper uniform contact of agents with pollutants is also an important factor. Activity and growth of microorganism, degradation mechanism of contaminants and efficiency of the process are broadly depended on various factors like moisture, pH, temperature, types of matrix, redox potential, availability of oxygen, mass transfer characteristics etc (Uqab et al., 2016). Mechanism of bioremediation basically depend on the unique property/tricks of living organisms involve in this process by the means of absorption, adsorption, uptake, conversion to simple no/less toxic materials, degradation and decomposition (Figure 1).

Adsorption

Adsorption is carried out by the binding of pollutants in the binding sites of microbial cellular structure. Extracellular polymeric substances (EPS) which is a reactive compound have a significant effect on acid-base properties and metal adsorption through the mechanism of proton exchange and micro-precipitation of metals (Dixit et al., 2015).

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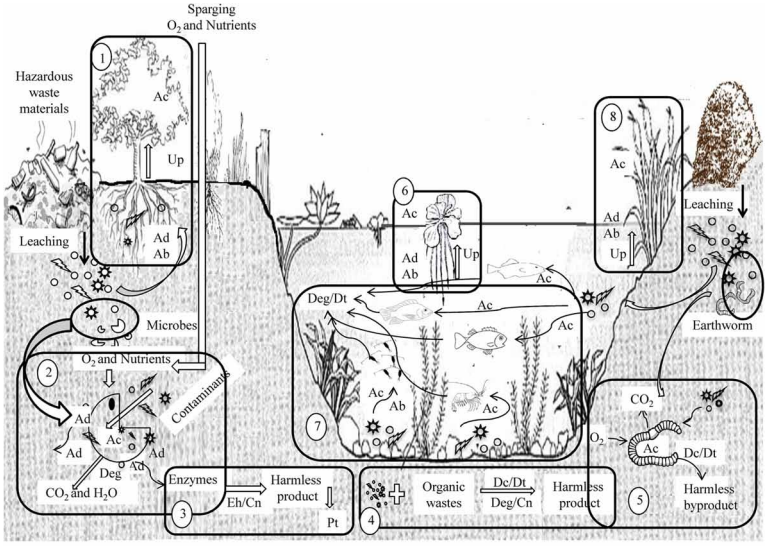
Figure 1. Mechanism of various bioremediation pathways driven by different living machines (biological components) in decontaminating and detoxifying the hazardous substances in environment (Up take- Up, Accumulation- Ac, Conversion- Cn, Enzymatic hydrolysis- Eh, Degradation-Deg, Decomposition-Dc, Absorption-Ab., Adsorption-Ad, Precipitation-Pt, Detoxification-Dt).



Plant tools- system 1, 6, 8 (phytoremediation); Microbial tools- system 2, 7 (microbial remediation); Enzyme tools- system 3 (enzymatic remediation); Animal tools- system 5,7 (zooremediation); Organic waste- system 4 (biosorption)

For the plant species surface of the roots binds many pollutants. Interaction of the plant root and microbes resulted into secretion of proton, organic acids, enzymes and phytochelatins increase the metal dissolution in rhizosphere zone (Revathi et al., 2013).

Biosorption

By the biosorption process positively charged heavy metal ions get absorbed by the negatively charged microbial cell membranes and polysachharides. In this process contaminants first entered in to the cell cytoplasm through cell membrane by the help of transporter proteins. From the surface, the metals are transported into the cell cytoplasm through the cell membrane with help of transporter proteins. Specific binding sites present in the transporter proteins binds and transports ions from outer side to inside of the cell (Sinha et al., 2013).

Precipitation

Precipitation of metals occurs by compartmentalizing and/or converting to more innocuous form. Micro-organism precipitate metals in different forms like metal sulphides, metal oxides, metal protein aggregates or elemental metal crystals. These forms of metals form particulates which are closely associated with cytoplasmic membrane (Bhakta, 2016).

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Detoxification

Possible mechanisms of the detoxification of contaminants by microorganisms are 'valence transformation', by 'extracellular chemical precipitation' or by 'volatilization'. In general by redox conversion of inorganic pollutants or conversion of inorganic pollutants to organic forms, detoxification occurs by microbial population. Aerobic bacteria produce harmless CO_2 and water by the degradation of natural and synthetic hazardous organic substance on the other hand anaerobic bacteria are responsible for the degradation of halogen and nitrosamine, reduction of epoxides to olefins, reduction of nitro groups. Microbial methylation of metals is another aspect of detoxification. Living organisms are used for biomethylation of arsenic to gaseous arsines, selenium to volatile dimethyle selenide and lead to dimethyl lead (Sinha et al., 2013).

Enzymatic Bioconversion

Microbial enzymes act as a biocatalysis which facilitate the bio-conversion of substrates into products. Different types of enzymes like monooxygenase, dioxygenase, laccase, lignin peroxidase, manganese peroxidase, versatile peroxidase, lipase, cellulase and protease are involved in oxidoreductase and hydrolysis of toxic materials (Karigar and Rao, 2011).

Degradation/Decomposition

Several microbes has been identified which are involved in the breakdown of toxic organic substances and xenobiotics in the environment. Heterotrophic microbes which cannot produce their own food are involved in the decomposition process to gain their growth nutrients. These microbes utilize Oxygen (O_2), ammonia (NH_3), and phosphate (PO_4^{3-}) from the organic material as a nutrient source and produce harmless materials. Degradation process may be carried out in the absence (Anaerobic process) or presence (Aerobic process) of oxygen. Anaerobic process produces carbon dioxide (CO_2) to methane (CH_4) in the presence of the available hydrogen (H_2).

Hydrocarbons of waste organics (*Acetogens*) → Acetate + Organic Acids + CO_2 + H_2O

Organic Acids + CO_2 + H_2 (*Methanogens)* →Byproducts + Energy

On the other hand aerobic process produces CO_2 and water.

Organics + Molecular Oxygen (Aerobes) → CO_2 + H_2O + Other products + Energy (Sinha et al., 2013).

LIVING MACHINE (TOOL) OF BIOREMEDIATION

A vast array of biological components in ecosystem play important role in self-cleaning process of ecosystem as living machines or tools. Several studies determine and demonstrated their services and efficacy in remediation of polluted/contaminated environment. Therefore, it is well established that

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biological agents have potent capacity in bioremediation by removing and/or transforming from higher to lower toxic forms. Biological components act a very important role in biotransformation and biodegradation of contaminants to less toxic substances. Biotransformation deals with the amendment of the structure of a substrate by microorganisms, where biodegradation deals with the breakdown of organic and biotransformation of inorganic compounds into non-toxic compounds. Bioremediation utilize different types of biological agents like bacteria, fungi, algae, plant, etc. to clean up the contaminated sites. This technology promotes the growth of the microorganism in contaminated sites and can be enhanced by adding nutrients, adding terminal electron acceptor; maintaining temperature and moisture content (Singh et al., 2014).

Bacteria

Microbes have been widely used for environmental clean-up. Microbial degradation process involved in metal reduction, methylation, demethylation, enzymatic reduction, metal organic complexion, metal ligand degradation (Okeke et al., 2014). Different types of species of which are extensively utilized for the management of contaminated sites like *Streptomyces*, *Pseudomonas* and *Bacillus* for metal biosorptions. Few others commonly use microorganisms are the species of *Achromobacter, Citrobacter, Escherichia, Cinetobacter, Flavobacterium, Micrococcus, Mycobacterium, Norcardia, Pseudomonas* and *Rhodococcus* etc. (Bhatnagar, & Kumari, 2013; Kumar et al., 2011). Versatile properties of these microorganisms can change in metal mobility, speciation, toxicity and mineralization and thus helps in the degradation and transformation of the huge variety of compounds viz., metals, hydrocarbons, chlorinated solvents, chlorinated phenol, BITEX, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pesticides, radionuclide (Joutey et al., 2013). Bioremediation can be classified into 3 phases i) by natural attenuation ii) by supplying nutrients and iii) by adding microbes to the system (Seo et al., 2009). Many factors like pH, temperature, moisture, and availability of nitrogen, phosphorous, carbon, production of toxic metabolites, solubility of contamination and concentration of pollutants influence the existence of microorganism population and the capability of degradation (Naik and Duraphe, 2012). Hence, there is an urge for the preparation of high potential microorganism to work a wide range of environmental condition and thus genetically engineered microorganisms (GEM) came into the scenario. Four principle approaches for the development of GEMs for bioremediation application are i) identification of the microorganism which are suitable for modification ii) pathway construction and regulation iii) adaptation of enzyme specificity and affinity and iv) bioaffinity, bioreporter sensor applications in chemical sensing, toxicity reduction and end point analysis (Kulshreshtha, 2013). Some examples of GEMs are *Alcaligenes eutrophus* 2050, *A. eutrophus* H850Lr, *Burkholderia. cepacia* BRI6001, Comamonas testosteroni VP44, *E. coli* FM5/pKY287, *Pseudomonas* sp. B13, *P. putida* KT2442, *Pseudomonas* sp. FR1, *Pseudomonas* sp. LB400, *P. pseudoalcaligenes* KF707-D2, *P. putida* TVA8, *P. fluorescens* HK44, *P. fluorescens* 10586s/pUCD607 and *P. fluorescens* 10586s/pUCD607. These microorganisms are used in the process monitoring, end point analysis, stress response and toxicity assessment (Menn et al., 2008).

Fungi

Morphological, physiological and genetic features of fungi are important to make them unique in bioremediation process. They can easily persist and colonize in all matrices in the environment and thus play an important role in the reduction, elimination and transformation of contaminants. Air is the main

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vehicle for fungal propagules, though aquatic environment is steadily colonized by fungi but the major habitat is soil. Fungi can be found in different ecological niche extended from arctic tundra to the desert sand dunes. All fungi are heterotrophic in nature and utilize organic substance in their growth by three ways: saprophytism, parasitism and mutualistic symbiosis. One or more fungal species can degrade almost all natural organic compounds by producing a variety of enzymes viz., amylases, lipases, and proteases. They degrade natural polymers like keratin, chitin, and lignin, which are mainly complex and resistant to microbial attack. Wood fungi can degrade numerous aromatic and aliphatic, xenobiotic compounds, different pollutants like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and herbicides. White-Rot Fungi, Brown-Rot Fungi, Litter Fungi, Soil Fungi and Mycorrhizal Fungi are some examples which are extensively used in the bioremediation process (Anastasi et al., 2013). Some examples of fungi and their application in pollution remediation are listed in Table 1.

Yeasts show the capability to resist under adverse environmental condition. The major application of yeast is dye decolourization of food industry effluents. Different types of yeast species like *Clavispora, Candida, Rhodosporidium, Pichia* and *Rhodotorula* etc. are used in the bioremediation process (Bhatnagar, & Kumari, 2013).

Algae

Algae are important bioremediation agents, used in pollutant abatement in waste water. The major advantage of algae as a bioremediation agent is its high biomass yield capability which leads to high absorption and accumulation of metals, tolerance to heavy metals, capability to grow both autotrophically and heterotrophically, large surface area/volume ratios and potential for genetic manipulation (Chekroun, & Mourad, 2013). Algal species are used broadly for the bioremediation of heavy metal, oil, pesticides, toxins, radioactive and several organic compounds (Prabha et al., 2016). A list of some algal species and their bioremediation of specific pollutants has been enlisted in Table 2.

Table 1. List of some potential fungi used in bioremediation

Fungi	Application
Phanerochaete chrysosporium	Degrade lignin macro molecules, organopollutants (PAH's, PCBs) dioxins, synthetic dyes, pesticides, nitrocranditics, chlorolignins, chlorophenols
Phanerochaete flavido-alba	Decolorize olive oil mill wastewater
Trametes versicolor	Degrade lignin, PAHs, polychlorinated biphenyl mixture and synthetic dyes. Delignify, dechlorinate and decolorize bleach kraft pulp
Pleurotus ostreatus	Degradation of PAHs
Pleurotus tuber-regium	Ameliorate crude oil polluted soil
Lentinus squarrosulus	Mineralization of soil tainted with crude oil and thus at the end nutrient contents increased in the soil
Pleurotus pulmonarius	Management of cement and battery polluted soils

Adenipekun, & Lawal, 2012.

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Table 2. Potential algae involved in pollutant removal from diverse field

	Algal species	Elements/Contaminants
Heavy metal removal	*Anabena doliolum*	Cu^{2+} and Fe
	Sargassum fluitans	Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}
	Cladophora fascicularis	Cu^{2+}
	Padina sps	Cu^{2+}
	Spirulina	Pb^{2+}
	Chlorella vulgaris	Cu^{2+}, Cd^{2+} and Pb
	Spirogyra	Pb^{2+}
	Spirogyra hyaline	Cd^{2+}, Hg^{2+}, Pb^{2+}, As and Co^{2+}
	Scenedesmus obliques	Oil effluents
	Scenedesmus obliquus	Cd^{2+}
	Sargassum sinicola	Cd^{2+} and Cu^{2+}
	Dunaliella	Hg^{2+}, Cd^{2+} and Pb^{2+}
	Enteromorpha algae and its silicates bonded material	Pb
	Spirulina platensis	Cu^{+} and Cu^{2+}
	Tetraselmis chuii	Cu^{2+}
	Spirogyra sp., *Nostoc* commune	Se
	Anabaena variabilis, *Aulosira* sp., *Nostoc muscorum, Oscillatoria* sp. and *Westiellopsis* sp.	Cr^{6+}, Ni^{2+}
	Chlorella minutissima	Cr^{6+}
	Chlorella pyrenoidosa	Zn^{2+}, Cu^{2+}, As, Pb^{2+}, Cd^{2+}, Cr, Ni, Hg^{2+}
	Ascophyllum nodosum	Au^{+}, Co^{2+}, Ni^{2+}, Pb^{2+}
	Caulerpa racemosa	B, As, Zn^{2+}, Ni^{2+}
	Laminaria japonica	Zn^{2+}
	Micrasterias denticulata	Cd^{2+}
	Phormedium bohner	Cr
	Platymonas subcordiformis	Sr
	Sargassum filipendula	Cu^{2+}
	Sargassum natans	Pb^{2+}
	Sargassum vulgare	Pb^{2+}

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Plants

Use of plants is a low cost and eco-friendly tool for effective and efficient remediation process of pollutants. It plays a significant role in the removal of toxic materials from contaminated soil and water. Plant species provide advantages by its unique and selective uptake capabilities of root, accumulation and degradation of pollutants by whole plant. Pollutants accumulation capacity varies from plant to plant and thus high accumulator plants known as 'hyperaccumulator' which can take up toxic materials up to the levels of thousand ppm (Tangahu et al., 2011). Examples of some hyper accumulator plants are *Armeria maritima* (Seapink thrift), *Ambrosia artemisiifolia* (Ragweed), *Brassica juncea* (Indian

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Table 2. Continued

	Algal species	Elements/Contaminants
Wastewater treatment	*Chlorella vulgaris* and *Scenedesmus dimorphus*	NH_3 and P
	Oscillatoria	Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)
	Chlorella vulgaris, Spirulina platensis and *Dunaliella* saline	COD and Phenolic Compounds
	Chlorella vulgaris and *Scenedesmus quadricauda*	PO_4^{3-}, NO_3^-, COD and BOD
	Chlorella minutissima	P and NO_3^-
	Oscillatoria, Synechococcus, Nodularia, Nostoc and *Cyanothece*	BOD, COD, Dissolved Oxygen, NH_3, NO_3^-, Mg, Organic and Inorganic Phosphates
	Isochrysis zhanjiangenesis	P, NH_3, N, NO_3^- and NO_2^-
	Spirogyra sps. and *Oscillatoria* sps.	Cd^{2+} and Ni^{2+}
	Aphanocapsa sps., *Chlorella autotrophica, Coccochloris elabens, Dunaliella tertiolecta, Oscillatoria* sps., *Scenedesmus obliques, Synechococcus elongates* and *Volvox*	Crude Oil
	Chlorella vulgaris	Textile waste effluents (Color and COD)
Bioremediation of oil	Cyanobacteria (Blue-green algae)	Benzene, toluene, naphthalene, phenanthrene, pyrene
	Mycobacterium sp.	n-Undecane
	Strains of *Pseudomonas putida*	Phenol cresols
	Trichosporon pullulans	Paraffins
	Acinetobacter calcoaceticus	Petroleum derivatives
	Microcystis aeruginosa	Acrylonitrile
	Aeromonium sp.	Total petroleum hydrocarbons
Pesticides	*Chlamydomonas* sp.	Mirex, Lindane, naphthalene, phenol,
	Selenastrum capricornutum	Benzene, toluene, chlorobenzene, 1,2-dichlorobenz ene,nitrobenzene naphthalene, 2,6- dinitrotoluene, phenanthrene, di-nbutylphthalate, pyrene
	Cylindrotheca sp	Dichlorodiphenyltrichloroethane (DDT)
	Euglena gracilis	DDT, parathion
	Scenedesmus obliquus	DDT, parathion, Naphthalene sulfonic acid
	Chlorella sp.	Toxaphene, methoxychlor, Lindane, chlordimeform
	Chlorococcum sp.	Mirex
	Dunaliella sp.	Mirex, DDT, naphthalene

Prabha et al., 2016; Chekroun, & Mourad, 2013; Priyadarshani et al., 2011.

mustard), *Brassica napus* (Rape, Rutabaga, Turnip), *Brassica oleracea* (Flowering/ornamental kale and cabbage, Broccoli), *Festucaovina* (Blue/sheep fescue), *Helianthus annuus* (Sunflower), *Thalspi rotundifolium* (Pennycress), *Triticum aestivum* (Wheat), *Zea mays* (Corn) (Paz-Alberto and Sigua, 2013). Plants have a very efficient mechanism and highly specific to attain essential micronutrients when present in low concentration. Plant root produces chelating agent and thus make pH change and redox reaction which helps to solubilize and uptake the nutrients. Not only for uptaking, but these same mechanisms are involved in the translocation of storage of pollutants in different parts of the plant. There are several

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Table 3. Examples of some plant species used in remediation process

Plant Species	Toxic Compounds
Ambrosia artemisifolia and *Apocynum cannabinum*	Pb^{2+}
Brassica juncea	Se, Pb^{2+} and Cu^{2+}
Helianthus annus	As and U
Medicago sativa	Benzopyreneand PAHs
Melastoma malabathricum	Al
Nephrolepis exaltata	Hg^{2+}
Pteridium esculentum	As
Pteris vitata	As, Hg^{2+}, Cs and Sr
Salix viminlais	Cd^{2+}, Zn^{2+} and Cu^{2+}
Raphanus sativus	Cu^{2+}
Silene vulgaris and *Thlaspi caerulescens*	Cd^{2+} and Zn^{2+}
Brassica juncea, hybrid poplars grasses	As, Cd^{2+}, Cr, Cu^{2+}, Pb^{2+} and Zn^{2+}
Brassica juncea, pennycress, alyssum sunflowers, hybrid poplars	Ag^{2+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Mo, Ni^{2+}, Pb^{2+}, Zn^{2+} 90Sr, 137Cs, 239Pu, 238,234U
Helianthus annus, *Brassica juncea*, water hyacinth	Metals and radionuclides
Poplars, alfalfa black locust, *Brassica juncea*	Chlorinated solvents
Stonewort black willow, bald cypress hybrid poplar	Organic compounds, chlorinated solvents phenols, herbicides
Red mulberry, grasses, hybrid poplar, cattail, rice	Organic compounds (TPH, PAHs, pesticides chlorinated solvents PCBs)
Vetiveria zizanioides L.	As^{3+} As^{5+}, Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Pb^{2+} and Hg^{2+}

Bhatnagar, & Kumari, 2013; Pandey, & Bagga, 2013; Paz-Alberto, & Sigua, 2013.

mechanisms of pollutant uptake by plants, these are phytoremediation phytoextraction, phytostabilisation, rhizofiltration, and phytovolatilization (Tangahu et al., 2011). A list of some plants involved in phytoremediation process presented in Table 3.

Not only for water and soil, plant species are extensively used to remediate pollutants from the air. These types of plants should have certain properties like evergreen, big leaved, coarse bark, native, low water requisite, high absorption of pollutants, agro-climatic suitability, pollution tolerance and dust scavenging capacity etc. *Tamarindus indicus, Mangifera indica, Derris indica, Thespepsia populnea, Polyalthea longifolia, Azadirchta indica, Bombax ceiba, Delonix regia, Ficus religiosa, Jacaranda mimosifolia, Lagerstroemia indica, Plumeria rubra, Syzygium cumini* are suitable for pollutants elimination from air (Kumar et al., 2013).

Animals

Animal induced bioremediation capacities are not widely known and are rarely used for bioremediation for its ethical concern. Animal mediated bioremediation can be achieved by the introduction, culture, and harvest of animals from the contaminated sites. Some examples of animal involved in aquatic system bioremediation are oysters, mussels, clams, fish, polychaetes and sponges. This process is termed as 'zooremediation' (Gifford et al., 2006). The mechanisms employed are zooextraction, zoostabilisation, zootansformation and animal metal-hyperaccumulation. This remediation process occurs in two ways i)

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by taking part in the process, increasing in number and soil metabolic activity. ii) as a good indicator of contaminated soil, to evaluate the toxicity and risk of the end product (Haimi, 2000). Aquatic animals accumulate contaminants in several orders of magnitude higher than the surrounding water. Accumulation is depend on several factors like temperature, pH and salinity of the matrix and biological factors like age, sex, sexual maturity stage of premeditators (Gupta and Singh, 2010). Earthworms also found as a potential species for the removal of contaminants. It involves in the remediation of pesticides, heavy metals and lipophilic organic micropollutants like the polycyclic aromatic hydrocarbons (PAH) from the soil. In the soil the area of earthworm and pollutants interactions is known as "drilosphere system" and the process of remediation called as "Vermiremediation" (Sinha et al., 2009). Some names of decomposer animal are listed in Table 4.

Organic Wastes

Organic manures/wastes have been extensively used throughout the world for the improvement of soil fertility by adding organic matter and nutrients (Anyanwu, & Okorie, 2013; Umar et al., 2013). Like other agents application of organic waste is a promising tool in bioremediation process (Bahadure et al., 2013). Basically addition or amendment of the soil by organic waste increases the microbial population and activity by providing nutrients (Chijioke-Osuji et al., 2014).

Table 4. Name and groups of some animals involved in bioremediation process

Animal Group	Species
Earthworms	*Eisenia fetida/Andrei* *Aporrectodea caliginosa* *Lumbricus terrestris*
Enchytraeids	*Enchytraeus albidus*, also other species
Collembola	*Folsomia candida* several species, e.g. *Folsomia fimetaria* and *Orchesella cincta*
Mites	*Platynothrus peltifer*
Isopods	*Porcellio scaber* *Trichoniscus pusillus*
Nematodes	*Plectus parietinus*
Protozoans	*Colpoda cucullus*
Animal-Hyperacculators	*Crassostrea virginaca* *Mytilus edulis* *Pinetada albino albina* *Crassotrea rhizophorea*
Molluscs	*Pera viridis.* *Chione fluctifraga* *Mytilus edulis*
Sponges	*Chondrilla nucula* *Hymeniacidon perleve* *Halichondria panicea* *Spongia officinalis*
Arthropods	Carabid beetle *Poecilus cupreus* *Pterostchus oblogopunctatus*

Haimi, 2000; Okeke et al., 2014.

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SOME CASE STUDIES

Bacterial Bioremediation

Case 1

Singh and Fulekar in 2010 isolated *Pseudomonas putida* strain MHF 7109 for biodegradation of benzene, toluene and o-xylene (BTX). By this process, they successfully degrade BTX (50mg/L) within a time period of 48, 96, and 168 h, respectively, but higher concentration of BTX (250 and 500mg/L) repressed the action of microorganisms. 100 mg/L benzene and toluene was completely degraded within 120 and 168 h respectively where same concentration of o-xylene was degraded within 168 h by 62%.

Case 2

A pilot scale study was conducted by Mukherjee, & Bordoloi (2011) for the reclamation of petroleum oil hydrocarbons contaminated soil. Bacterial consortium (20% v/w) consisting three strains (*Bacillus subtilis* DM-04 and *Pseudomonas aeruginosa* M and NM) were used for these remediation processes for a period of 180 days. After the experimental period, results showed a significant degradation of contaminants in polluted soil by 76%. An ecotoxicity study by observing seed growth of Bengal gram (*Cicer aretinum*) and green gram (*Phaseolus mungo*) in contaminated and remediated soil was carried out where 72–74% seeds were germinated in the remediated soil (after 180 days experiment) which is very much similar to uncontaminated soil.

Case 3

In the year of 2013, Ahluwalia, & Goyal reported 100% removal of chromium (VI) from the metal processing industry effluent. In this study a non living biomass (*Aspergillus terreus*) was used as a biosorbent to remove chromium. Removal efficiency up to 10 cycles and 100% removal of metal up to 5 weeks made this process more cost-effective and commercially viable.

Case 4

Pilot scale studies were carried out at different oil refineries in India for the purpose of the removal of petroleum hydrocarbon. Four species of bacterial consortium were used for remediation of 48,914 tons of different types of oily waste. Initially, total petroleum hydrocarbon (TPH) content varied 83.50 to 531.30 gm/kg of oily waste in 44 contaminated sites. This process successfully degraded 10 gm/kg of oily waste within the time period of 2-12 months (Mandal et al., 2012).

Case 5

A new metal resistance lactic acid bacterial (LAB) strain was isolated (*E. faecium* Pb12) for the purpose of the removal of metal contaminants. This strain shows minimum inhibitory concentration of 120 mg/L for cadmium and 800 mg/L for lead. The researchers successfully removed cadmium and lead by

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0.0377 mg/h/g and 0.0460 mg/h/g of cells (wet weight) respectively. Thus, a potential metal resistant probiotic strain has been discovered which can be used for heavy metal removal from fish intestinal milieu (Bhakta et al., 2012).

Case 6

A mixture of 6 microbial consortiums was used for the remediation of oil contaminated area in upper Assam, India. From 2009 to 2010, they were able to remediate about 1210 metric ton (MT) and 5045 m^3 of contaminated soil and water respectively. After 7-13 months 74-90% degradation was occurred in soil and in case of water, 90% contaminants were degraded within 4-6 months (Agrawal et al., 2010).

Case 7

Mandal et al. (2012) utilized a four species of bacterial consortium for the degradation of TPH of the oily waste. After the period of 2-12 months of successful application of the microbial consortium, 95% degradation of TPH was occurred.

Case 8

Jové et al. (2016) studied on the degradation potentiality of anthracene in cork by three ligninolytic white-rot fungi and three non-ligninolytic fungi. *Aspergillus niger, Penicillium simplicissimum and Mucor racemosus* were selected as ligninolytic white-rot fungi and *Phanerochaete chrysosporium, Irpe lacteus and Pleurotus ostreatus* were selected as non-ligninolytic fungi. After 61 days of experimental period, *P. simplicissimum* was capable to degrade the highest amount of contaminant (86%) followed by *P. chrysosporium* (40%) and *I. lacteus* (38%) in cork.

Case 9

Mouhamadou et al. (2013) studied bioremediation of polychlorinated biphenyl (PCB) using different autochthonous filamentous fungal strains. From this research *Myceliophthora thermophila, Thermoascus crustaceus, Aspergillus fumigates, Doratomyces nanus, Phoma eupyrena, Doratomyces purpureofuscus, Doratomyces verrucisporus* strains showed >70% degradation ability of PCBs. Among all these strains *Aspergillus fumigatus* S2-9 has degraded 84.99% of PCB.

Case 10

Lee et al. (2015) carried out the bioremediation of Polycyclic Aromatic Hydrocarbons (PAHs) in Creosote contaminated Soil by *Peniophora incarnata* KUC8836 strain. After 2 weeks, concentration of phenanthrene, fluoranthene, and pyrene were degraded by 86.5%, 77.4%, and 82.6% respectively. Total initial PAHs concentration (229.49 mg/kg) was reduced by 85.7% after 4 weeks of incubation period.

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Algal Bioremediation

Case 1

El-Sheekh et al. (2016) treated a mixture of wastewater (sewage, sea and well) by fresh water (*Chlorella vulgaris*) and marine (*Chlorella salina*) algae. Both alga species were successfully reduced total dissolved solids (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), nutrients concentration (nitrate, ammonia, phosphate, sulphate, calcium, magnesium, sodium, potassium) and heavy metals concentration (Zn, Cu, Mn, Ni, Co, Fe and Cr) after 10 days of experiment. Overall *C. vulgaris* was more efficient in pollutants removal than *C. salina*.

Case 2

Alcohol distillery wastewater treatment has been done by using a new strain of *Chlorella sorokiniana* using a high-density photobioreactor. 92.5% removal of COD, 95%, 77%, 35% removal of nitrate, phosphate and sulfate, respectively were achieved by this process (Solovchenko et al., 2014).

Case 3

Degradation of Triclosan, a widely used antimicrobial agent, was carried out by *Chlorella pyrenoidosa,* a ubiquitous green alga. After 96 h of experiment, 77.2% degradation was achieved. Degradation of Triclosan leads to the disruption of the chloroplast and the release of organic material into the aquatic body and thus affects the membrane metabolism.

Case 4

Spirulina platensis was successfully used as a biosorbent for the removal of azo dye, C.I. Basic Red 46 (C.I. BR 46). After 1 h of wastewater treatment, for the particular algal species maximum dye biosorption was accomplished as 25.46 mg/g (Deniza, & Kepekcib, 2015).

Case 5

An experiment on the bioremediation rate of deepwater horizon crude oil was carried out using *Aphanocapsa* sp., *Chlorella autotrophica*, *Coccochloris elabens*, *Dunaliella tertiolecta*, *Oscillatoria* sp., *Scenedesmus obliquus, Synechococcus elongatus* and *Volvox aureus*. Maximum 34.99% crude oil degradation was observed by *Coccochloris elabens*. Hence it can be concluded that algae is potential degrader of crude oil and can be flourish in the high crude oil environment (Cao et al., 2013).

Case 6

A pilot scale study was conducted for the treatment of chrome-sludge generated from electroplating industry. *Desmococcus olivaceus* (Persoon et Acharius) J.R. Laundon VIAT029 was utilized for the treatment process. In this open pond system TDS, total suspended solid (TSS), ammonia, nitrate, phosphate and chromium were successfully removed by the algal species (Sivasubramanian et al., 2010). Another

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pilot scale study as well as World's first phytoremediation plant has been established at Ranipet, India. From 2006 this pond is in operation. About 30-40 kiloliters of effluent has been generated from alginate industry every day and 100% sludge has been achieved by this process. A blue green alga *Chroococcus turgidus* has been used for this treatment process (Sivasubramanian, 2011).

Chlorella vulgaris was used for the treatment of raw effluent of a Confectionery industry in Tamil Nadu, India, which generates 50-70 kiloliters of effluent per day. Algal pretreatment has been employed at the flow rate of 3500 L/h before anaerobic digestion, because this pretreatment process helps to maintain pH, reduce BOD, COD and sugar level (Sivasubramanian, 2011).

Plant Mediated Bioremediation

Case 1

Reclamation of a 1600000 m^2 (approx.) metal-contaminated site known as Ahangaran lead and zinc mine of Malayer city, southwest of Hamedan, was successfully done by 12 plant species (*Euphorbia macroclada Boiss, Centaurea virgata Lam, Reseda lutea* L, *Echinophora platyloba DC, Cichorium intybus* L, *Tamarix ramosissima Ledeb, Cirsium congestum Fisch and C. A. Scrophularia scoparia Pennell, Chaerophyllum macropodum Boiss, Cardaria draba* (L.) *Desv, Scariola orientalis (Boiss.) Sojak, Reseda alba* L.). Mainly from the top 20 cm of the soil was contaminated with heavy metals such as Zn, Mn, Cu, Pb and Fe. These hyper accumulator plants showed suitable remediation efficiency for the reclamation of this contaminated site (Cheraghi et al., 2011).

Case 2

Phytoremediation of heavy metals was successfully done by *Typha latifolia, Eichhornia crassipes, Salvinia molesta and Pistia stratiotes* through constructed wetland. The source of effluent was a rare earth separating industry, Kerala, India, which contain high concentration of lead, arsenic, cadmium and copper. 100 x 45 x 45 (cm) plastic tubs were constructed for the remediation purpose. Lead, copper, arsenic and cadmium were significantly removed by *Typha latifolia, Eichhornia crassipes, Salvinia molesta and Pistia stratiotes* from the effluents of Travancore Titanium Products (TTP). Initial concentration of lead, arsenic, copper and cadmium in TTP effluent were 2.984 ± 0.021 ppm, 0.016 ± 0.004 ppm, 0.096 ± 0.012 ppm and 0.253 ± 0.019 ppm, respectively. (Sukumaran, 2013). Maximum lead was removed by *Eichhornia* sp. (1.012 ± 0.11 ppm residual), arsenic, copper and cadmium by *Typha* sp. (0.002 ± 0.0003, 0.024 ± 0.002 and 0.102 ± 0.015 ppm residual).

Case 3

A highly sulfonated textile dye Remazol Red (RR) was completely degraded by a macrophyte (*Alternanthera philoxeroides Griseb*). Initial concentration of dye was 70 mg/L which was completely degraded within 72 h. Several enzyme activities like azoreductase and riboflavin reductase was found in the root and stem tissues respectively. On the other hand, lignin peroxidase, laccase and dichlorophenolindophenol (DCIP) reductase activity were present in leaf tissues (Rane, 2015).

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Case 4

Amaranthus dubus which is leafy high biomass content vegetable crop, effectively applied for decontamination of metallic elements such as Fe, Cd, Co, Pb, and Cr in Patancheru, Hyderabad, India. Its rapid growth and huge biomass content make it suitable for phytoremediation. *Amaranthus tricolor*, *Amaranthus dubius* wild I and *Amaranthus dubius* wild II were used in combination with Phosphate Solubilising Bacteria (PSB) and solely for the remediation purpose. *Amaranthus dubius* wild II accumulate 2.54 fold and 3.56 fold elevated Cr and Cd concentrations, respectively than control one. In the case of Co *Amaranthus dubius* wild I show highest accumulation than other treatment (2.70 fold than control). *Amaranthus tricolor* with the combination of PSB shows the highest removal of Pb (26.8 mg/kg) (Shankar, 2011).

Case 5

A heavy metal (Zn, Cu, Cr, Ni, Pb, Cd) contaminated area (6,667 m^2) in Chang-Hwa City, Taiwan, was selected for the decontamination of pollutants through plant species. *Jatropha curcas* was used for the remediation purpose. About 800 plants were planted with the density of 0.12 plant/m^2. From 0-30 cm depth, soil sample was collected. After 2 years of plantation, plant species were successfully removed Cd, Cr, Cu, Ni, Pb and Zn by 51.16, 12.80, 38.88, 14.10, 17.61, 17.88%, respectively (Chang, et al., 2014).

Animal Assisted Bioremediation

Case 1

Kaur & Hundal (2015) successfully established the metal accumulation potentiality of earth worm (*Eisenia fetida*). Organism was able to removal of 42.3%, 24.5% and 8.5% for lead, chromium and nickel respectively from contaminated soil. This experiment was carried out in the contaminated soil collected from the vicinity of Buddha Nullah at Ludhiana.

Case 2

Cadmium was removed by the *Anodonta woodiana* from cadmium contaminated synthetic water. Cd was accumulated in different tissues of the mussels. Maximum Cd accumulation was found in the digestive gland (0.142 mg/g) followed by gills and mantle of the mussels. Though it is an experiment but make a print of evidence of pollutants accumulation by animal species (Bhakta & Munekage, 2008).

Case 3

Kundu et al. (2016) observed the accumulation of lead (Pb) in East Kolkata Wetland (22°27' N 88°27' E), India through fish (*Oreochromis niloticus)*. Lead concentration in fish *was* highest in intestine (0.0182 µg/mg) and lowest in fin (0.0004 µg/mg) with an order as intestine > liver > skin > muscle > scale > bone > fin.

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Case 4

Removal of phenol was successfully carried out by Mohan Krishna et al, 2011 using *Eisenia foetida*. Different concentration of phenol contaminated (20 to 100 ppm) were taken for the experiment. As a result *Eisenia foetida* established as a potential tolerant species for phenol removal than other two earthworm species (*Eudrillus eugenia* and *Anantapur* speciesand can uptake upto 100 ppm phenol completely with in 72hours.

Case 5

Eisenia fetida and green waste compost (GWC) were to desalinate a coastal saline soil (38° 46' N, 117°13' E) in Tianjin, North China. Mean annual temperature of this area is 14°C, where the mean monthly temperature ranges from -2 °C in January to 28 °C in July. Maximum soil salinization occurs during March-May moths in the topsoil. 60 number of *E. fetida* were used in per m^2 area and municipal waste was used as green waste compost which moisture content was 60% (w/w) and the C/N ratio of 25-30. Results revealed increased contents of humic acid, available N, and available P in the GWC-amended soil in reclaimed soil. Modeling from this study predict that total salt content of the saline soil would decrease by > 2 g/kg when 29-90 individuals per m^2 of *E. fetida* (Zhang et al., 2015).

Case 6

A successful bioremediation of polluted water was carried out in off the coastline of the urban center of Zanzibar-Stone Town by the implementation of sponge and pearl oyster mariculture. The experiment reveals the strong pollution filtration abilities of both species. Sponges and oysters help to decrease the phosphate concentration of polluted water from 3.93 ug/L to 1.33 and 1.73 ug/L, respectively. Marine sponges also reduce the turbidity level within 36 h (Oakland, 2013).

Waste Based Bioremediation

Case 1

Hara et al. (2013) used food waste compost in order to remediate oil contaminated site in Japan. Bioremediation was carried out in an oil factory site in Japan from the month of August to November, 2006. Climatic condition such as temperature was recorded as 9.5 to 31.5 °C and precipitation was 0 to 50.5 mm per day during the experiment time. The experiments were carried out taking 2,000 kg of contaminated soil in 4 sections in such as control section, compost section (3.8% [w/w] compost), chemical nutrient section (0.5% [w/w] ammonium sulphate and 0.1% [w/w] phosphorus fertilizer), mushroom section (3% [w/w] *Merulius tremellosus*) and biofertilizer section (0.2% [w/w] bionutrients and TerraXyme). In the food waste compost treatment maximum degradation was occurred from the concentration 4,700 ppm to 2,300 ppm of TPH after 74 days followed by other treatments.

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Case 2

In the Southeast of Mexico, drilling mud-polluted site (contaminated with petroleum hydrocarbons) was reclaimed by composting in biopiles with addition of urea and K_2HPO_4 were added as nitrogen and phosphorous sources to achieve optimum C/N/P ratio. Biopiles were amended with the addition of nutrients to get a C/N/P ratio of 100/3/0.5 and straw as a bulking agent (30 kg of bulking agent per each ton of soil). A polluted mudpit site near an oil well drilled in the early 1970s, at the Mexican State of Tabasco was chosen for the remediation purpose. The average atmospheric temperature was in the range of 26 °C to 35 °C during the experimentation period. Soil was clay loam and slightly alkaline (pH 7.9) in nature with the water content of 25% and an existing C/N/P ratio of 6089/76/1. Average TPH concentration of contaminated soil was 99300 ± 23000 mg per kg soil. After 180 days TPH concentration was reduced by 77% (22900 ± 7800 mg per kg soil as residue) in the soil (Rojas-Avelizapa et al, 2007).

Case 3

Three types of organic wastes such as goat manure, poultry droppings and cow dung, were used for the treatment of oil contaminated soil due to pipeline vandalization and local refinery activity, collected from Isaka Mangrove, in Okirika Local Government Area of Rivers State, Nigeria. Organic wastes were mixed with the soil in the ratio of 10/1 (soil/organic waste). Total count of heterotrophic bacteria, hydrocarbon utilizing bacteria and heterotrophic fungi were increased gradually during the experimental tenure while TPH concentration were decreased by 87.1%, 76.6%, 70.7%, and 32.1% after treated with goat manure, poultry droppings and cow dung, respectively after the 28 days experiment (Obiakalaije et al., 2015).

CONCLUSION AND FUTURE PROSPECTS

Bioremediation is a natural way to clean the environment without having any adverse effect on the society. As the process involves all the biological organisms, such as bacteria, fungi, algae, plant and animals, it is considered as a safe technology, environmental friendly and aesthetically pleasant and also of low cost as compared to other physical or chemical treatment methods. These agents effectively remediate pollutants from contaminated matrix by the diverse mechanism of absorption, adsorption, precipitation, enzymatic hydrolysis, detoxification and degradation. Each and every agent has particular niche and unique mechanism to deals with the contaminants. It is very easy to implement and maintain and also can be done on-site or off-site. Though there several benefits but the process is not without its drawbacks, long time taking, limitation in contaminants degradation, difficult to extrapolate from bench and pilot scale study, lack of potential biological agents, lack of proper knowledge are the main setback of bioremediation process.

Prior to go for bioremediation, meticulous knowledge of the environment must be taken and proper selection and characterization of the bioremediation agents should be done. Time taking nature of the process can be overcome by the development of modified versions of the species by the help of biotechnological techniques which may serve very effective, less time consuming process. It will also enhance the capacity of the agents for biotransformation of most toxic contaminants present in the environment. Recently, application of potential biological tools in designing the engineered ecosystem for the benefit

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of both human and environment is an emerging field. On the basis of decontamination efficacy of various useful biological tools/component, the ecosystem can be designed following the ecological engineering technology, which would be an important environmental friendly solution for cleaning up the contaminated domain of the environment.

Future research in the area of protocol evaluation, innovative site characterization techniques, model improvement and the capabilities of bioremediation to deep will open the new frontiers in bioremediation. Special focus on understanding the biological agent's communities, their responses towards natural environment and pollutants, technology development for the degradation of complex mixture of contaminants may open the new door in bioremediation history. On the other hand a wide variety of potential bioremediation agents are waiting to be explored. However with the existing laboratory scale process development, field trials of the technology for the remediation of organic compounds, metals, metalloids, radionuclides and complex polycyclic hydrocarbons should be employed immensely. Improvement of the microbial genomics studies will be providing several robust technologies for the bioremediation of contaminated waters and land contaminated with metals. Though, the concept of potential biological tool based-engineered ecosystem is in very infancy stage, it has significant future prospect in sustainable development of pollutants free environment.

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KEY TERMS AND DEFINITIONS

Biological Tools: It refers to organisms or biological substances used in any systems.

Bioremediation: It is an eco-friendly biological process employed in remediation of environmental problems (such as, pollution, contamination, etc.) using biological system or organisms.

Contaminants: Presence of unwanted substances in any matrix which cause several physicochemical changes and made the substrate polluted, toxic, unsafe, harmful to environment as well as causes health hazards.

Decontamination: The process involved in the elimination or neutralization of contaminants.

Eco-Friendly: It refers to method or product or system having no negative impacts on environment.

Ecological Engineering: It refers to an emerging technology for designing the sustainable ecosystem by integrating human society with its natural environment for the benefit of both or the fusion of engineering and ecology for the development of human and environment by the design, construction and management of ecosystems which are beneficial for both human and environment.

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Ecosystem Services: Services provided by the ecosystem by the means of provisioning, regulating, cultural and supporting services. This is a self-regulating mechanism driven by the ecosystem components which fulfill the basic needs of human beings.

Living Machine: Biotic system or organisms used in bioremediation process to protection environment from degradation/destruction.

Phytoremediation: Use of different types of plants in the bioremediation, such as purification of wastewater, air and reclamation of contaminated soil are known as phytoremediation.

Zooremediation: It is a kind of bioremediation process driven by the animal systems using the mechanism of uptake, accumulation, and transformation of contaminants.

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Chapter 55
Effective Management of Agro-Industrial Residues as Composting in Mushroom Industry and Utilization of Spent Mushroom Substrate for Bioremediation

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ABSTRACT

Different types of edible mushrooms like Agaricus, bisporus, A. bitoriqus, Pleurotus spp., Volvariella volvacea, Lentinula edodes, Calocybe indica, Flamullina, Ganoderma lucidum etc. are cultivated in industrial scale. Majority of edible fungi secretes extracellular Ligninocellulolytic enzymes like Laccase, lignin peroxidase, manganese peroxidase, cellulase etc. for effective conversion of ligninocellulolytic substrate to compositing form which led to fruiting of mushrooms. Consequently, an adequate disposal method is needed for the high quantities of spent mushroom substrate (SMS) generated in this agro-food industrial activity. On the other side, textile industry among the largest water consuming industries in the world and approximately, 10,000 different dyes and pigments are used at industrial scale. It is estimated that nearly 40% of the total dyes used in the dyeing process may find their way in wastewater. So, there is an attempt to utilize the ligninolytic enzymes rich SMS of different mushroom for efficiently biodegradation of textile wastewater & polyaromatic pollutants.

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1. INTRODUCTION

Mushroom cultivation is a common practice all over the world and is a major income source in China and other developing countries which also suffer from serious pollution. Total edible species of mushrooms are approximately 2000 and total edible species under cultivation are nearly 20 at commercial level. World mushrooms production annually is greater than 25 million ton (Li, 2012). Total annual mushroom production in India is 1, 20, 000 tons (DMR, 2014). Annually, world production of major lignocellulolytic biomass waste is around 1088.258 million tons (FAO). Mushroom cultivation offers a highly efficient method capable of not only biodegradation and bioremediation of agro-industrial waste but also biotransformation into proteinaceous food that can sustain food security in the developing countries (Ingale & Ramteke 2010; Narain et al. 2011; Philippoussis & Diamantopoulou 2011; Kulshreshtha et al. 2010). Many basidiomycetes fungi are edible mushrooms whose industrial production generates significant amount of spent mushroom substrate (SMS) with residual high levels of lignin-degrading extracellular enzymatic activities. Annual spent mushroom substrate required to be disposed of in India is around 6,00,000 tons (Table 1) . Spent mushroom substrate (SMS), has recently gained importance because of its unique physical, chemical and biological properties. Spent mushroom substrate (SMS) is a biomass waste generated from mushroom production. About 5 kg of SMS is generated for every kg of mushroom produced (Williams et al., 2001). Spent mushroom substrate (SMS) is the substrate left over after mushroom harvesting. The rapid growth in mushroom production worldwide has resulted in large quantities of SMS (about 13.6 million tons per year) (Williams et al., 2001; Uzun, 2004). These massive amounts of waste can cause environmental problems, which has led to increased research to develop technologies for treating these type of waste substrate. SMS mainly contains lignocellulosic materials, such as sawdust, wheat straw, paddy straw, wheat bran, chicken manure and cotton seed hulls, which have been decomposed and permeated by mycelium.

The composting of spent mushroom substrate yields a product that is valuable for agricultural utilization and soil reclamation. Mushroom produces don't reuse this spent mushroom substrate (SMS), because disease incidence, nutrient depletion and growth factor depletion. SMS has rich heterogeneous microbial populations with remains of mushrooms mycelia, actinomycetes and bacteria. It has a high organic content and low concentration of essential plant nutrient contents.

Activities in mushroom industry is steadily growing, the quantity of mushroom waste (SMS) generated annually is increasing. In recent years, the mushroom industry has faced challenges in storing and disposing these waste substrates. The obvious solution is to explore new applications and development of new technologies for the management and effective utilization of SMS. In last decades, there has been considerable discussion recently about the potential of using SMS for bioremediation of environmental pollutants.

The increasing industrialization has specially put pressure on natural resources like water bodies, agricultural land and the physical area by adding unwanted chemicals in the environment. The manufacturing and use of dyes and pigments is a multibillion-dollar industry. The use of these chemicals is an integral part of almost all manufacturing processes. Dyes are synthetic chemical compounds having complex aromatic structures, which are extensively used in the textile, cosmetics, plastic, food, paper printing, colour photography and pharmaceuticals industries. Approximately 10,000 different dyes and pigments are used at industrial scale and over 0.7 million tonnes of synthetic dyes are produced annually, worldwide (see Figure 1 and Table 1).

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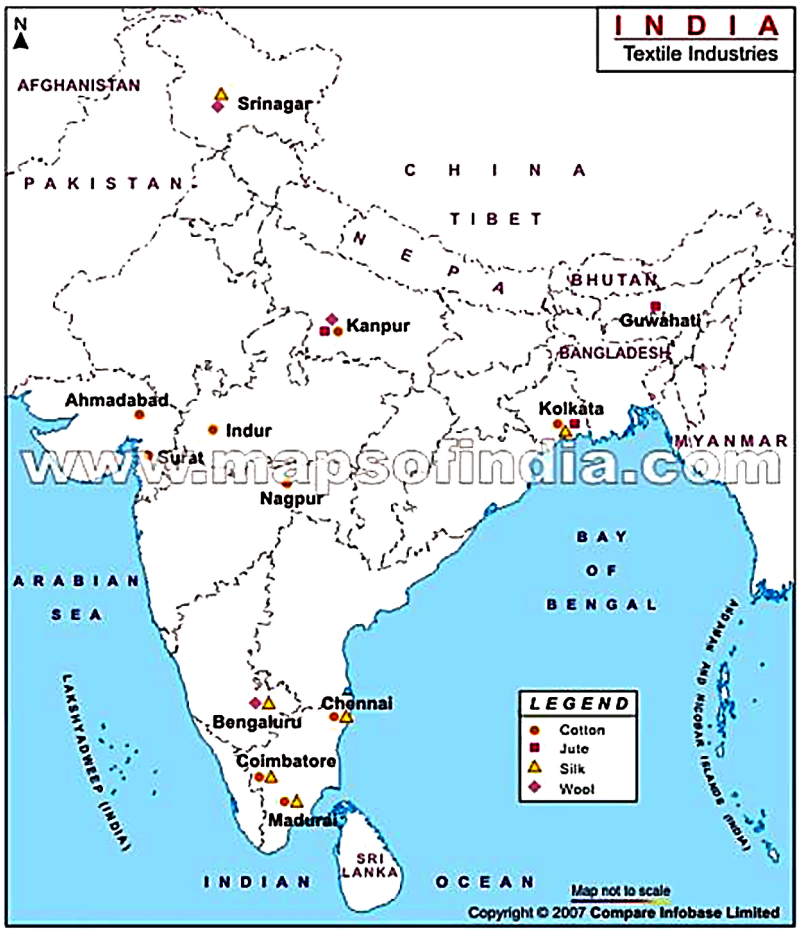
Figure 1. Location of major textile industries in different parts of India



When such wastewater effluent is discharged onto the land adjoining the agriculture crops, it causes the gradual deterioration of land quality and ultimate reduction in crop yields. Colour is the first recognised contaminant in textile wastewater and has to be removed before discharging it into receiving water body. Among various industrial effluents involved in an increase of chemical load (COD) of water systems, effluents from textile dyeing industries are the major source, resulting discharge of coloured water causing toxicities to aquatic life. The presence of a variety of dyes in the wastewater emanating from textile dyeing industries is a serious concern because of their resistance to environmental conditions like light, temperature and pH, resulting in low biodegradability. The presence of high level of heavy metals viz., copper, zinc, cadmium, chromium in wastewater further aggravates the problem. Available physical and chemical methods used for wastewater treatment have limitation due to high cost, low efficiency and in-applicability to a wide variety of dyes. Hence feasible and environmental friendly approach that is Bioremediationis used. The use of microorganisms to detoxify environmental pollutants is generally referred as bioremediation. Environmental issues are now of increasing concern and biological methods are being more directed towards technologies to minimize pollution or to remediate it if it occurs. Mushroom species like, *Pleurotus*, *Agaricus*, *Volvariella, Lentinula, Ganoderma* spp. along with white rot fungi and their ligninolytic enzymes appear to have wide industrial applications (Figure 2).

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Table 1. Worldwide annual mushrooms production and spent mushroom substrate (SMS) waste generation

S.No.	Country	Crop	Annual mushrooms production (tonnes)	Approximate spent mushroom substrate production (tonnes) (Annual mushrooms productions × Five times SMS)(tonnes)
1.	Australia	Mushrooms and truffles	49954.00	249,770.00
2.	India	Mushrooms and truffles	40000.00	200,000.00
3	Belgium	Mushrooms and truffles	42000.00	21,0000.00
4	China	Mushrooms and truffles	7076842.00	35384210.00
5	Taiwan	Mushrooms and truffles	8700.00	43,500.00
6	South Korea	Mushrooms and truffles	5700.00	28,500.00
7	Denmark	Mushrooms and truffles	10936.00	54680.00
8	France	Mushrooms and truffles	104621.00	523105.00
9	Germany	Mushrooms and truffles	59884.00	299420.00
10	Hungary	Mushrooms and truffles	19000.00	95,000.00
11	Indonesia	Mushrooms and truffles	39682.00	198410.00
12	Iran	Mushrooms and truffles	87675.00	438375.00
13	Ireland	Mushrooms and truffles	63600.00	295,000 (Barry et al. 2012)
14	Israel	Mushrooms and truffles	10000.00	50,000.00
15	Italy	Mushrooms and truffles	792000.00	39,96000.00
16	Japan	Mushrooms and truffles	61500.00	
17	Netherlands	Mushrooms and truffles	323000.00	800,000 (Oei and Albert 2012).
18	New Zealand	Mushrooms and truffles	10116.00	307500.00
19	Poland	Mushrooms and truffles	220000.00	11,00000.00
20	Republic of Korea	Mushrooms and truffles	25502.00	127510.00
21	South Africa	Mushrooms and truffles	14284.00	71420.00
22	Spain	Mushrooms and truffles	149700.00	825,000.00 FAO, 2007
23	United Kingdom	Mushrooms and truffles	79500.00	397500.00
24	United States of America	Mushrooms and truffles	406198.00	2030990.00
25	others	Mushrooms and truffles	Nearly 400000.00	2000000.00

Source= FAOSTAT 2013

The biotechnology based processes involving dead or live microbial cells or their components, as biota agents are more user friendly under such conditions, as these restrict the introduction of new forms of chemicals in the environment. Mushroom cultivation is an eco-friendly method of converting a wide range of agro-residues and agro-industrial wastes in to a protein rich food in the form of mushrooms. After several cycles of mushroom cultivation, the mushroom productivity decreases and the residual by-product, generated in the form of spent mushroom substrate (SMS) required to be properly disposed of to maintain hygiene and avoid environmental problems. If not properly disposed of, it leads to environmental problems, such as soil and water contamination, due to high load of organic carbon, nitrogen and salt in SMSs of different mushrooms. The biological component of SMS is also very important,

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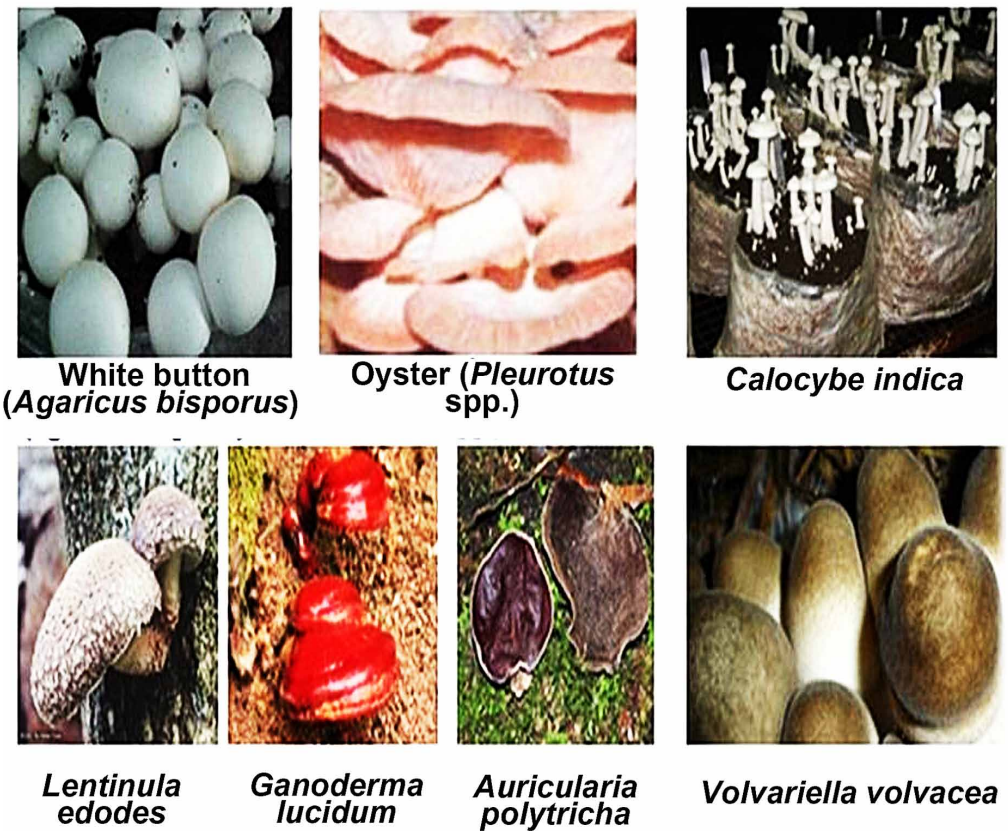
Figure 2. Different species of edible mushrooms cultivated in India and worldwide



as it is constituted of mushroom mycelial biomass along with high population of heterotrophic bacteria, actinomycetes and the fungi having potential to produce full range of ligninolytic enzymes (Singh et al., 2013a, 2013b). The past studies have also supported the role of laccase, lignin peroxidase and manganese dependent peroxidase along with some more enzymes in decolourisation of colouring dyes. Highly immobilized microbial cultures in the form of SMS tend to have a higher level of bioremediative activity and are more resilient to environmental perturbations such as pH and toxic chemicals than the suspended cultures. Besides this, the immobilized cultures offer other advantages like reusability of the same biocatalyst, control of reactions, and the non-contamination of products. Immobilized form of living microorganisms have also been described more effective in biological wastewater treatment and treatment of polyaromatic hydrocarbons than the suspended form of microorganisms. The overall objective of this book chapter is to introduce with the effective management of agriculture waste residue for mushroom composting and waste generated from mushroom can be efficiently used for treatment of textile wastewater and polyaromatic hydrocarbons or others pollutants which led to bioremediation of environmental pollutants and generation of green technology.

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2. CURRENT STATUS OF MUSHROOM CULTIVATION

Worldwide, the top three mushroom species cultivated are the white button mushroom (*Agaricus bisporus*), shiitake (*Lentinula edodes*) and oyster mushroom (*Pleurotus* spp.) (Suguimoto et al. 2001; Li 2012). Cultivation of these mushrooms represents a major industry in the countries of Southeast Asia (Mehta et al. 1990; Ragunathan & Swaminathan 2003). Amongst the different cultivated species, genus *Pleurotus* is an industrially important and occupying a third place in worldwide production of edible mushrooms, i.e., 16.3% of the total production (Chang, 1996). *Pleurotus* spp. can grow and produce fruit bodies in temperate and tropical zones and does not require any pretreatment of substrate. The production of *Pleurotus* spp. results in a large amount of protein (as extra-cellular enzymes) on substrates consisting primarily of wide agro-industrial and forestry waste materials (Poppe, 2000). In South Korea, the area of mushroom cultivation has increased to 1,102 km^2 and 117,600 t of mushroom was produced in 2000 (Ko et al., 2005). It has been reported that approximately five times of SMS is produced in South Korea annually, of which 58% is from *Pleurotus ostreatus* cultivation.

In the United States, the annual production of *Pleurotus* spp. has reached 880 t in 1996 and it has increased by 120-fold in 2002 (Royse et al., 2004). In 2010/2011, the oyster mushroom production has exceeded 3,700 tonnes in the United States (United States Department of Agriculture 2012). In Ireland, mushroom production is an appreciable industry and has been estimated to contribute approximately £90 million to the economies of both Northern Ireland and the Republic of Ireland. In Northern Ireland, 24,000 t of mushrooms are produced annually, offering 3,000 jobs to the nation. (Russell et al. 2005; Williams et al. 2001).

3. PRESENT WORLDWIDE SCENARIO OF SPENT MUSHROOM SUBSTRATE

Wheat straw, the above-ground biomass remaining after wheat harvest, was estimated to be around 70.9 million tons only in the U.S (Johnson et al., 2006). Individually, yard trimmings and wheat straw have exhibited low degradability due to their lignocellulosic recalcitrance (Cui et al., 2011; Zhao et al., 2014a).Although paddy straw, wheat straw, soybean, wheat bran, chicken manure are the traditional substrates for*Agaricus* spp.*Pleurotus* spp., different biological efficiencies (BE) have been reported by various authors (Ragunathan et al., 1996; Zhang et al., 2002). Other non-traditional substrates used alone or in combination with the traditional substrates include cotton stalks (BE, 32.69–41.42%) maize stover (BE, 25.18–35.39%), coir pith (BE, 26.11–27.33%), sorghum stover (BE, 32.17–36.84%), saw dust (BE, 73.5%), banana leaves (BE, 10.25%), mango leaves (BE, 5.96%), bagasse (BE, 34.29–41.31%), peanut shell, corn cobs, coffee pulp, *Eupatorium adenophorum, Populus deltoids* etc. (Ingale & Ramteke 2010; Moonmoon et al. 2010; Patrabansh & Madan 1997; Ragunathan & Swaminathan 2003). *Pleurotus sajor caju* is grown commercially on supplemented rubber-wood sawdust. For every 200 g of mushroom produced, about 800 g of spent mushroom substrate (SMS) is available. An average farm discards about 24 tons of SMS per month. The SMS consists of mycelium, extracellular enzymes produced by fungus during growth and unutilized lignocellulosic substrate. The disposal of SMS is a major problem to farmers. Of the total spent compost produced in Malaysia, 69% is dumped in landfill sites, 28% is applied to agricultural land and remaining 3% is incinerated (Vigneswaran et al., 1997). However, most spent compost is produced in large urban areas and it can be extremely expensive to transport it to farming areas where it is given free to farmers. A further difficulty is that farmers only require compost at certain

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times of the year whereas spent compost is produced all year round. On the other hand, the incineration of compost is an alternative method of disposal whereby it offers a large reduction in the volume of the solid waste to be disposed of, along with the elimination of nuisance from biological decomposition. The method of incineration requires smaller space, relatively to land application but has the disadvantage of generation of ash (25 - 40% of the incoming load on a dry basis) which can have high polluting qualities (Vigneswaran et al., 1997). As both the main methods currently employed for the disposal of compost has some drawbacks, it becomes necessary to explore new applications of the spent mushroom compost.

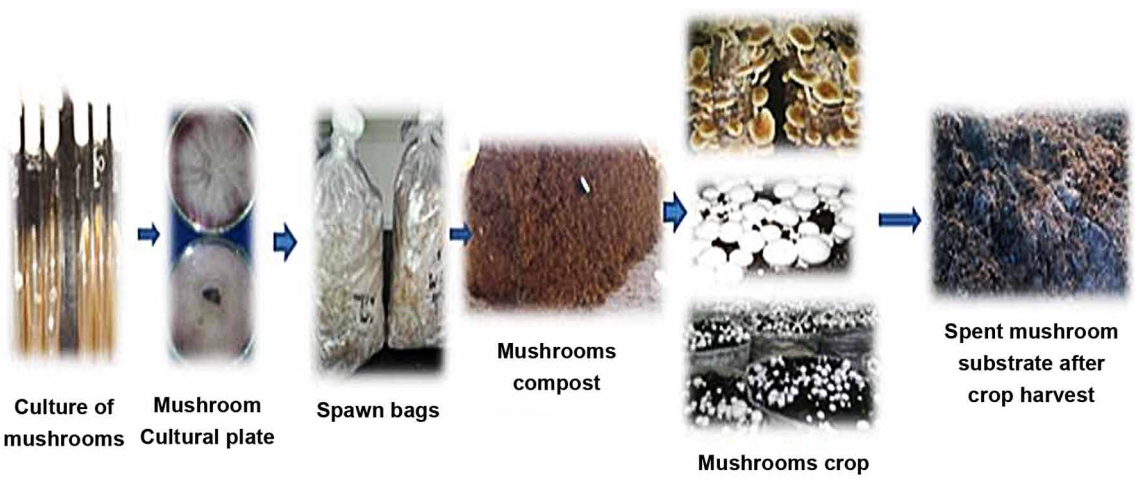
SMS is commonly made from renewable agricultural residues such as sawdust, sugarcane bagasse, oil palm empty fruit bunch, wheat straw-bedded horse manure, hay, poultry manure, ground corncobs, cottonseed meal, cocoa shells, gypsum and other substances (Jordan et al., 2008). One of the main difficulties in the management of SMS is the lack of waste management supervision (Magette et al., 1998).

The current largest mushroom producer of mushrooms, China has attained more than 20 mt and accounted for over 80% of the world's mushroom production (Li, 2012). An average farm discards about 24 t of SMS per month (Singh et al. 2011). In Ireland, approximately 254,000 t of SMS is generated each year (Barry et al. 2012) and in The Netherlands, more than 800,000 t of SMS is produced per year (Oei & Albert 2012). In some countries, waste management of SMS is a major problem faced by farmers. Apparently, the obvious solution is to increase the demand for SMS through exploration of new applications for utilization (Figure 3).

4. PHYSICO-CHEMICAL PROPERTIES OF SPENT MUSHROOM SUBSTRATE (SMS) OF DIFFERENT MUSHROOMS

The major physico-chemical properties of fresh spent mushroom substrate of different mushrooms were determined and the pH of spent substrates varied between 7.7 in *Agaricus bisporus* to 6.8 in *Pleurotus sajor-caju* SMS. Moisture content was higher (64%) in SMS of *Agaricus bisporus*, followed by spent

Figure 3. Schematic diagram for development of mushroom culture, spawn, compost, cultivation and spent mushroom substrate generation



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substrate of *Pleurotus sajor-caju* (55%). Moisture content (64%), Nitrogen (1.8%), Sodium (105 ppm), Potassium (275 ppm) and Calcium (1045 ppm) were higher in spent substrate of *A. bisporus* (Table 2) compared to SMS of *P. sajou-caju* with an exception of Carbon (33.2%). The values of Carbon, Nitrogen, Sodium, Potassium and Calcium were 42%, 1.7%, 48 ppm, 134 ppm and 896 ppm, respectively in spent substrate of *Pleurotus sajor-caju.* These results indicate that spent substrate of both *Agaricus bisporus* and *Pleurotus sajor-caju* provides good nutrient source for the growth of different bacteria and fungi (Table 2).

5. MICROFLORA OF SPENT MUSHROOM SUBSTRATE

SMS is the left over substrate after harvesting mushrooms; it is harboring both bacteria and fungi. The microorganisms from SMS were characterised as *Enterobacter sp, Bacillus polymxa, Micrococcus roseus, Citrobacter fruedi, Bacillus subtilis, Clostridium perfringens, Pseudomonas aeruginosa, Bacillus cereus, Bacillus licheniformis, Escherichia coli* (Table 3)and the fungi fromSMS were characterized as *Trichoderma hazianum, Trichoderma polysporum, Trichoderma viride, Pencillium janthinellum, Mycogene perniciosa and Aspergillus bisporus* (Viji et al., 2003). All the three SMS namely, *Agaricus bisporus*, *Pleurotus* spp., and *Volvariella volvacea* have fungal isolates namely *Penicillum* spp, *Rhizopus* sppand *Aspergillus niger* with potential for dye decolourization (Table 4). Among these,*Aspergillus niger* showed greaterdecolourization potential during 16 days incubation. Decolourization may be due biosorption,which is dependent on functional groups in the dye molecule in fungal biomass. The SMSisolates are able to decolourize and detoxify highly concentrated effluent (Manikandan et al., 2012). The catalytic stability is often improved by immobilization, microorganisms may degrade higher concentration of toxic components than their free cell counterparts.

6. BIOREMEDIATION OF POLYAROMATIC HYDROCARBONS BY SPENT MUSHROOM SUBSTRATE

Bioremediation of PAH-contaminated soils is based either on the biostimulation of the indigenous microbiota (Sayara et al., 2010) or on the addition of exogenous microbes, the latter approach being

Table 2. Physico-chemical properties of spent mushroom substrate (SMS) of different mushrooms

Physico-Chemical Properties	Spent Mushroom Substrate	
	Agaricus bisporus	*Pleurotussajor-caju*
Moisture (%)	64.00	55.00
pH	7.70	6.80
Total Nitrogen (%)	1.8	1.70
Total Carbon (%)	33.2	42
Sodium (ppm)	105.00	48.00
Potassium (ppm)	275.00	134.00
Calcium (ppm)	1045.00	896.00

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Table 3. Bacterial population in spent substrate of different mushrooms

Spent Substrate	Bacteria Isolates	Isolates Identified by Gene 16S rRNA Gene Sequencing
A. bisporus CFU[(16.1×10^7)/ml]	DMRB-3	*Bacillus subtilis*
A.	DMRB-1	*Bacillus pumilus*
A.	DMRB-6	*Sphingobacterium multivorum*-I
A.	DMRB-7	*Sphingobacterium multivorum*-II
P. sajor-caju CFU[(35.74×10^7)/ml]	DMRB-2	*Bacillus licheniformis*
	DMRB-4	*Bacillus subtilis*
	DMRB-9	*Rummelibacillus stabekisii*
	DMRB-10	*Pseudomonas fluorescens*-I
	DMRB-11	*Pseudomonas fluorescens*-II
V. Volvacea CFU[(29.6×10^7)/ml]	DMRB-3	*Bacillus pumilus*

Table 4. Fungal population in spent substrate of different mushrooms

Spent Substrate	Fungal Isolates	Isolates Identified by Gene 5.8S rRNA Gene Sequencing
Agaricus bisporus CFU[(5x10^4)/ml]	DMRF-1	*Aspergillus fumigatus*
Pleurotus sajor-caju CFU[(14.5x10^4)/ml]	DMRF-2	*Aspergillus fumigatus*
	DMRF-7	*Schizophyllum commune*
	DMRF-8	*Pezizomycotina* sp.
Volvariella volvacea CFU[(4x10^4)/ml]	DMRF-6	*Aspergillus fumigatus*
	DMRF-4	*Paecilomyces variotii*
	DMRF-5	*Pichia guilliermondii*

referred to as bioaugmentation (Haritash & Kaushik, 2009). Bioaugmentation with lignin-degrading fungi (LDF) to perform the clean-up of PAH-contaminated soils has received increasing attention in recent years due to its reported efficacy (Covino et al., 2010b; Federici et al., 2012a). LDF are known to produce extracellular lignin-modifying enzymes (LME) with low substrate specificity which enables them to degrade a wide range of organic pollutants, including PAH (Covino et al., 2010c). The main LME enzymes include multi-copper oxidases, such as laccase, and heme-peroxidases (Mn-peroxidase (MnP), versatile peroxidase and lignin peroxidase).Contaminant degradation by Lignin degrading fungi (LDF) in soil requires the addition of lignocellulosicmaterials either as amendments, or inoculum carriers (Covino et al., 2010a). The use of these additives has been found to have a favorable impact on the resident microbiota, including specialized populations (Federici et al., 2012a). PAH degradation via bioaugmentation with LDF has been shown to involve either synergistic or antagonist interactions between the fungi added and the autochthonous microflora.

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The use of spentmushroom substrate of some ligninolytic fungi as a source of viable inocula for soil clean up applications has been proposed (Li et al., 2012). However spent *Agaricus bisporus* substrate (SAS), without previous treatment, has never been used for bioremediation of PAH polluted soil. Spent substrate of *Agaricus bisporus*, has been shown to enhance the ability of the fungi to endure the toxic effects of both cadmium and lead in a PAH-contaminated substrate (García-Delgado et al., 2013a). Marín-Benito et al., (2014) reported the ability of pesticide degradation by spent substrate of *Agaricus bisporus*used as composted with spent substrate of *P. ostreatus*(75:25) and its adsorption capacity for fungicides with low polarity that reduce their mobility in the environment. In addition, spent substrate of *A. bisporus* has been reported to be an excellent source of LME, mainly laccase that were able to biodegrade PAH in aqueous solutions (Mayolo-Deloisa et al., 2011). The annual production of this organic waste in Europe has been estimated at 3.5 × 106 t (Pardo-Giménez & Pardo-González, 2008) consequently its potential use in bioaugmentation applications would certainly help to reduce this amount (Table 5).

This needs a variety of manipulations of the waste prior to its application, to gain more insight into its ability to act as an organic amendment, fungal carrier or a supplier of exogenous complex microbiota or microflora.The addition of the sterilized spent *A. bisporus* substrate to polluted site was effective in stimulating the resident soil bacteriawhich resulted in higher levels of 3-ring PAH being removed. Bio-augmentation treatments with spent substrate of *A. bisporus*, were more effective in removing 5, 6-ring PAH. The wide availability of this agro-waste combined with its proved efficacy in PAH biodegradation make its use technically feasible for environmental remediation purposes. Another field of the use of spent mushroom substrate from commercial production of edible fungi is bioremediation of soil contaminated with different organopullutants. Spent substrate of *A. bisporus* was successfully used in remediation of soil contaminated with chlorophenols, hydrocarbons and volatile organic compounds (Semple et al., 2001). The ability to degrade chemically different compounds was attributed to the extracellular enzyme systems (lignin peroxidase, manganese-dependent peroxidase and laccase) and production of reactive free radicals (Field et al., 1993). Several species of cultivated and medicinal mushrooms (e.g. *Pleurotus ostreatus*, *Agrocybe aegerita*, *Kuehneromyces mutabilis*, *Trametes versicolor, Stropharia rugosoannulata* were also found to be able to degrade different organopollutants (Sack & Fritsche, 1997; Song, 1999).

Many factors influence the effectiveness of fungal soil bioremediation and one such include the concentration of respective pollutants in the soil. Eggen (1999) successfully applied spent oyster mushroom substrate to remediation of soil with initial concentration of poly -aromatic hydrocarbon of 1900 mg/kg. In this study we used a similar substrate for remediation of soil in which PAH concentration was three times as high. Polycyclic aromatic hydrocarbons (PAHs) belong to a class of organic compounds that are persistent and recalcitrant in the environment. Biodegradation of PAHs especially by white-rot fungus *Pycnoporus sanguineus* is considered environmentally friendly when compared to the conventional physical–chemical remediation which might lead to secondary contamination and the need for additional post-treatment (Annuar et al. 2009). Similarly, Vikineswary et al., (2006) have shown that a higher laccase productivity (7.60 U/g substrate) during solid substrate fermentation of sago hampas was achieved as compared to oil palm frond parenchyma tissue (7.52 U/g substrate) and sawdust (5.68 U/g). The capacity of *P. sanguineus* to remove PAHs like anthracene, phenanthrene and pyrene was attributed to the enzyme laccase secreted (Munusamy et al., 2008).

Now, the potential of SMS in bioremediation of PAH has attracted more attention. Bioremediation by employing crude extracts containing PAH-degrading enzymes from SMS are supposed to be more economical compared to pure enzyme/s. Purification of pure enzyme is often expensive and has limited application in bioremediation. However, it could not be a one-to-one relationship between PAH degra-

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Table 5. Bioremediation of pollutants by spent mushroom substrate

S.No.	Type of Spent Mushroom Substrate	Type of Pollutants	References
1.	*Pleurotus sajor-caju*	Textile dyes	Singh et al., 2010, 2011
2.	*Pleurotus* spp. *Agaricus bisporus*	Phenolic and non-phenolic aromatic compounds	Rodriguez et al., 2004 Trejo-Hernandez et al. (2001)
3.	*Pleurotus pulmonarius*	Removal of petroleum from industrial soil	Chiu et al., 2009
4.	*Pleurotus pulmonarius*	Biocide pentachlorophenol	Law et al., 2003
5.	Mixed spent mushroom substrate	Polycyclic aromatic hydrocarbons	Garcia Delgado et al., 2013
6.	*Pleurotus ostreatus*	Creosote contaminated soil	Eggen, 1999
7.	Mixed spent mushroom compost	Detoxification and benzo(a)pyrene	Russo et al., 2012
8.	*Lentinus polychrous*	Remazol brilliant blue R	Khammuang et al., 2007
9.	*Pleurotus ostreatus*	Polycyclic aromatic hydrocarbons	Ayotamuno et al., 2010
10.	*Agaricus bisporus* *Agaricus bisporus* (75%) and *Pleurotus* sp. (25%) *Pleurotus pulmonarius*	Fungicides Biocide and fungicides Fungicides	Ahlawat et al., 2010 Kadian et al. (2008) Chiu et al. (1998) Law et al. (2003) Córdova Juarez et al. (2011)
11.	*Pleurotus ostreatus*, *P. eryngii*, and *P. cornucopiae*	Remazol brilliant blue R and Congo red	Lim et al., 2013
12.	*Agaricus bisporus*	Fungicides (metalaxyl, benalaxyl, penconazole, tebuconazole, pyrimethanil, cyprodinil, iprovalicarb and azoxystrobin)	Marín-Benito et al., 2012
13.	*Pleurotus sajor-caju*	Methyl violet 2B	Singh et al., 2013
14.	*Pleurotus ostreatus, Pleurotus sajor- caju, Agaricus bisporus*	Rhodamine B, Chicago sky blue, Methyl violet 2B	Singh et al., 2013
15.	*Lentinula edodes, Agaricus bisporus, Volvariella volvacea* *Pycnoporus sanguineus* *Lentinus polychrous*	Textile azo dyes Synthetic textile dyes Dyes	Ahlawat et al., 2009 Annuar et al. (2009) Khammuang and Sarnthima (2007)
16.	*Lentinula edodes*	Heavy metals	Chen et al. (2005)

dation rate and a particular enzyme activity, since crude extracts contained more than one enzyme. An intergraded waste management approach by combining ozone oxidation pre-treatment and SMS-mediated aerobic biological treatment of benzo(α)pyrene was granted successful (Russo et al. 2012). The matrix of *Pleurotus pulmonarius*-degraded paddy straw consist predominantly –OH groups which hypothetically contributed by the cellulosic cell wall of plant matter and they facilitated the biosorption of PAHs (Lau et al., 2003). Laccase was found in the SMS of *P. pulmonarius* and its activity was 1.5-fold higher than that of manganese peroxidase (MnP). More recently, pilotscale PAH removal capacity of spent substrate of *P. ostreatus* in Nigerian oil-based drill cuttings has been investigated and after 56 days, the degradation of total PAHs was as high as 92.38% (Ayotamuno et al. 2010). Besides that, the highest total degradation rate of 15 PAHs were achieved by adding crude extracts from spent substrate of *Pleurotus eryngii*, followed by *A. bisporus*, *P. ostreatusand Coprinus comatus* (Li et al. 2010). Interestingly, laccase activity from the crude extracts of spent substrate from *P. eryngii* was not the highest amongst all. This showed

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that the laccase activity was not positively correlated to the PAH degradation rate, implying that natural mediators present in different crude extracts might contribute to the degradation rate, rather than laccase alone. Oxidation of phenol by crude extracts of spent substrate from *A. bisporus* was reported and laccase was identified as the main enzyme responsible for the oxidation (Trejo- Hernandez et al. 2001).

7. COCKTAIL OF LIGNINOLYTIC ENZYMES GENERATED FROM SPENT MUSHROOM SUBSTARTE

Mushroom enzymes reported in the literature are derived from mycelia of macro-fungi grown in submerged fermentation. Enzymes can also be extracted from solid substrate fermentation technology which is a process mimicking nature (Pandey et al. 2000). After mushroom crop harvesting, the spent mushroom compost will have plenty of extra-cellular enzymes. Of all the enzymes, laccase (EC 1.10.3.2) is the most reserved and common in spent substrate from *Agaricus bisporus* (Mayolo- Deloisa et al. 2009), *Pleurotus sajor-caju* (Kumaran et al. 1997; Singh et al. 2003), *P. ostreatus*, *Lentinula edodes*, *Flammulina velutipes* and *Hericium erinaceum* (Ko et al. 2005). However, lignin peroxidase productivity (per microgram of SMS) was found to be the highest from the spent substrate of *P. sajor-caju* (Singh et al. 2003) and it was two-, 22-, 30-, 86-fold higher than that of β-glucosidase, laccase, xylanase and cellulase, respectively. It is believed that the type of enzymes produced by mushroom during cultivation is directly affected by the ingredient of growing substrates and the species of mushrooms (Ball and Jackson 1995).A total of eight dyes from the triphenylmethane, azo and polymeric/heterocyclic dye group were decolourized by enzyme cocktail extracted from five month old spent compost of *Pleurotus sajor-caju* with lignin peroxidase as the main enzyme (Singh et al., 2010).So far spent compost of *Agaricus bisporus* has been employed for the recovery of laccase (Ball & Jackson, 1995; Mayolo-Deloisa et al., 2009). The decolourisation of Remazol brilliant blue R by laccase from the spent compost of *Lentinus polychrous* Lev. has also been reported (Khammuang & Sarnthima, 2007). Spent mushroom compost of *Pleurotus* spp. which represent the second largest group of cultivated basidiomycetes, has only been implicated in the bioremediation of polyaromatic hydrocarbons (Chiu et al., 1998; Eggen, 1999; Lau et al., 2003).

However, the potential of enzymes from the spent compost of *Pleurotus* spp. for the decolourisation of dyes has not been explored. However, there has been an earlier report on the extraction of high titers of lignin peroxidase (LiP) from the spent compost of *P. sajor-caju* and its potential in thedecolourisation of selected synthetic dyes (Avneesh et al., 2002). Decolourisation of azo dyes by the cultures of *P. sajor caju* has already been reported (Chagas & Durrant, 2001). Since azo dyes make the largest group of synthetic colourants used in textile industries which were released into the environment, decolourization of azo dyes by the enzyme cocktail from the spent compost offers economical bioremediation alternative.

Simona Di Gregorio et al., 2010 also demonstrated that the enzyme showed also a significant stability with respect to the temperature of incubation, and all the characteristics previously de-scribed make the laccase from spent substrate of *P. ostreatus* showed extremely attractive for industrial application, suggesting the exploitation of the SMS not only as a low cost substrate with oxidative capacity, but also as a source of robust laccase. In this context, the induction of laccase production could be advantageous for enzyme-purifying purpose, even though, in the experimental condition here explored, an effect of induction of the chromo baths on the ligninolytic battery of enzymes eventually associated to the SMS was absent.

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8. ROLE OF SPENT MUSHROOM SUBSTRATE IN DYES DECOLOURISATION

Mushrooms are ligninolytic fungi and represent an important organism in natural recycling events and in bioremediation (Gadd 2001). The enzyme systems of mushrooms contain lignin peroxidase, laccase and manganese-dependent peroxidase which catalyses metabolisation of many ligninlike structures, for example, PAHs and phenols. However, only in this decade, greater attention has been drawn to reuse SMS and the enzymes recovered from it as an economical approach in bioremediation of such pollutants (Eggen & Sasek 2002).

Textile industry is one of the largest water consuming industries in the world. The manufacturing and use of dyes and pigments is a multibillion-dollar industry. The use of these chemicals is an integral part of almost all manufacturing processes. Dyes are synthetic chemical compounds having complex aromatic structures, which are extensively used in the textile, cosmetics, plastic, food, paper printing, colour photography and pharmaceuticals industries (Forgacs *et al.,* 2004). Approximately 10,000 different dyes and pigments are used at industrial scale and over 0.7 million tonnes of synthetic dyes are produced annually, worldwide (Knapp *et al.*, 1997). United States Department of Commerce has predicted a 3.5 fold increase in textile manufacturing by 2020 (Ganesh *et al.,* 1994; Walsh *et al.,* 1980). In India, an average textile mill producing 60 x 10^4 m of fabric per day is likely to discharge approximately 1.5 Megalitres per day (MLD) of effluents (COINDS, Comprehensive Industry Document Series, 1999-2000). During industrial dyeing process a substantial amount of dye is lost in the waste water. It is estimated that nearly 40% of the total dyes used in the dyeing process may find their way in wastewater (Vaidya *et al.,* 1982).Evenin modern days of industrialization, an industrial waste effluent is being often discharged into water bodies without any adequate pre treatment. When such wastewater effluent is discharged onto the land adjoining the agriculture crops, it causes the gradual deterioration of land quality and ultimate reduction in crop yields. This has led to an enhanced concern and awareness, forcing Government of India to strict legislations for controlling the discharge of untreated effluents into the environment, may it be land, water or air.

Major classes of synthetic dyes are azo, anthraquinone and triaryl methane, and majority of them are toxic and even carcinogenic with long turnover times. With the increased use of a wide variety of dyes, pollution due to dye wastewater is becoming increasingly alarming. Colour is the first recognised contaminant in textile wastewater and has to be removed before discharging it into receiving water body (Padamavathy *et al.,* 2003). The presence of high level of heavy metals viz., copper, zinc, cadmium, chromium in wastewater further aggravates the problem (Pagga & Taeger, 1994). Textile industry is also one of the water intensive industries, which consumes large quantity of water for various processes and discharges equally large volume of wastewater containing a variety of pollutants. According to an estimate, a mill having production capacity of 35,000 m cloth per day consumes 1,000 kl water and produces effluents of 800 kl day^{-1}. Textile industry in India is one of the oldest industries. Large textile mills are (Fig. 1) mainly situated in Ahmadabad, Surat, Mumbai, Coimbatore, Kanpur and Delhi.The exact data on the number of processing houses operating in the cottage and household sector is not available and it has remained by and large unorganized. The textile units are scattered all across the country and out of 21,076 units, Tamilnadu tops with 5,285, whereas Maharashtra has the next highest number of units (ISPCH, 1995).

Physical processes if followed by chemical or biological process have shown good results. However, wide variation in BOD and other parameters necessitates the requirement of equalization of various physio-chemical processes viz., chemical coagulation / flocculation, adsorption, ion exchange, etc.

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Chemical coagulation employing various chemical coagulants followed by setting, have proven to be highly efficient in removing solids, BOD and COD from textile effluents and attained its reliability as physical and chemical unit (Mohan *et al.,* 1997; Robinson *et al.,* 2001 a). Removal of colour from the effluents is difficult by using conventional physico-chemical treatment system. However, biological treatment may be the best alternative, as the operational costs involved in it are relatively low compared to conventional technologies (Arutchelvan *et al.,* 2003).

Mushroom cultivation is an eco-friendly method of converting a wide range of agro-residues and agro-industrial wastes in to a protein rich food in the form of mushrooms. After several cycles of mushroom cultivation, the mushroom productivity decreases and the residual by-product considered as spent mushroom substrate which required to be properly disposed off to maintain hygiene and avoid environmental problems. If not properly disposed off, it leads to environmental problems, such as soil and water contamination, due to high load of organic carbon, nitrogen and salt in SMSs of different mushrooms.

Syntheticdyes find application in different industrial divisions including textile industry. An annual consumption of about 0.7 million tons of synthetic dyes has been reported (Deveci et al., 2004).Textile industry alone ac-counts for two-thirds of the total dyestuff market. Accordingly, discoloration of textile wastewaters is one of the major environmental concerns since last decades. However, it is worth to mention that *P. ostreatus* and many other basidiomycetes are edible mushrooms and their industrial cultivation produces a significant amount of spent mushroom substrate (SMS), reported as harboring high levels of residual oxidative enzymatic activity (Ball et al, 1995). Thus, SMS would be a low cost source of ligninolytic enzyme and their use for bioremediation for environmental pollutants (Trejo Hernandez et al., 2001; Karla et al., 2009). Gregorio et al., 2010 also studied that the low cost organic substrate, the SMS deriving from the cultivation of the basidiomycetes *Pleurotus ostreatus*, is able to discolor anthraquinonic, diazo and monoazo-dyes when incubated in dying chromo-reactive and chromo-acid baths containing surfactants and anti-foams, where the concentrations of the different dyes are exceeding the one recovered in the corresponding wastewaters.

9. BIOREMEDIATION OF FUNGICIDE/INSECTICIDES

Disposal of Spent Mushroom Substrate (SMS) generated after button mushroom cultivation is a matter of great concern as it is produced nearly five times to the quantity of mushrooms produced. The bulk of SMS makes its disposal more arduous besides the involvement of finance for its disposal. Moreover, unplanned disposal causes considerable land and water pollution along with nuisance in the surroundings. SMS have potential to bioremediate several agricultural grade fungicides and pesticides (Ahlawat *et al*., 2010, 2011).

10. DISCUSSION

Many fungal species are cultivated either for culinary or medicinal purposes, and some of the fungi are produced on large scales. The spent substrate left after fruit body collection is partly recycled in open field agriculture, but partly it causes environmental problems as bulk waste material. However, the spent substrates might represent a potential tool to cure polluted environment especially soils. Up to now spent mushroom substrate from only from few species i.e. *Agaricus bisporus*, *Lentinula edodes*, *Pleurotus*

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spp., *Trametes versicolor* have been studied either under lab conditions or in field scale. In the research work performed, spent oyster mushroom substrate demonstrate higher degradation capability to degrade 3-ring PAH compounds even in soil with initial concentrations.Of many different spent substrates from edible and medicinal mushroom cultivation. Only a few have been tried in soil remediation up to now. Results obtained are variable; on one side, encouraging data on depletion of PCP and PAHs from contaminated soil using spent substrate of *Lentinula edodes*, *Pleurotus pulmonarium* and *P. ostreatus* have been published (Okeke et al., 1993, 1996; Chiu et al., 1996; Eggen, 1999). The advantage of the use of spent mushroom substrate in soil restoration is rgar it is a cheap inoculums source and its application can to some extent reduce the cost of its disposal.

11. CONCLUSION

It could be concluded that the enzymes extracted from the spent compost of *P. sajor-caju* offers an economical advantage of obtaining industrially important enzymes, which have potential in the bioremediation of synthetic dyes. Furthermore, the utilization of spent compost for the extraction of enzymes can also offer a possible solution for the problem posed due to the disposal of large amounts of spent mushroom compost. It has being shown that enzymes extracted from the spent compost of *P. sajor-caju* have potential in the decolourisation of chemically different dyes. In addition, the effect of certain physical parameters on the rate of decolourisation of each dye was also shown. The study also provided insight on how the knowledge of these parameters can help in the optimization of processes employing enzymes for bioremediation on an industrial scale. Moreover, the *in vitro* treatment of environmental pollutants with crude ligninolytic enzymes of white rot fungi represents a simpler and effective method as compared to the direct application of the fungi by eliminating the need to grow biomass and absorption effects of the pollutants on the mycelia. The utilization of SMS for the extraction of enzymes offers an economical advantage of obtaining industrially important enzymes without long incubation periods and additional cost of specialized fermentations.

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Chapter 56
Bioremediation of Pharmaceutical Wastes

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ABSTRACT

The astounding increase in the use of pharmaceuticals in the last decade has raised concerns over their occurrence in the soils and wastewaters posing potential dangers to the general public health and environment. Considering the limitations of chemical remediation measures in treatment of recalcitrant xenobiotics, several bioremediation measures are being currently investigated and proposed for removal of pharmaceutical contaminants from the environment. Several bacterial, fungal and plant species have shown promising bioremediation potential with regard to the removal of pharmaceuticals. Varying configurations of anaerobic and aerobic reactors have been utilized for pharmaceutical wastewater treatment. This chapter is intended to give a compilation and overview of the various types of bioremediation measures currently being employed or investigated to remove the pharmaceutical pollutants.

INTRODUCTION

Pharmaceuticals comprise the broad group of synthetic as well as naturally obtained chemicals, intended for human or veterinary use as medicines. The use of pharmaceuticals and personal care products (PPCPs) has shown an astonishing increase in the last decade. Pharmaceutical industry production involves a wide range of raw materials, solvents, antibiotics, drugs and cosmetic products and hence, pharmaceutical effluents contain a wide variety of potentially harmful constituents (Dixit & Parmar, 2013). Pharmaceuticals enter the waste water, ground water, surface waters and soil through various means (Deziel, 2014). These include the sewage carrying excreta of patients on prescription or over the counter medicines, uncontrolled and unaccountable disposal of drugs by individuals as well as organizations, errant production houses lacking proper facilities for the disposal of drug waste, etc. The most frequently detected classes of pharmaceuticals in wastewater are NSAIDs, antibiotics, beta-blockers, lipid-regulators, steroids, antiepileptics, X-ray contrast media and tranquilizers (Drewes, 2007). The

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sewage treatment plants employed for treating wastewaters have been found to act upon the previously conjugated pharmaceutical residues (bound to a bile acid) excreted from the patients. The latter undergo de-conjugation, yielding higher levels of free pharmaceutical substance in the plant outlet than in its incoming water. Wastewater reuse in areas with water scarcity leads to contamination of drinking water with pharmaceuticals like sulphamethoxazole, ibuprofen and carbamazepine in low levels (Luo, Guo, Ngo, Nghiem & Hai, 2014). Limited studies have shown that presence of these low level pharmaceutical contaminants in wastewaters can be potential dangers to human health (Pomati et al, 2006).

Further, the continual input of antibiotics into the environment is leading to emergence of newer antibiotic-resistant strains of microorganisms (Larsson, 2014). Currently, the antibiotic contamination is being recognized as a global environment issue. The recalcitrant nature of antibiotics sprouting from their inherent resistance to biodegradation due to their antimicrobial properties further complicates the issue in comparison with other classes of pharmaceuticals. This antibiotic contamination can promote the mobilization as well as the fixation of resistance genes among human and animal commensal bacteria along with other environmental and clinically-relevant species (Baquero, Tedim, & Coque, 2013; Kristiansson et al, 2011)). Several studies have shown the harmful effects of wastewater contamination on various animal species. Hormonal drugs have demonstrated capability of feminizing or masculinizing fish (Gilbert, 2012). Further, the non-steroidal anti-inflammatory drug (NSAID) diclofenac, can cause damage to the gills and lungs in fish populations (Gilbert, 2012).

The concerns regarding the presence of pharmaceuticals in the environment are many (Patneedi & Prasadu, 2015), and concrete remedial measures are yet to gain momentum but, this relatively recent field is rapidly acquiring eminence with several bioremediation measures being investigated and proposed for removal of pharmaceutical contaminants from the environment. Chemical methods can possibly lead to the generation of newer xenobiotics which can persist in the environment and may not be amenable to biological transformation. Biological processes utilizing microorganisms, plants and enzymes represent an eco-friendly approach towards the removal of pollutants from the environment. This book chapter is intended to explore and compile the various types of bioremediation approaches currently applicable (or holding considerable future promise) to successfully treat pharmaceutical industry effluents.

PHARMACEUTICAL WASTES AND THEIR ENVIRONMENTAL IMPACT

In recent times, concerns are being raised over the occurrence of pharmaceuticals in the environment and their potential adverse effects on general public health, flora and fauna and the aquatic environment. The pharmaceuticals may be categorized into four classes based on their occurrence in environment and their risk effects as:

1. Hormonal drugs and their derivatives, found in effluents at nanogram levels but pose a health risk due to their high potency and potential effects as endocrine disruptors,
2. Antineoplastics (anticancer) agents, with cytotoxic, carcinogenic, mutagenic and embryotoxic potential on account of their high reactivity,
3. Anti-infective agents, including antibiotics, and
4. Halogenated compounds such as X-ray contrast media, which are highly resistant to biodegradation and hence, highly persistent in the environment and food chain.

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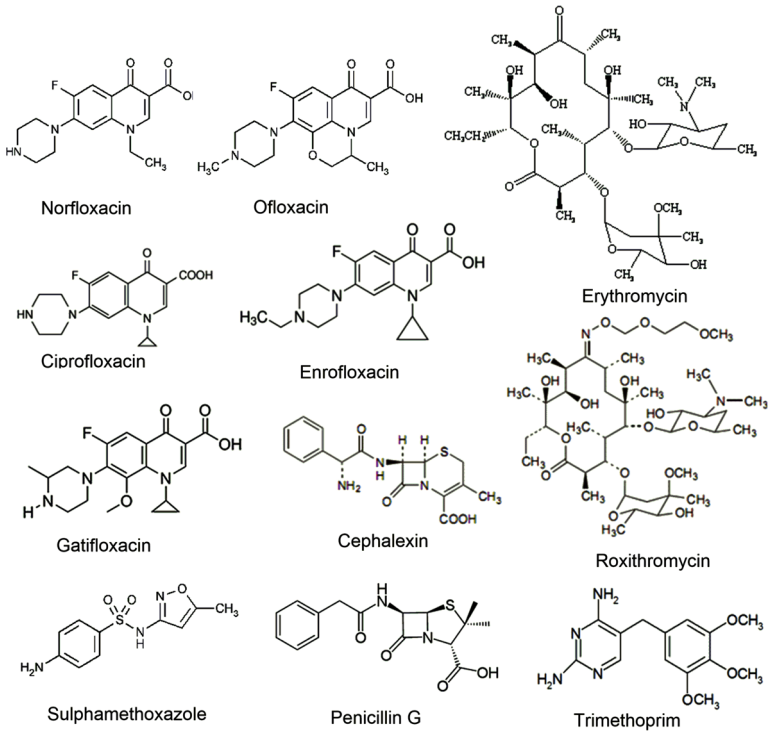
Several studies have highlighted the toxicity concerns of pharmaceuticals in wastewater, particularly, their potential to induce DNA damage and to cause lipid peroxidation effects (Mansour, Mosrati, Barillier, Ghedira, & Chekir-Ghedira, 2012). The US-EPA and other international agencies have listed the antibiotics (Figure 1), analgesics and other drugstore products (Figure 2) as top priority pollutants. The large scale production and use of antibiotics both in clinical and veterinary medicine, aquaculture, horticulture and agriculture has led to significant discharges of antibiotics into the environment. The bacterial isolates in the pharmaceutical effluents get exposure to sub-optimal dose of antibiotics produced by the factories and these constitute a major threat to public health. Many antibiotics are known to be persistent in the environment (Zuccato, Calamari, Natangelo, & Fanelli, 2000). A three year study conducted on seventy two pharmaceuticals and personal care products concluded that the half-lives for antibiotics when they reach agricultural soils can be phenomenally high, e.g., 55 to 578 days for tetracycline and 120 to 2310 days for ciprofloxacin (Walters, McClellan, & Halden, 2010). There have been several reports on isolation and characterization of newer antibiotic-resistant bacterial strains from pharmaceutical industrial wastewaters demonstrating varying patterns of multi-drug resistance (Tahrani et al., 2015).

A wide array of chemical as well as biological treatment methods are being employed by pharmaceutical industries for disposal of wastewater (Deegan et al., 2011). These include the use of ozone, Fenton's method, coagulation, electrocoagulation (Dixit & Parmar, 2013), pH correction, oxidation, sand filtration (Saleem, 2007), sedimentation, membrane separation, UV irradiation, photelectrocoagulation, peroxi-photelectrocoagulation, peroxi-electrocoagulation, adsorption, chlorination, distillation, reverse osmosis, bacterial treatments (Madukasi, Dai, He, & Zhao, 2010), phytoremediation methods including algal treatment, methods using membrane bioreactor (MBR) (C. Chang, J. Chang, Vigneswaran, &

Figure 1. Antimicrobials (antibiotics and sulphonamides) as pharmaceutical wastes



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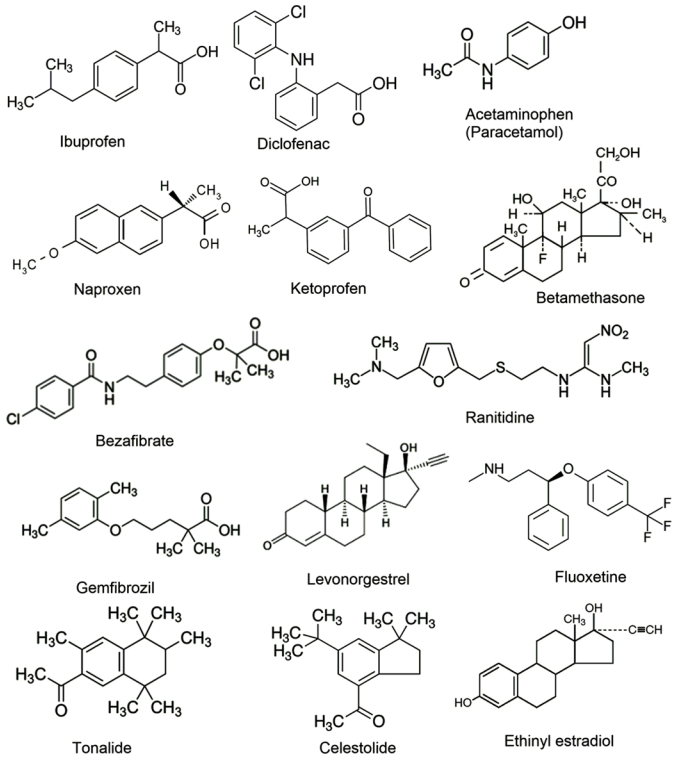
Kandasamy, 2008), fungal treatment (Spina, Anastasi, Prigione, Tigini, & Varese, 2012), anaerobic fixed film reactor (Rao, Naidu, Prasad, Rao, Mohan, Jetty, & Sharma, 2004), aerobic sequencing batch reactor (ASBR) (Patil, Kulkarni, S. Kore, & V. Kore, 2013), membrane-aerated biofilm reactor (MABFR) (Wei et al., 2012) and activated sludge method (Mayabhate, Gupta, & Joshi, 1988).

Chemical/physicochemical purification methods utilize costly chemicals and treatment units, which are difficult to manage at the industrial unit level and they can also possibly generate additional by-products with complex pharmacological/toxicity profiles, e.g., chlorination of phenols resulting in more toxic chlorinated products (Krug, Ziegler & Straube, 1985; Lee, Lu, & Chuang, 1994). Microorganisms play a critical role in the degradation of xenobiotics and in maintaining the steady-state concentration of chemicals in the environment (Misal, Lingojwar, Shinde, & Gawai, 2011). Their incredible versatility to catabolize, degrade or transform various contaminants has been increasingly investigated for removal of different types of non-pharmaceutical and pharmaceutical contaminants. The development of various types of aerobic and anaerobic biological reactors employing these microorganisms has revolutionized this field and this has become a prime area of research today. Further, phytoremediation and enzyme based approaches are being explored and encouraging results are generating novel leads in this area which can open up newer avenues in future.

Figure 2. Selected non-antibiotic pharmaceutical contaminants in wastewaters



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BIOREMEDIATION APPROACHES OF PHARMACEUTICAL WASTES

Different types of bioremediation approaches for treatment of pharmaceutical wastewaters rely on specific strains of bacteria and fungi which have the capability to degrade or transform the pharmaceutical pollutants under anaerobic or aerobic conditions. Various types of anaerobic and aerobic reactors have been designed employing bacterial and fungal consortia as bioremediation measures. Besides these, plants and certain enzymes have also been explored as a means of removal of pharmaceuticals from industrial effluents and wastewaters.

BACTERIAL BIOREMEDIATION

Several bacterial strains like *Pseudomonas, Enterobacter, Streptomonas, Aeromonas, Acinetobacter* and *Klebsiella* have been shown to demonstrate upto 44% reduction in the chemical oxygen demand (COD) in anaerobically treated spent wash (Ghosh, Verma, Mengoni, & Tripathi, 2004). Soil bacteria such as *Arthrobacter* and *Pseudomonas* predominantly present in rhizospheric soil, possess a special phenolic biodegradation potential. Numerous bacteria from the genera *Comamonas, Rhodococcus and Ralstonia* have been shown to degrade phenolic and other complex organic compounds and hence, have potential utility in degrading the pharmaceutical pollutants as well. Some *Clostridium* species (fermenting bacteria) can degrade resorcinol (Kavitha & Beebi, 2003). Thermophilic bacterium *Bacillus thermoglucosidasius* A7 has been shown to degrade phenols/cresol at 65^0C *via* the meta-cleavage pathway (Duffner, Kirchner, Bauer, & Muller, 2000). The bacterium *Pseudomonas fluorescence* has also been reported to demonstrate the capability to degrade phenols and chlorophenols (Agarry & Solomon, 2008). Biodegradation kinetics of phenol and catechol has been studied using *Pseudomonas putida* MTCC 1194 (A. Kumar, S. Kumar, & S. Kumar, 2005). Phototropic bacterium *Rhodobacter sphaeroides* has been used for treatment of pharmaceutical wastewater and 80% COD removal was achieved (Madukasi et al., 2010).

The specific bacterial species acclimatized in presence of the compounds needing remedial methods can be assets in bioremediation approaches and several of these have been investigated. Many researchers have worked on the isolation and identification of species from the sludge of biological treatment plants in pharmaceutical industries and have used those bacteria for utilization of other pharmaceutical ingredients. Bacteria highly resistant to a large number of antibiotics and non-antibiotics have been identified in such studies. The same bacteria, however, have also been seen to demonstrate a good potential to degrade and bioremediate some other non-antibiotic pharmaceutical effluents (Basu, Dastidar, Mukhopadhyay, & Gangopadhyay, 2012). Effective bioremediation of pharmaceutical waste water by *Pseudomonas putida* mt-2 has been recently reported (Mansour et al., 2012; Mansour, Dellai, & Ayed, 2012). *P. putida* was found to be very efficient in reducing the chemical oxygen demand (COD), total dissolved solids (TDS), and turbidity of solution (85.5, 89.1, and 81.5%, respectively). Further, genotoxicity evaluation studies on the effluent showed that the chromosomal aberrations and lipid peroxidation effects induced by the pharmaceutical wastewater (PW) were significantly reduced on bioremediation with *P. putida. Pseudomonas putida* IFO 14671 has also been isolated, and identified from the *Gomeya*/cow dung microbial consortium as a high-potential phenol degrader (Rao et al., 2004; Singh & Fulekar, 2009). *P. putida* isolated from cow dung microflora has been demonstrated a potential to degrade benzene (Singh

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& Fulekar, 2010). Bioremediation of effluents with *P. putida* has been shown to completely remove the murine chronotoxicity to pharmaceutical wastewater (Dridi, Bchir, Zouiten, Tahrani, & Mansour, 2013). Recently, biodegradation of the pharmaceutical waste, 4-nitrophenol has been shown with *P. putida* (Guleria, 2014).

Antibiotics, on account of their inherent properties, pose problems to bioremediation measures. However, there are several reports where these have been biodegraded in presence of consortium of microbes under specific conditions such as the absence of alternative sources of carbon and nitrogen, presence of moisture, etc. (Drillia et al., 2005; Gartiser, Elke, Radka, & Kümmerer, 2007). Streptomycin and cycloheximide have been reported to be biodegraded by soil bacteria and fungi (Badalucco, Pomaré, Grego, Landi, & Nannipieri, 1994). In a recent study, the bacteria and fungi from aquatic environment have been shown to degrade a mixture of two broad spectrum antibiotics, ciprofloxacin and erythromycin (Nnenna, Lekiah, & Obemeata, 2011).

Gomeya/cow dung has been used traditionally as an excellent, cheap and effective bioremediation measure against harmful pollutants. Randhawa and Kullar (2011) have reviewed the available studies on the bioremediation of a vast range of pharmaceuticals, pesticides, and petrochemicals with gomeya/cow dung. Manure (cattle dung) has been shown to effectively degrade the antibiotic enrofloxacin due to the presence of the known strains of coprophilous basidiomycetes, particularly, *Cyathus stercoreus* (Freer & Detroy, 1982; Wicklow, 1992). Reports are there in literature showing degradation of the antibiotics such as erythromycin, streptomycin, penicillin and bacitracin present in manure within 30 days (Gavalchin & Katz, 1994; Wang, Bradford, Zheng, & Yates, 2006). The sulphonamide drug sulfadimethoxine is shown to undergo biodegradation in manure and its degradation kinetics has also been studied (Wang et al., 2006).

FUNGAL BIOREMEDIATION (MYCOREMEDIATION)

Several fungal strains play an important role in the bioremediation of industrial effluents. Fungi, especially, the white-rot fungi are ubiquitously present in nature and these have adaptability to extreme conditions, thus, making them good biodegraders. These produce enzymes like lignin peroxidase, laccase and manganese peroxidase which are involved in degradation of lignin in their natural lignocellulosic substrates. This ligninolytic system of white rot fungi is directly involved in the degradation of various xenobiotics including pharmaceutical drugs and dyes by causing one-electron oxidation of aromatic compounds, with subsequent formation of aryl cation radicals, which spontaneously decompose by various pathways. (Christian, Shrivastava, Shukla, Modi, & Vyas, 2005; Tripathi, Harsh, & Gupta, 2007). Manganese peroxidase catalyzes the oxidation of Mn^{2+} to Mn^{3+}, which in turn can cause oxidation of several phenolic substrates (Sayad and Ellouz, 1995). However, fungal bioremediation (mycoremediation) measures suffer from certain drawbacks in terms of long growth cycle and spore formation.

Studies have shown that some fungal strains like *Bjerkandera adusta* MUT 2295, *Aspergillus niger, Aspergillus fumigatus, Penicillium decumbens* and *Penicillium lignorum* are effective in causing COD reduction in industrial effluents (Jayaraman, Muthuswamy, & Swaminathan, 2003; Mohammad et al. 2006). A comparative study was conducted by Spina et al. (2012) in which effectiveness of fungal treatment (Bjerkandera adusta MUT 2295) was compared with the activated sludge for treatment of pharmaceutical industrial wastewater. A 91% reduction in COD was noted with the fungal method, which was significantly higher than that observed from the activated sludge (78%). The degradation of enrofloxacin,

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a fluoroquinolone antibacterial drug used in veterinary medicine, has been investigated with the brown rot fungus *Gloeophyllum striatum* presumably by an oxidative mechanism. The findings suggest that the brown rot fungi are capable of producing highly reactive hydroxyl radicals, which can transform the xenobiotics by oxidative metabolism (Wetzstein, Schmeer, & Karl, 1997). Azo dyes are used extensively in the pharmaceutical and other industries and these are known to possess potentially mutagenic and/or carcinogenic properties. *Phanerochaete chyrosporium,* a major wood rotting fungus is capable of degrading a wide range of recalcitrant xenobiotics including azo-dyes through its non-specific hydrogen peroxide dependent extracellular lignin degradation enzyme system (Aust, 1990; Cripps, Bumpus, & Aust, 1990). *Aspergillus niveus,* a litter degrading fungus has been found useful in the biotreatment of distillery effluent (Angayarkanni, Palaniswamy, & Swaminathan, 2003). Recently, degradation of pharmaceuticals in non-sterile urban wastewater by white-rot fungus *Trametes versicolor* was reported in a fluidized bed bioreactor (Cruz-Morató et al., 2013). In a similar study, a fungal bioreactor based on *Trametes versicolor* pellets was reported as a new alternative for pre-treatment of hospital wastewater resulting in efficient removal of pharmaceuticals and endocrine disruptor compounds (Cruz-Morató et al., 2014). Further, the degradation of pharmaceuticals by *Trametes versicolor* has been found to be enhanced by addition of external nutrients (Badia-Fabregat et al., 2015). Very recently, *Trametes versicolor* has been applied for the removal of pharmaceuticals from a veterinary hospital wastewater and sixty-six per cent removal was achieved in a non-sterile batch bioreactor inoculated with *T. versicolor* pellets (Badia-Fabregat et al., 2016). Biodegradation by the fungus *Pycnoporus sanguineus* is another promising method for the mineralization of recalcitrant compounds present in pharmaceutical effluents (Watanabeet al., 2012).

Periconiella species of fungus isolated from cow dung has been reported to be an excellent degrader of biomedical waste and thus, represents a cheap, safe, and environment friendly method of biomedical waste disposal (Pandey & Gundevia, 2008). The efficiency of two white-rot fungi, *Trametes versicolor* and *Ganoderma lucidum*, to eliminate thirteen pharmaceutical pollutants has been recently investigated. Total removal of the drugs diclofenac, gemfibrozil, ibuprofen, progesterone and ranitidine was noted with the method whereas, lower removals were achieved for 4-acetamidoantipyrin, clofibric acid, atenolol, caffeine, carbamazepine, hydrochlorothiazide, sulfamethoxazole and sulpiride (Vasiliadou et al., 2016).

ENZYMATIC BIOREMEDIATION

In the last two decades, the application of enzymes as biocatalysts for environmental remediation has been widely studied as these offer advantages over living systems like microbes or fungi with respect to high reaction kinetics of degradation under subtle conditions of pH or temperature. Further, these are selective and are not affected by the biological activity of the targeted compounds. Enzymes can act on specific recalcitrant pollutants to remove them by precipitation or transformation to other products. The enzymes like oxidoreductases EC1 (*i.e.*, peroxidases, polyphenol oxidases (PPO), hydrolases EC3 (*i.e.*, proteases, esterases, lipases and cellulases) and lyases EC4 have been recommended for various wastewater treatment applications including pharmaceutical wastewaters and their effectiveness extends to wide range of pharmaceutical substances like phenolic drugs, antibiotics and other drugs. The application of oxidoreductive enzymes to catalyze the removal of phenol from wastewater has been investigated extensively. An example of such a method employs hydrogen peroxide and an immobilized derivative of soybean peroxidase, covalently bound to a glass support in a continuous tank reactor to remove phenol from aqueous solutions with 80% removal efficiency (Gómez et al. 2008). A recent article discusses the

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effectiveness of peroxidase based enzymatic treatment for continuous removal of phenol from wastewater (Chiong, Lau, Khor, & Danquah, 2014). A pharmaceutical effluent has been bio-remediated using yeast and amylase as the active agents (Uwadiae, Yerima, & Azike, 2011). Based on this technology, several types of enzymatic reactors have been designed (EMRs).

PHYTOREMEDIATION

Phytoremediation of wastewater is an emerging low-cost technique which utilizes the natural or transgenic green plants to bio-accumulate hazardous substances, particularly, metal ions such as lead and cadmium, and other xenobiotics (Campos, Merino, Casado, Pacios, & Gómez, 2008). The method has an advantage over microbial techniques as the microorganisms don't absorb heavy metals easily. This technique has a great potential for commercialization particularly in Europe and United states (Campos et al., 2008; McIntyre & Lewis, 1997; Watanabe et al., 1997). The method is still in preliminary stage and some reports on usage of aquatic plants as bioremediation measures are there. A recent review has addressed phytotoxicity of common pharmaceuticals and bioremediation potential of plants (Carvalho, Basto, Almeida, & Brix, 2014).

- **Aquatic Plants:** Phytoremediation through aquatic macrophytes treatment system for the removal of pollutants and contaminants from various natural sources is an accepted environmental protection technique. The biosorption capacity of the water hyacinth (*Eichhornia crassipes*), a highly invasive aquatic weed, in minimising various contaminants present in the industrial wastewater has been extensively studied (Priya & Selvan, 2014). Water hyacinth and the plants *Typha latipholia* and *Phragmitis karka* have been used in some studies to demonstrate their usefulness in reducing COD, BOD levels in pharmaceutical wastewaters (Billore et al., 2001). The algae are effective in hyper-accumulation of heavy metals and can bring about bio-degradation of xenobiotics (Suresh & Ravishankar, 2004). *Dunaliella* algae have been found effective in causing biological removal of heavy metals from wastewater at concentrations of about 85 mg/l (Qari & Hassan, 2014). Biodegradable adsorbents are being developed for the treatment of contaminated waters due to their low cost and greater efficiency in the removal of organic and inorganic pollutants. The application of marine algae and derivatives as potential adsorbents for pharmaceutical products is being studied as an inexpensive and eco-friendly alternative. Different types of marine algae and hydrogel beads of alginate and chitosan have been reported for the bio-removal of antibiotics such as amoxicillin, enrofloxacin, penicillin G and other non-antibiotic drugs such as caffeine.
- **Aerial Plants**: Several plants are being investigated for their potential to remove xenobiotics from soils. The phytoremediation potential of *Cicer arietinum* (black chick pea) has been evaluated for aspirin (Gahlawat, Makhijani, Chauhan, Valsangkar, & Gauba, 2014) and tetracycline (Makhijani, Gahlawat, Chauhan, Valsangkar, & Gauba, 2014) under hydroponic conditions. Recently, Gahlawat & Gauba (2016) have evaluated the phytoremediation of aspirin and tetracycline by *Brassica juncea.*
- **Plant Root Remediation:** Peroxidases (EC 1.11.1.7) are versatile heme-containing biological catalysts that have been used for wide spectrum applications in a number of enzyme based industrial processes to preserve water quality (Ashraf & Husain 2010). Hairy roots in various plants offer an attractive cost-effective alternative to enzyme-based methods in this regard, as their exudates

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contain enzymes like peroxidase, and some metal chelating compounds to sequester harmful inorganic or organic pollutants, including phenol (Angelini, Orejas, Medina, & Agostini, 2011). Plant root remediation of contaminated soils and groundwater is being recognized as having a great potential for future development due to its environmental compatibility and cost-effectiveness (Zhou, Tang, & Wu, 2013). Phytoremediation of 2,4-dichlorophenol and phenol by *Brassica napus* hairy roots cultures has been reported (Agostini, Coniglio, Milrad, Tigier, & Giulietti, 2003; Angelini et al., 2011; Coniglio et al., 2008). Phytoremediation of phenol at pilot scale has been carried out by tobacco hairy roots and various parameters suggested that these could provide adequate matrix for the successful removal of phenol (Sosa Alderete, Ibáñez, Agostini, & Medina, 2012).

- **Constructed Wetlands:** Constructed wetlands have been viewed as a promising approach for the removal of pharmaceuticals from waters and wastewaters (Li et al., 2014). Constructed wetlands are engineered wetlands that utilize natural processes involving wetland soil, vegetation, and consorted microbial aggregations to assist in treating polluted waters (Helt, Weber, Legge, & Slawson, 2012). Five different wetland plant species have been evaluated for their efficiency in scavenging commonly used recalcitrant fluoroquinolone antibiotics ciprofloxacin, gemifloxacin mesylate, ofloxacin and gatifloxacin from aqueous medium. *Taxodium distichum* was found to be the most suitable for the removal of ofloxacin, gatifloxacin and ciprofloxacin and *Canna indica* was the most effective in the removal of gemifloxacin mesylate (Tandon et al., 2013).

A particular concern in viewing the phytoremediation methods as viable alternative bioremediation techniques is that several of the reported studies have not clearly addressed the relation between the xenobiotic removal and plant uptake of pharmaceuticals. In such studies, photo-degradation and oxidative degradation could also be additional possible contributors and their contribution needs to be ruled out as a possible cause of drug removal. Results from phytoremediation plants show that in many cases, the plant uptake usually represents a low percentage of the mass depleted from the systems. However, it has been debated that phytoremediation depends both on the plant uptake and the rhizospheric microbial communities; therefore, removal efficiencies must be analysed in terms of the overall processes involved (Carvalho et al., 2014).

IMPORTANT BIOREMEDIATION TECHNOLOGIES

Biological treatment technologies in pharmaceutical industrial wastewater treatment are broadly based on aerobic and anaerobic methods (Deegan et al., 2011). Several high-rate reactors have been designed for the biological treatment of pharmaceutical effluents at full-scale operation.

Aerobic Methods

Activated Sludge Process

The conventional activated sludge process (CAS) uses a microbial biomass to treat the influent wastewater. The typical configuration consists of a primary clarifier, aeration tank, a secondary clarifier and a process for returning a portion of the secondary sludge. In the aeration tank, the wastewater is mixed and aerated with the microbial suspension. Under well-controlled operating conditions, the classical

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aerobic AS reactors can be relatively efficient for the removal of poorly biodegradable persistent drug pollutants diclofenac, sulfophenylcarboxylates and antibiotics, like tetracycline or erythromycin, and hardly-degradable micropollutants, such as carbamazepine.

Several researchers have reported the aerobic biological treatment of pharmaceutical wastewater (Altaf and Ali, 2010; Khan and Mostafa, 2011; Lapara, Nakatsu, Pantea, & Alleman, 2001) with significant reductions in the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) amounting to 75-98%. The use of activated sludge process (ASP) for treatment of wastewater from herbal pharmaceutical industry resulted in 68.98–91.02% reduction in COD, 76.90–97.26% reduction in BOD and 74.61–95.54% reduction in suspended solids (Vanerkar, Satyanarayan, & Dharmadhikari, 2013). The **aerobic** sequencing batch reactor (ASBR) and activated sludge process are the most commonly employed aerobic methods for the treatment of industrial wastewater.

Sequencing batch reactors (SBRs) carry out the activated sludge process in a sequential, time-oriented manner employing a single vessel for all the phases of the process. These offer advantages over the ASP in being more cost-effective due to lower operating costs, amenability to online control, a reduced site space, and adaptability to suit variable wastewater compositions and flow rates (Al-Rekabi et al., 2007). Sequencing batch reactor (SBR) has been used to treat the mixed pharmaceutical industrial resulting in significant removal in BOD (approximately 85%), COD (approximately 87%), ammonia (approximately 96%), suspended solids (approximately 98%), and phosphate (approximately 5%) (Ileri, Sengil, Kulac, & Damar, 2003). Another similar study with sequential batch reactor (SBR) has been reported by Altaf and Ali (2010). Optimization of SBR operating conditions for treatment of high-strength mixed pharmaceutical wastewater with reduction in BOD (94%) and COD (83%) has been carried out by Elmolla et al. (2012).

Rotating Biological Contactor (RBC) Biofilm Process

The rotating biological contactor (RBC) biofilm process is an important biofilm process (attached growth process) in existing treatment facilities for municipal and industrial wastewater treatment with medium strength (COD concentration is 600–2000mg/l) of organic substances but has not been applied yet to pharmaceutical effluents (Akunna & Jefferies, 2000; Vidal, Ba˜nares-Alc´antara, Rodr´ıguez-Roda, & Poch, 2002). The RBC process has the advantages of a high microbial concentrations in good condition, high suitability for fluctuations in flow rate and organic concentration and high efficiency for organic degradation (Chen, Wen, Wang, & Li, 2006; Wang, Liu, Zhang, & He, 2009). RBC also has the advantages of simultaneous nitrification and denitrification accompanied by carbon removal (Hiras, Manariotis, & Grigoropoulos, 2004; Tawfik, Klapwijk, El-Gohary, & Lettinga, 2005). Further, low water content in the sludge causes it to easily settle, allows easy operation and its lower energy consumption makes it a economically viable option as well (Taseli, G¨okc¸ay, & G¨urol, 2008; Torkian, Yazdani, & Alinejad, 2003). Recently, high-strength antibiotic pharmaceutical residual liquid mixed with ordinary wastewater has been treated by a simple three-stage RBC system with resultant COD removal efficiency of 45% and BOD removal efficiency of 85% at low ambient temperatures thus, showing the effectiveness of RBC for such an inherently bio-recalcitrant wastewater (Su et al., 2015). Another study has been reported involving a two-stage RBC for biological removal of the pharmaceuticals belonging to different therapeutic classes including caffeine, sulfamethoxazole, ranitidine and carbamazepine and the maximum removals achieved for all the drugs were greater than 85% (Vasiliadou, Molina, Martínez, & Melero, 2014).

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Nitrifying Activated Sludge (NAS) Method

An alternative procedure employing nitrifying bacteria (e.g., *nitrosomonas europaea*) is the nitrifying activated sludge (NAS) method which has been demonstrated to be more effective in the removal of pharmaceuticals. This method has been successfully employed to remove ethinyl estradiol (Vader et al., 2000) and other estrogens (Anderson, Siegrist, Halling-Sorensen, & Ternes, 2003; Kanda & Churchley, 2008) in sewage treatment plants. Batt et al. (2006) have reported higher removal of the drugs iopromide and trimethoprim in the NAS compared to conventional AS method in lab batch reactors as well as full-scale plants. Another comparative study has shown the complete removal of trimethoprim (poorly removed by AS and primary sewage treatments), sulfamethazine, sulfamethoxazole and sulfathiazole in NAS batch experiments on laboratory scale (Perez, Eichhorn, & Aga, 2005). Tran et al (2009) have also reported higher laboratory scale removal of ten APIs (clofibric acid, gemfibrozil, ibuprofen, fenoprofen, ketoprofen, naproxen, diclofenac, indomethacin, propyphenazone and carbamazepine) by the NAS method compared to CAS method. Good removal of the drugs fluoxetine, citalopram, ethinyl estradiol, ibuprofen, naproxen, diclofenac, carbamazepine, trimethoprim, roxithromycin, sulfamethoxazole, erythromycin, galaxolide, tonalide, celestolide and diazepam has been reported with NAS system (Suarez, Lema, & Omil, 2010).

Anaerobic Methods

Anaerobic treatment of the pharmaceutical industrial wastewater (PIWW) involves the step-wise decomposition of the organic material into gaseous methane and CO_2 with the help of microorganisms in the absence of molecular oxygen. Anaerobic treatment systems do not require an energy consuming aeration system and offer several additional advantages over aerobic methods such as good removal efficiency even at high loading rates and low temperature, slow sludge production, need of low nutrient amount and production of biogas (>50% methane) which can be utilized as a renewable energy source for energy production (Nandy & Kaul, 2001; Seghezzo, Zeeman, van Lier, Hamelers, & Lettinga, 1998). Typically, pharmaceutical wastewater is characterized by high chemical oxygen demand (COD), and some pharmaceutical wastewaters can have COD as high as 80,000 mg/l. Due to their high organic content, anaerobic technology is being viewed as a promising alternative for treatment of pharmaceutical effluents. Various reactor configurations are available such as up-flow anaerobic stage reactor (UASR), upflow anaerobic sludge blanket reactor (UASB), anaerobic filter, anaerobic contact reactor (ACR), fluidized bed reactor (FBR) and anaerobic fixed film reactor (AFFR) to treat wastewaters from different industries.

Up-Flow Anaerobic Stage Reactor (UASR)

An up-flow anaerobic stage reactor (UASR) has been investigated as a pre-treatment system at an existing pharmaceutical production plant to reduce the antibiotics in the trade effluent. The pharmaceutical wastewater originally containing macrolide antibiotics (Tylosin and Avilamycin) showed 95% reduction in Tylosin concentrations on UASR treatment (Chelliapan, Wilby, & Sallis, 2006).

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Up-Flow Anaerobic Packed Bed Reactor

A fully packed up-flow anaerobic packed bed provides a quiescent inlet region for large dense biomass aggregates to develop, which are not prone to washout. Furthermore, the reactor provides a surface to facilitate biofilm accumulation. This assures a shorter start-up period due to greater amount of retained inoculum. An anaerobic packed bed reactor has been recently designed and employed to treat highly polluted of pharmaceutical wastewater of Samarra Drug Factory (SDI) in Iraq showing best hydraulic retention time (HRT) of 24 hours for anaerobic stage and removal efficiencies of COD and BOD as 87% and 90% (Hashimi, Al-Ali, & Abbas, 2011). A similar treatment of highly polluted pharmaceutical wastewater employing an anaerobic packed bed reactor has also been reported by Chelliapan et al., (2011). An Up-Flow Anaerobic Packed Bed reactor has been employed to treat pharmaceutical wastewater containing recalcitrant antibiotics. Results from the study showed a COD reduction of 60–70% at an organic loading rate (OLR) of 1.5–4.6 kg $COD.m^{-3}.d^{-1}$, suggesting that the biomass had acclimated to the antibiotics (Chelliapan & Golar, 2011). Antibiotic wastewaters containing a high proportion of spent fermentation broths usually require long HRT for efficient treatment (Lapara et al., 2001), presumably, on account of their complex organic carbon content. Hence, this factor can limit the performance of the packed bed reactor at lower HRT (2 d).

Wastewaters from pharmaceutical industry usually contain a high concentration of sulphate as a result of sulphate use during down-stream processing of fermentation broth. The production of sulphide during anaerobic treatment of sulphate containing wastewaters can inhibit methanogens and can precipitate the nutrients required by the methanogens (Ozdemir, Cirik, Akman, Sahinkaya, & Cinar, 2013). An anaerobic reactor system has been developed employing phase separation (especially at high OLRs) by accomodating different microbial populations in different stages according to their favourable substrate conditions. This two-stage anaerobic digestion system has been recently utilized for anaerobic treatment pharmaceutical wastewaters with high sulphate content (Chelliapan & Sallis, 2015).

Upflow Anaerobic Sludge Blanket (UASB) Reactor

A hybrid upflow anaerobic sludge blanket (UASB) reactor is a single tank process in an anaerobic centralised or decentralised industrial wastewater or blackwater treatment system achieving high removal of organic pollutants. A UASB reactor operates as a suspended growth system where microorganisms attach themselves to each other or to small particles of suspended matter to form agglomerates of granules which settle easily. The latter form an active suspended sludge blanket that filters and treats the wastewater as it flows upwards through it. The process combines the advantages of the UASB and anaerobic filter (AF) concepts. This method has been widely used for the treatment of wastewater from the beverage, brewery, food and tannery industries (To´th, Gergely F, & Mizsey, 2011) and is reported as a preferred option for certain chemical synthesis-based pharmaceutical wastewaters due to several operational advantages over other reactor configurations. These advantages include high organic loadings, greater efficiency, low energy requirements, shorter hydraulic retention time (HRT) and easy reactor construction. (Oktem, O. Ince, Sallis, Donnelly, & B. Ince, 2007). It is a popular anaerobic reactor for both high and low temperatures. Among the recently developed high-rate processes, it has attracted most commercial and research interests (Lettinga, van Velsen, Hohma, de Zeeuw, & Klapwijk, 1980). A study by Rodriguez-Martinez et al (2005) in an Up-Flow Anaerobic Sludge Bed (UASB) treating

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pharmaceutical wastewater containing Penicillin G antibiotics has shown a COD removal efficiency of 90% at an OLR of 1.5 kg $COD.m^{-3}.d^{-1}$ and HRT 11 d. The performance of a pilot-scale UASB reactor, treating an antibiotic chemical synthesis-based pharmaceutical wastewater, has been recently evaluated under different operating conditions with good results (Rao, Habiulla, Prasad, & Anand, 2014).

The hybrid UASB reactor has been evaluated for efficacy in reduction of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of bulk drug pharmaceutical wastewater containing hazardous compounds like phenol, l,2-methoxy phenol, 2,4,6-trichloro phenol, dibutyl phthalate, 1-bromo naphthalene, carbamazepine and antipyrine. After the treatment, all the pharmaceutical compounds degraded almost completely except carbamazepine. Thermophilic *methanothrix* and *methanosaetae* like bacteria were present in the granular sludge (Sreekanth, Sivaramakrishna, Himabindu, & Anjaneyulu, 2009). Herbal pharmaceutical wastewater treatment has been reported by Satyanarayan et al (2009) by a pilot scale UASB reactor resulting in COD, BOD and suspended solids (SS) removal in the range of 86.2%-91.6%, 90.0%-95.2% and 62.6%-68.0% respectively.

Low-temperature or psychrophilic ($< 20^0$C) anaerobic digestion (PAD) has recently been demonstrated as a cost-effective option for the treatment of solvent containing pharmaceutical wastewater (Enright, McHugh, Collins, & O'Flaherty, 2005). Two UASB reactors with different operating temperatures, mesophilic (35 ± 1ºC) and thermophilic (54 ± 1ºC) have been studied for the treatment of a non-penicillin based product factory waste water (ISA, Kutty & Bin Abd Rahim, 2010) affording the highest percentage of COD removal for the mesophilic and thermophilic reactors as 95% and 93% respectively.

Structured Packing Rotating Biological Contactor (spRBC)

A removal process of the antibiotic enrofloxacin has utilized a biological treatment unit consisting of a structured packing rotating biological contactor (spRBC). The removal rate reached a maximum of 70% in this biological unit and removal efficiency for a combined system including spRBC and an ultraviolet radiation unit was 94% (Zamanpour & Mehrabani-Zeinabad, 2014).

Anaerobic Fixed Film Reactor (AFFR)

The anaerobic fixed film reactor (AFFR) possesses a biofilm support structure for biomass attachment. Utilization of the anaerobic fixed film reactor (AFFR) is reported to be more effective due to simplicity of construction, stability, higher threshold to absorb toxic shock load and faster recovery. An AFFR may employ glass beads, red drain clay, polyurethane foam, waste tyre rubber, splintered glass, polyacryl nitrile acrylamide, corrugated plastic, coconut coir, and charcoal or nylon fibre as a support media (Borja, Sanchez, Marin, & Jimenez, 1996; Garcia, Rivas, Figueroa, & Monroe, 1995; Perez, Romero, Nebot, & Sales, 1997). The laboratory scale bio-methanation of high strength herbal pharmaceutical wastewater has been achieved with anaerobic fixed film fixed bed reactor system (Nandy & Kaul, 2001) with COD removal efficiencies ranging from 76 to 98%. Studies have been carried out on the treatment of wastewater from a bulk drug industry employing an AFFR designed and fabricated in the laboratory The AFFR has been shown to be very efficient in lowering COD, total dissolved solids (TDS) and total suspended solids (TSS) (Rao et al., 2004).

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Anaerobic Fluidized Bed (AFB) Reactor

The anaerobic fluidized bed (AFB) reactor comprises small media, such as granular activated carbon or sand to which the bacteria attach. High flow rate around the particles results in decreased clogging. The large pore spaces formed through bed expansion and high specific surface area of the carriers significantly improves the efficiency of the fluidized bed reactors. The expanded granular sludge bed (EGSB) reactor is a modification of the AFB reactor with a difference that the fluid's upward flow velocity is not as high which results in partial bed fluidization (Rittmann & McCarty, 2001). Bioaugmentation and anaerobic treatment of pharmaceutical effluent has been carried out in fluidized bed reactor affording maximum COD removal of 91.2% (Saravanane, Murthy & Krishnaiah, 2001a). The treatment of cephalexin drug-based pharmaceutical effluent in an upflow anaerobic fluidized bed system coupled with bio-augmentation also resulted in 88.5% COD removal (Saravanane, Murthy & Krishnaiah, 2001b). A large quantity of concentrated effluent resulting from the production of cephradine, a cephalosporin antibiotic (COD of 14000-18000 mg/l) has been treated using a fluidized bed reactor under anaerobic conditions with bioaugmentation (Saravanane, Murthy & Krishnaiah, 2001c). Degradation of phenol has been studied in anaerobic fluidized bed reactors (AFBR) packed with polymeric particulate supports including polystyrene, polyvinyl chloride (PVC) and polyethylene terephthalate (PET). Excellent removal efficiencies of ranging from 90-100% have been demonstrated (Sancinetti et al., 2012).

Anaerobic Suspended Film Contact Reactor

Bio-treatability studies have been reported on the effluents from a bulk drug industry using an anaerobic suspended film contact reactor (Mohan, Prakasham, Satyavathi, Annapurna, & Ramakrishna, 2001). The COD reduction was found to be in the range of 60 to 80% for organic loading rates varying from 0.25 kg/m^3/day to 2.5 kg/m^3/day.

Membrane Bioreactors (MBR)

MBR technology is a combination of the activated sludge (AS) process with a micro- or ultrafiltration membrane system (Mutamim, Noor, Hassan, & Olsson, 2012). The activated sludge treatment is responsible for the biodegradation of the organic waste compounds, and the membrane system (pore diameter 0.01-0.1 μm) physically separates the solids from the liquid (Hoinkis et al., 2012). The membrane bioreactors (MBR) have been reported to be much more efficient than classical AS systems (Kimura, Hara, & Watanabe, 2007; Radjenović, Petrovic, & Barcelo, 2009). At worst, these systems perform as well as activated sludge treatment (Clara et al., 2005; Joss et al., 2005). Recently, several reports have come up emphasizing the relevance of this technique in the current bioremediation scenario. Membrane bioreactor (MBR) has been used for the large-scale wastewater treatment of industrial wastewater in the pharmaceutical industry (C. Chang, J. Chang, Vigneswaran, & Kandasamy 2008). MBRs can operate at high suspended solid concentrations because the membrane separation step is not limited by sedimentation capacity, which will result in longer solid retention times (SRTs) (Cirja, Ivashechkin, Schäffer, & Corvini, 2008). These conditions can be favourable for API (active pharmaceutical ingredient) biodegradation as more diverse microbial population can flourish at longer SRTs resulting in diverse biodegradation pathways (Clara, Kreuzinger, Strenn, Gans, & Kroiss, 2005). Moreover, the extended contact time gives the bacterial biomass an opportunity to acclimate to certain xenobiotics by broadening their enzymatic

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(Suarez et al., 2010) or metabolic capabilities (Ternes, Joss, & Siegrist, 2004). An external loop airlift membrane bioreactor (ELAMBR) has been applied for treatment of a synthetic pharmaceutical wastewater and the performance of this system was evaluated in removal of acetaminophen as the main pollutant of the pharmaceutical wastewater. The removal efficiency was found to be significantly higher in the ELAMBR system compared to the AS process and 100% of the acetaminophen was removed within two days (Shariati et al., 2010). Another comparative study has been conducted with a laboratory-scale MBR and the AS process on pharmaceutical wastewater containing several drugs like diclofenac, ketoprofen, ranitidine, gemfibrozil, bezafibrate, pravastatin, ofloxacin, ibuprofen, naproxen, acetaminophen, paroxetine, and hydrochlorothiazide. Pharmaceuticals were, in general, removed to a greater extent by the MBR integrated system than by the AS process (Radjenović et al., 2009). Treatment of pharmaceutical wastewater containing three NSAIDs (acetaminophen, ketoprofen and naproxen) and three antibiotics (roxithromycin, sulfamethoxazole and trimethoprim) has been reported in two MBRs with sludge retention times (SRTs) of 15 (MBR-15) and 30 (MBR-30) days over a period of 4 weeks. The NSAIDs were removed with higher efficiency compared to the antibiotics, and the MBR-30 afforded better removal efficiencies than the MBR-15 for all the drugs (Tambosi et al., 2010). A very similar study with similar results has been reported by Schröder et al. (2012) with wastewater containing three NSAIDs (acetaminophen, ketoprofen and naproxen) and three antibiotics (roxithromycin, sulfamethoxazole and trimethoprim) performed MBR-15 and MBR-30. Removal rates ranged from 55% (sulfamethoxazole) up to 100% (acetaminophen, ketoprofen). An efficient removal of ammonia, total organic matter and four corticosteroids, levonorgestrel, betamethasone valerate, betamethasone dipropionate (Betha-D) and medroxyprogesterone acetate, has been achieved in a laboratory-scale submerged membrane bioreactor (MBR) treating wastewater from a pharmaceutical industry. Chemical analysis of MBR effluent revealed that all the corticosteroids were removed at high percentages (> 93%) in all the cases (López-Fernández, Martínez, & Villaverde, 2012). The application of membrane separation technology (MBR) on pharmaceutical wastewater has been recently reviewed (Cazes, Abejón, Belleville, & Sanchez-Marcano, 2014; Fazal, Zhang, Zhong, Gao & Lu, 2015).

Combined Anaerobic-Aerobic Processes

Although, innumerable reports have come up relating to the successful organic removal from pharmaceutical wastewater employing varying configurations of anaerobic reactors, yet, there have been differences in anaerobic treatment performances possibly explained by the differing wastewater characteristics including salinity/toxicity and presence of refractory compounds poorly biodegraded under anaerobic conditions. In light of the tightening legislations on effluent water quality standards, a subsequent aerobic process is required for further removal of organic residues from the anaerobic effluents (Chen, Ren, Wang, Zhang, & Shi, 2008). Application of activated sludge system as an aerobic post-treatment process has been shown to further enhance the COD removal rate from 62% to 96.4% in the treatment of purified terephthalic acid wastewater (Pophali, Khan, Dhodapkar, Nandy, & Devotta, 2007). This sequential two stage process has been widely employed for the treatment of paper and pulp industry effluents (Tezel, Guven, Erguder, & Demirer, 2001), textile wastewaters, food solid waste leachates, etc. Agdag and Sponza (2005) have employed the combination of an anaerobic sludge blanket reactor (UASB) and completely stirred tank reactor (CSTR) systems for the treatment of municipal landfill leachate. Isik and Sponza (2008) have reported the anaerobic/aerobic treatment of a simulated textile wastewater. Recently, granular sludge was successfully cultivated employing an intermittent anaerobic

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and aerobic reaction phase strategy using synthetic textile wastewater containing mixed dyes with 93% removal of COD and ammonia (Muda, Aris, Salim, Ibrahim, & Yahya, 2012). The application of sequential anaerobic/aerobic treatment to pharmaceutical wastewater treatment has been fairly recent and relatively fewer applications have been reported. In a recent study, pharmaceutical wastewater with high total dissolved solids (TDSs) and chemical oxygen demand (COD) content has been treated through a sequential anaerobic–aerobic treatment process. For the anaerobic process, application of up-flow anaerobic sludge blanket (UASB) resulted in COD removal efficiency of 41.3 ± 2.2% achieved with an organic loading rate of 8.11 ± 0.31 g COD/l/d. Significant improvement was achieved by treating the UASB effluent by a membrane bioreactor (MBR) and a sequencing batch reactor (SBR). Both the UASB + MBR and UASB + SBR systems have demonstrated an excellent organic removal efficiency, with COD removal of 94.7% and 91.8% respectively. Best performance was noted with UASB + MBR system in terms of organic removal as well as nitrification (Shi, Lefebvre, K. Ng, & H. Ng, 2014) The continuous sequential biological anaerobic/aerobic treatment of Samarra Drugs Factory wastewater has included a pilot plant of upflow anaerobic filter (UAF) (with mesophilic bacterial growth at a temperature range of 35-37 °C) for the anaerobic stage followed by an air diffuser for the aerobic stage. However, there was no significant advantage in terms of the removal efficiency of COD and BOD in anaerobic/aerobic stage (92% and 93% respectively) over the anaerobic stage alone (87% and 90% respectively) (Hashimi & Abbas, 2007). A pilot-scale system composed of an anaerobic baffled reactor followed by a biofilm airlift suspension reactor has been designed for removing organic matter from the high-strength pharmaceutical wastewater containing antibiotics ampicillin and aureomycin (Zhou, Su, Li, Qian, 2006). Recently, ozone and thermal hydrolysis pre-treatment has been employed to improve anaerobic digestion (AD) efficiency to reduce tetracycline resistance genes in municipal and pharmaceutical waste sludge. Thermal hydrolysis pre-treatment was found to be more efficient than ozone for reduction after AD (Pej, Yao, Ren & Yu, 2016).

Coupling Bioremediation with Alternative Techniques

Bioremediation measures have also coupled with other alternative or conventional wastewater management processes to ensure more effective removal of the pollutants. An example is provided by a recent report wherein, distinct laboratory scale biological processes: suspended activated sludge and attached-growth biomass or moving bed biofilm flow-through reactors have been investigated for wastewater treatment to remove pharmaceuticals including ibuprofen, naproxen, ketoprofen, carbamazepine and diclofenac and an active metabolite of the lipid regulating agent clofibric acid. The suspended activated sludge process resulted in 74% removal of ibuprofen, naproxen and ketoprofen but removal of clofibric acid, carbamazepine and diclofenac was inconsistent. However, the coupling of the attached-growth biomass biological treatment with UV treatment and hydrodynamic cavitation/hydrogen peroxide process afforded excellent removal efficiencies for clofibric acid (>90%) and carbamazepine and diclofenac (>98%), while the remaining compounds were reduced to levels below their limits of detection (LOD). A combined treatment process (solar photo-Fenton + immobilized biomass reactor) was utilized for the treatment of pharmaceutical industrial wastewater containing nalidixic acid (an antibiotic pertaining to the quinolone group), which is not easily biodegraded. This process resulted in 95% reduction in COD out of which, 62% reduction was accounted for by the immobilized biomass reactor (Sirtori et al., 2009). The coupling of solar photo-Fenton process with aerobic sequencing batch reactor attained COD removal of 98% in pharmaceutical wastewater (Adishkumar, Sivajothi, & Banu, 2012).

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FUTURE RESEARCH DIRECTIONS

The emerging field of bioremediation of pharmaceuticals is quite challenging due to the plethora of information still waiting to be explored not only in relation to their removal from to the environment but also for gaining insight into their chemical characteristics and susceptibilities. The structural diversity of the pharmaceuticals encompasses a vast organic chemical space, hence, diverse range of approaches are required to be explored for their effective and complete removal from the environment. There is a need to have comprehensive information on the most common pharmaceutical contaminants in the environment. Further, there is limited information on the deleterious impact of low level pharmaceutical contaminants on human and animal health. As drug selection in different geographical regions varies depending upon economic and social factors, the potential bioremediation measures need to be customized according to the contaminants present. Generation of comprehensive database of common pharmaceutical pollutants in different geographical regions of the world should be the first step in this direction. In-depth and accurate analysis of industrial effluents and wastewater and ground water needs to be carried out in order to assess the most common pharmaceutical pollutants present. Particularly recalcitrant and stubborn drugs and pharmaceuticals need to be identified in terms of their prevalence in wastewater, groundwater and soils to chalk out a future course of action for devising specific bioremediation measures. Pharmaceutical research is a fast evolving field and with the introduction of newer pharmaceuticals in therapeutic arena, newer challenges will arise for their safe disposal.

CONCLUSION

Presence of wide variety of pharmaceuticals in the environment is a cause of concern on account of their harmful effects to the humans and also due to their deleterious effects on terrestrial as well as aquatic plant/animal life. Bioremediation of pharmaceuticals is still an emerging field. In recent times, there has been a growing awareness about this global issue but the real gravity of the problem is yet to be recognized and understood completely. The chemical diversity of pharmaceuticals, frequent introduction of newer pharmaceuticals into the market and poor existing information about the susceptibility of different types of plant and animal species to their toxic effects adds up to the complexity of the problem. Several bioremediation measures have been proposed in the recent times utilizing the versatility of various types of microorganisms such as bacteria and fungi to catabolize or degrade different types of pharmaceutical contaminants. Several configurations of anaerobic and aerobic reactors have been devised which have demonstrated their potential to detoxify pharmaceutical industrial effluents by removing the various drugs, solvents and other non-pharmaceutical raw materials used in the pharmaceutical manufacturing. Enzyme based studies have also yielded encouraging results but their costs involved could preclude their wide applicability. Phytoremediation has been utilized for removal of a number of non-pharmaceutical industry effluents but recently, this is gaining prominence for its potential to degrade pharmaceuticals as well. All these represent green or eco-friendly approaches towards conservation of the environment and in the coming times, this field in expected to grow tremendously because the scientific community as well as the general population is getting increasingly sensitized towards alleviation of this problem.

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KEY TERMS AND DEFINITIONS

Aerobic: A process requiring the presence of oxygen.

Anaerobic: A process occurring in the absence of oxygen.

Bacterial Bioremediation: Treatment of wastewater with bacteria having the capability to consume or digest the chemical contaminants including drugs and pharmaceuticals.

BOD: Biochemical oxygen demand or biological oxygen demand. It is an important water quality parameter representing the amount of dissolved oxygen needed for biodegradation of organic material present in a given water sample at certain temperature over a specific time period.

COD: Chemical oxygen demand is a water quality parameter (unit mg/L) based on chemical oxidation methods employing strong oxidizing agents.

Membrane Bioreactor: Wastewater treatment process in which a membrane filter process like microfiltration or ultrafiltration is integrated with a biological process like suspended growth bioreactor yielding high quality treated effluent.

Mycoremediation: Bioremediation method employing fungi to degrade or accumulate organic and heavy metal contaminants in the environment.

Phytoremediation: Use of green plants and solar energy for degradation and removal of environmental contaminants.

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Section 5

Organizational and Social Implications

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Chapter 57
Legislation for Solid Waste Management

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ABSTRACT

The legal and institutional framework, as well as the international trends in solid waste management, serves as the basis for the formulation of a policy framework that seeks to improve solid waste management (SWM) practices in the future. Recently, SWM has become a global concern, especially for urban environments such as Malaysia, whose economy could potentially be adversely affected. To address these issues, the authors has reviewed several laws, including the Federal Constitution 1957; Local Government Act (Act 171) 1976; Town and Country Planning Act (Act 127) 1976; Environmental Quality Act (Act 127) 1974; Street, Drainage, and Building Act (Act 133) 1974; and Solid Waste and Public Cleansing Management Act 2007. Relevant international norms and principles at the federal, state, and local levels have also been reviewed. Exploring this topic generates an overview of SWM implementation in the context of Malaysia and the rest of the world.

INTRODUCTION TO SOLID WASTE MANAGEMENT

Scope and Focus of the Chapter

This chapter outlines the legislation for solid waste management (SWM) in Malaysia and the world. The background of SWM legislation, including the types of solid waste and SWM controls are provided. The development of waste management control is discussed with a focus on the waste hierarchy principles, such as reduction, reuse, recycling and composting, energy recovery, and treatment and disposal. The solid waste legislation under the review of SWM for the past and currently applied in Malaysia is then discussed.

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The SWM Act of Malaysia, which covers the period from 1950 to the present, is described in this chapter as well. The establishment, governance, jurisdiction, and operational issues are addressed. An overview of the Malaysian Legal Framework in Integrated Solid Waste Management is also highlighted. The roles of federal and states agencies as well as international trends in SWM, including those in the U.S, Europe, and Sweden, are discussed. The chapter ends with a brief conclusions regarding the Malaysian legislation on SWM.

Types of Solid Waste

The US Environmental Protection Agency (2013) stated that Municipal Sold Waste (MSW) consists of everyday items that are used and then thrown away; MSW includes product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances, paint, and batteries. The sources of such waste are homes, schools, hospitals, and businesses. MSW is a term usually applied to a heterogeneous collection of wastes produced in urban areas, the nature of which varies from region to region (UNEP, 2005).

The Malaysia Solid Waste and Public Cleansing Management Act (2007) defines solid waste as controlled solid wastes that include commercial solid waste, household solid waste, institutional solid waste, and public solid waste. "Solid waste" includes the following:

1. Any scrap material or other unwanted surplus substance or rejected products arising from the application of any process.
2. Any substance required to be disposed of as being broken, worn out, contaminated, or otherwise spoiled.
3. Any other material that according to this Act or any other written law is required by the authority to be disposed.

The Act also categorizes controlled solid waste as follows:

1. **Commercial Solid Waste:** Any solid waste generated from any commercial activity such as shoplots supermarkets etc. (e.g. plastic packaging, food residues etc.)
2. **Construction Solid Waste:** Any solid waste generated from any construction or demolition activity, including improvement, preparatory, repair or alteration works.(e.g. wood, bricks, concretes, gypsum board, tiles etc.)
3. **Household Solid Waste:** Any solid waste generated by a household, and of a kind that is ordinarily generated or produced by any premises when occupied as a dwelling house, and includes garden waste (e.g. HDPE bottles, food residues, broken plates etc.)
4. **Industrial Solid Waste:**
    a. Processed Solid Wastes
        - Wastes generated from manufacturing process (product rejects, trimmings, surplus etc.)
        - Wastes generated from packaging of products, raw materials (wood pallets, carton boxes, plastic sheets etc.)
        - Could be very specific type and homogenous.
    b. Non-Process Solid Wastes
        - Wastes generated from canteens / food courts (food wastes, plastic bottles, tin cans etc.)

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- Wastes generated from office (computer papers, magazines, plastic bags, aluminium cans etc.)

5. **Institutional Solid Waste:** Any solid waste generated by:
   a. Any premises approved under any written law or by the State Authority for use wholly or mainly for religious worship or for charitable purposes.
   b. Any premises occupied by any Federal or State Government department, any local authority or any statutory body.
   c. Any educational premises.
   d. Any healthcare facilities including hospitals, clinics and health centres.
   e. Any premises used as public zoos, museums, libraries and orphanages.
6. **Imported Solid Waste:** Any solid waste generated in other countries and imported to Malaysia for processing or disposal.
7. **Public Solid Waste:** Any solid waste generated by public places, which are under the supervision or control of any local authority. This include any open spaces, parking spaces, garden, recreation and pleasure ground or square etc.

Development of Waste Management Controls

Improving waste management is aimed at reducing the generation of waste and the amount of materials disposed in landfills. This objective is part of the overall goal of improving the quality of the environment and encouraging sustainable practices. The main goal of good waste management practices is to use materials resourcefully and consequently decrease the amount of waste in the final disposal. Implementing the waste hierarchy principle, such as to reduce, reuse, recycle, recover, and dispose, is an example of a good waste management practice that can be employed by clients. The implementation of best practices in waste management should thus involve the consideration of the waste hierarchy. In this way, the amount of waste generated in projects and subsequently disposed of in landfills is reduced (Wimalasena, 2011).

The Malaysian Solid Waste and Public Cleansing Management Act 2007 (MSWPCM) Act defines "waste hierarchy" as the ranking of waste management operations in accordance with their environmental benefits in the following order of priority: (1) reduction of waste generation, (2) reuse of waste materials, (3) recycling of waste materials for similar or new products, (4) utilization of energy from waste, and (5) disposal of waste such as landfilling. As presented in the hierarchy, the most environmentally friendly alternatives are ranked first (at the top) while the most undesirable option is ranked last.

Sources Reduction

Avoidance is the best approach with regard to material waste; however, this may not be possible or practical in most cases (Wimalasena, 2011). Source reduction is the next best alternative in regulating waste generation. Source reduction is defined as "the design, manufacture, purchase or use of materials to reduce their quantity or toxicity before they reach the waste stream" (USEPA). According to Vesilind et al., (2002), waste reduction may be implemented by three methods: (a) reducing the amount of material used per product, (b) increasing the lifetime of a product, or (c) eliminating the need for the product. Waste reduction also means the reduction of waste at the user level. The USEPA suggests that source reduction can;

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A. Save natural resources,
B. Conserve energy,
C. Reduce pollution,
D. Reduce the toxicity of our waste, and
E. Save money for consumers and businesses alike.

Reuse of Existing Materials

Reuse means using the materials exactly as it was originally intended to be used. It is the most valuable form of recycling. The reuse of waste materials is regarded as an effective technique for improving resource utilization before disposal (Wimalasena, 2011).

Recycling and Composting

The USEPA (2014) stated that recycling comprises a series of activities, including collecting used, reused, or unused items that would otherwise be considered waste; sorting and processing the recyclable products into raw materials; and remanufacturing the recycled raw materials into new products. Consumers provide the last link in recycling by purchasing products made from recycled content. Specifically, recycling prevents the emission of many greenhouse gases and water pollutants, saves energy, supplies valuable raw materials to industries, creates jobs, stimulates the development of greener technologies, conserves resources for our children's future, and reduces the need for new landfills and combustors. Guerrero et al. (2013) stated that the success of recycling depends not only on participation levels but also on the efficiency of the equipment and infrastructure.

Energy Recovery

The US Environmental Protection Agency (2014) defined energy recovery from waste as the conversion of non-recyclable waste materials into useable heat, electricity, or fuel through a variety of processes, including combustion, gasification, pyrolization, anaerobic digestion, and landfill gas recovery. This process is often called the waste-to-energy process.

Treatment and Disposal

Landfills are the most common form of waste disposal and make up an important component of an integrated waste management system. Landfills that accept MSW are primarily regulated by state, tribal, and local governments. Methane gas, a byproduct of decomposing waste, can be collected and used as fuel to generate electricity. After a landfill is capped, the land may be used as recreation sites such as parks, golf courses, and ski slopes. The guidelines on solid waste disposal and landfill establishments identify and explain issues that should be addressed in proposals for solid waste disposal and establishment of landfill facilities for municipal and hazardous waste. Specific proposals must focus on key issues. The matter identified in these guidelines provides guidance for setting up of solid waste disposal and landfill facilities. Guerrero et al. (2013) stressed that improper waste collection systems due, among others, to the lack of infrastructure or municipal inefficiencies encourages people to search for other waste disposal solutions, including domestic burning (combustible materials) and composting the putrescible fraction of waste.

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The management hierarchy concepts should be enforced with the implemention of MSWPCM Act. The enforcement of the act should be implement for all the types of waste stated in the act. Managing the waste is crucial for Malaysia to be in line with the future sustainable development.

SOLID WASTE LEGISLATION

Introduction

Environmental protection and conservation is gaining significance in the long-term national development plan. In this regard, Malaysia has reaffirmed its commitment toward the protection and conservation of its environment (JKR, 2008). The activities performed for pollution prevention must be supported by a solid legal framework because such activities require legal powers, jurisdiction, and sanction for effective implementation (Zubaidah & Mustafa (2008)). The legal and institutional framework in Malaysia provides the basis for assessing the existing framework for the environmental management and SWM in the country. This framework is an indicator of where we are now, given that legal and institutional frameworks are the foundations from which policies and practices grow (Victor, 2001).

Malaysia

Malaysian Legal Framework for Solid Waste Management

In general, SWM in Malaysia involves various government agencies, from the federal to the state and local authorities (LAs). These government agencies are involved in SWM either directly or indirectly. Malaysia is governed as a parliamentary democracy with three tiers of government, namely, the federal government, the state government, and the LAs. It has 14 states and 144 LAs. The LAs include the Municipal Council, District Council, City Hall, and Town Board (Sakawi, 2011).

The development of the Solid Waste Management Act of Malaysia is considered informal because of the indirect legislation on the SWM enforcement prior to the establishment of the MSWPCM Act. The development process is considerably time consuming. The previous SWM legislation is derived directly or indirectly from the following:

A. Federal Constitution 1957
B. Local Government Act (Act 171) 1976
C. Town and Country Planning Act (Act 172) 1976
D. Environmental Quality Act (Act 127) 1974
E. Street, Drainage and Building Act (Act 133) 1974
F. Solid Waste and Public Cleansing Management Act 2007

The development of the MSWPCM Act is not the end of the legislation but the start of SWM enforcement. A few regulations have been developed as a result of the power conferred by the Act.

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Federal Constitution 1957

The Ninth Schedule of the Federal Constitution divides the legislative power of the federal state into three lists.

A. Federal List (contains matters based on which the Parliament may make laws)
B. State List (contains matters based on which State Legislatures may make laws)
C. Concurrent List (contains common subject matters on which both the Parliament and State Legislatures have competence)

Operationally, the federal government is legally permissible to pass laws on all subject matters enlisted in the Federal List. These subject matters involve national policies, taxes, education, national defense, and internal security.

State governments are in charge of matters stated in the State List. Such matters may include religious affairs, lands, rivers, forests, and waterways. In terms of application, these laws have restricted applicability. Unlike federal laws, state laws are only applicable within the boundaries and territories of a particular state (Article 74i). As for the Concurrent List, the federal and state governments can share legislative powers and jurisdiction over matters such as culture, sports, antiquities, town and village planning, and conservation of wildlife (Yusof, 2013).

According to Victor (2001), the term "solid waste" or "municipal waste" does not appear in the Constitution, and an explicit reference on solid waste is unavailable. This statement was supported by Yusof (2013), who stated that the term "environment" is surprisingly unlisted in any of the legislative lists of the Federal Constitution. In addition, the term is not clearly listed in the Federal List, State List, or Concurrent List. This exclusion is probably due to the general state of Malaysia in previous years, back when Malaya, the former name of Malaysia, was largely an underdeveloped country. However, under the Concurrent List of the Constitution, solid waste is indirectly mentioned under public health, sanitation, and prevention of disease (Victor, 2001).

Victor (2001) contended that the general matters pertaining to local governments, such as sanitation and SWM, fall under the state's jurisdiction. However, the provision under Article 95A (National Council for Local Government) and the fact that sanitation is alluded in the Concurrent List indicate that SWM may indirectly fall under the jurisdiction of the federal and state governments. The provisions under Article 76 (1) also mean that for the sake of promoting uniformity in management, the federal government may enact a legislation on solid waste for the entire country, but such legislation must be accepted by each state government.

Local Government Act (Act 171) 1976

The Local Government Act 1976 was enacted in March 1976 and is applicable only in Peninsular Malaysia. The Act enumerates the powers and functions of the LAs. Generally, under the legislation, the LAs are responsible for the control and conservation of the environment, sanitation and public health, prevention of epidemial diseases, and the general welfare of the residents within the LAs area. However, the functions of the LAs can be extended to other areas.

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Victor (2001) stated that the Act indirectly refers to SWM in Sections 9, 69–72, 84, and 102. Generally, the Act empowers the state governments to provide direction on policies and the operational management of the areas under the jurisdiction of the LAs. The following are the areas in which the local authorities are empowered by the Act to carry out their duties pertaining to SWM:

A. The Act prohibits the disposal of any waste in any form into any drains, streams, or watercourses within the jurisdiction of the LAs.
B. The Acts empowers LAs to maintain public health in areas under its administration. The LAs are also specifically empowered to perform sanitary services, such as the removal of rubbish and other kinds of waste.
C. The Act empowers the LAs to make, amend, or revoke by-laws for the proper management and operation of sanitary services, such as the removal of rubbish and other kinds of waste.
D. The Act empowers the LAs to carry out legal actions against any person that may cause a nuisance willfully or through ignorance within the area of the LAs. The term nuisance can be broadly interpreted to cover the indiscriminate disposal of rubbish or waste.
E. The Act provides for the regulation and control of industries or activities that are obnoxious or could be a source of nuisance.

For example, Section 42 of the Act prohibits anyone from placing building materials on the road without a written permission from the LAs. In fact, the Act requires the occupier of a premise to clean the road in front of the entrance to the premise. Generally, littering or disposing of unwanted materials at public places within any LA area is prohibited by the Local Government Act and punishable through fines or jail time, or both.

This Act is probably the most significant SWM legislation. It generally empowers the LAs to take charge of SWM in their areas of jurisdiction. The areas of empowerment appear broad and comprehensive to cover SWM, operational activities, and the formulation of by-laws and prosecution guidelines. The current job function of the LAs in terms of SWM appears to be largely derived from this Act.

Town and Country Planning Act (Act 172) 1976

Act 172, or the Town and Country Planning Act, was enacted in 1976 to ensure proper control and regulation of town and country planning and development in Local Authority (LA) areas. Zubaidah and Mustafa (2008) explained that this act imposes a statutory obligation on the local planning authority to ensure that effective planning controls are introduced within its locality. Sinha and Kew (2004) supported this account and added that the act requires the preparation of a draft structure plan which, among other things, defines measures to improve the physical environment and communications of planning authorities.

Victor (2001) summarized that the act designates LAs as the local planning authorities for their respective areas. Generally, the act includes a provision for the planning and development of an area by the formulation of Structure and Local Plans. These plans are development control plans that determine whichareas should be developed and how, by studying the physical, social, economic, and environmental issues. These development plans are legally binding documents that provide general guidance on the direction and strategies to be employed to develop geographically large areas such as districts.

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Environmental Quality Act (Act 127) 1974

The Environmental Quality Act was enacted in 1974 for the prevention, abatement, and control of environmental pollution,as well as to enhance the general quality and ensure proper management of the environment.

The term "waste" could be defined as Scheduled Waste or other solid, semi-solid, and liquid substances, which could cause environmental pollution,as stated in Section 2. The act also provides the control or prevention of environmental pollution. Section 24 even specifies soil pollution to include refuse dump, garbage tip, or other solid wastesbased on their negative effect on human beings. Open burning of waste, which usually includes solid waste, is also regulated by Section 29 of this act.

According to Victor (2001), an important feature of this act is that it requires an Environment Impact Assessment (EIA) for prescribed activities before such activities can be carried out. The list of prescribed activities include the construction of infrastructure for municipal solid waste, such as incineration plants, composting plants, recovery/recycling plants,and solid waste landfill facilities. Lastly, the act empowers the Minister to issue regulations to control, prohibit, and improve the general quality of the environment (Section 51). Under this provision, the Minister may regulate the establishment of sites for the disposal of solid or liquid waste on or in any land.

Street, Drainage and Building Act 1974

The Street, Drainage and Building Act was enacted on 13 June 1974. The Streets, Drainage and Building Act (SDBA) was enacted to consolidate the legislation governing the streets, drainage and building in local authority areas. Victor (2001) explained that this act empowers the management of solid waste in public areas. Though this may seems redundant, but the act especially focuses on the cleanliness of public places as compared to solid waste management in general.

Solid Waste and Public Cleansing Management Act 2007

The history of the SWMPC Act as a major solid waste legislation was fraught with numerous challenges. According to Yahaya and Larsen (2007), in September 1995, the Government decided that solid waste management was to be privatized. After 10 years of privatization, the National Strategic Plan for Waste Management (NSP) was then endorsed by the Government in July 2005. In the same year, a Solid Waste Management Division was formed in the Ministry to prepare for the implementation of the plan. Less than a year after the adoption of the NSP, the Government approved the National Solid Waste Policy, which provides the overall direction of solid waste management. Act 672, or the SWMPC Act, was passed by the Parliament in July 2007 and published in the national gazette in August 2007. This act was administered by the Ministry of Housing and Local Government and was enforced on September 1, 2011 for every state in Peninsular Malaysia except Penang and Selangor. The main objectives of the act are to provide and regulate public cleansing and the management of controlled solid waste to maintain proper sanitation.

Act 672 requires all operators of solid waste and public cleansing management services and facilities to apply for license from the Director General of the National Solid Waste Management Department. The Act also requires prior written approval from the Director General of the National Solid Waste Management Department before any construction, alteration, or closure of prescribed solid waste management facilities. Furthermore, Act 672 covers the following:

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A. Control of solid waste generators and persons in possession of controlled solid waste;
B. Enforcement; and
C. Reduction and recovery of controlled solid waste.

Act 672 empowers the Federal Government to shoulder the management of solid waste and public cleansing from the LAs throughout Peninsular Malaysia and the Federal Territories of Putrajaya and Labuan. The implementation of Act 672 and its relatedregulations on solid waste and public cleansing management is expected to drive a major change in the modus operandi of solid waste and public cleansing management in Malaysia. Upon the enforcement of Act 672, all works on solid waste and public cleansing management will be handled fully by the Solid Waste and Public Cleansing Management Corporation (SWPCMC). Such enforcement involves the immediate takeover of solid waste and public cleansing management responsibilities from all LAs, as the LAs will lose jurisdiction over the collection and disposal of garbage, as well as the cleansing of public roads, public places, public toilets, and drains. SWPCMC will then assume the management and operation of all landfill sites previously under the LAs, including identifying and evaluating sanitary landfills, transfer stations, incineration technologies, and plant management.

Upon this Act's coming into effect, the Federal Government shall have executive authority with respect to all matters relating to the management of solid waste and public cleansing throughout Peninsular Malaysia and the Federal Territories of Putrajaya and Labuan.Yahaya and Larsen (2007) explained that with the enactment of the SWMPC Act 2007, the two previously existing Acts, which provided legal authority to the LAs on solid waste management, must be amended. Hence, in the same session, the Parliament approved the amendments on the relevant provisions in both the Local Government Act of 1976 and the Street, Drainage, and Building Act of 1974, therefore deleting any reference on Solid Waste Management.

Such amendments are necessary to ensure smooth implementation of the new act and to avoid any confusion during implementation. Another important piece of legislation that was also amended is the Town and Country Planning Act of 1976 (TCPA). Although both of the earlier legislations had the relevant sections deleted, the TCPA hada new provision inserted. The inserted provision is to ensure that a local planning authority will consider the provisions of the SWMPC Act of 2007 when addressing an application for planning permission. This provision is a long-term measure to ensure a coordinated approach to Solid Waste Management.

Enforcement of the Act

Additionally, certain regulations have been developed by the National Solid Waste Management Department to implement the power conferred to it by the SWMPC Act of 2007, which became operative on September 1, 2011. Such regulations include:

A. Solid Waste And Public Cleansing Management (Manner Of Appeal) Regulations 2011
B. Solid Waste And Public Cleansing Management (Prescribed Solid Waste Management Facilities And Approval For The Construction, Alteration And Closure Of Facilities) Regulations 2011
C. Solid Waste And Public Cleansing Management (Compounding Of Offences) Regulations 2011
D. Solid Waste And Public Cleansing Management (Licensing)(Management Or Operation Of Prescribed Solid Waste Management Facilities) Regulations 2011

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E. Solid Waste And Public Cleansing Management (Licensing) (Undertaking Or Provision Of Collection Services For Household Solid Waste, Public Solid Waste, Public Institutional Solid Waste And Solid Waste Similar to Household Solid Waste) Regulations 2011
F. Solid Waste And Public Cleansing Management (Licensing) (Undertaking Or Provision of Transportation Services By Long Haulage) Regulations 2011
G. Solid Waste And Public Cleansing Management (Licensing) (Undertaking Or Provision Of Public Cleansing Management Services) Regulations 2011
H. Solid Waste And Public Cleansing Management (Scheme For Household Solid Waste And Solid Waste Similar To Household Solid Waste) Regulations 2011

The another strategies added in order to be included with the enforcement were;

A. A two year grace period would be given to the public to get used to the practice before fines were imposed on those who failed to do so.
B. Within these two years, the three concessionaires in charge of solid waste management in the country will have to raise awareness on separation of waste at source.
C. All hosehold owners must know their duty to segregate their own waste before dumping it.

The most valuable finding from this section is the latest information gained from Yahaya and Larsen (2007) regarding the amendment of related acts as a result of the enactment of the SWMPC Act of 2007. A summary of the final findings is provided below.

A. All references on Solid Waste Management in the Local Government Act of 1976 and the Street, Drainage, and Building Act of 1974 were deleted. Such amendments are required to ensure smooth implementation of the new act and to avoid any confusion during implementation.
B. A new provision was inserted into the Town and Country Planning Act of 1976 (TCPA) to ensure that local planning authorities will comply with the provisions of the SWMPC Act of 2007 when dealing with an application for planning permission.
C. The establishment of the SWMPC Act of 2007 changed the modus operandi of solid waste and public cleansing management in Malaysia. Upon the enforcement of Act 672, all works on solid waste and public cleansing management will be assumed by SWPCMC, which includes the immediate takeover of solid waste and public cleansing management responsibilities from all LAs. This change is because the LAs will no longer have jurisdiction over garbage collection and disposal, as well as the cleansing of public roads, public places, public toilets, and drains.

All legislation related to solid waste management, such as the Local Government Act of 2007 (Act A1311) (as amended), the Street, Drainage, and Building Act of 2007 (Act A1312) (as amended), and the Town and Country Planning Act of 2007 (Act 1313) (as amended), are now vested upon the federation by Act 672. The uniformity of these Acts is imposed throughout Peninsular Malaysia and the Federal Territories of Putrajaya and Labuan (Abas and Seow, 2014).

Managing waste is an issue for all households and businesses. The SWMPC Act has a well developed waste management act that generates significant enforcement and regulation for the collection, transportation, and processing of waste. The waste hierarchy remains an important principle in the SWMPC Act. This ensures that SWMPC Act presents a holistic waste management enforcement from the initial

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Table 1. Summary and area of jurisdiction for the legislation

Legislation	Area of Jurisdiction
Federal Constitution, 1957	• Basis for the formulation of the NCLG and other related solid waste management legislation.
Local Government Act, 1976	• Authorizes the State government and the LAs to be responsible for solid waste management.
Town and Country Planning Act, 1976	• Authorizes the LAs to plan for the development of their area which also includes solid waste management especially in siting of waste management facilities.
Environmental Quality Act, 1974	• Regulates pollution from solid waste and the implementation of waste management facilities through the requirement of an EIA
Streets, Drainage and Buildings Act, 1974	• Authorizes the LAs to regulate and prohibit solid waste disposal in its area.
Solid Waste and Public Cleansing Management Act 2007	• To provide and regulate public cleansing and the management of controlled solid waste to maintain proper sanitation. - Control of solid waste generators and persons in possession of controlled solid waste; - Enforcement; and - Reduction and recovery of controlled solid waste.

Modified from Victor (2001)

generation of waste through to its ultimate disposal with chances to reduce waste at each step of the hierarchy. The implementation of SWMPC Act will benefit from more sustainable waste management. The summary and area of jurisdiction of legislation was presented in the Table 1;

Institutional Framework in Solid Waste Management

This section is an overview of the main parties involved in solid waste management in Malaysia. According to Victor (2001), these institutions comprise the main mechanism by which the legislative framework is translated to operate and manage solid waste on the ground.

The overall institutional framework of the Malaysian government is headed by the Cabinet, which comprises of various Ministers, who are elected as the representatives of Malaysian citizens. Several councils assist the Cabinet in guiding the development of the country by formulating policies and providing directions for growth. These councils comprise various members of the Cabinet, as well as representatives from the State governments. Some of these councils function as liaisons between the Federal and State governments.

Under the Federal Government, the administration of Municipal Solid Waste Management (MSWM) is under the purview of the Ministry of Housing and Local Government (MHLG). This ministry has two units involved directly with MSWM, namely, the National Solid Waste Management Department (NSWMD) and the Solid Waste and Public Cleansing Management Corporation (SWPCMC). The roles of the Federal Government in MSWM are principally of an advisory and coordinating nature. This chapter presents the roles of NSWMD and SWPCMC as the primary federal agencies responsible for this matter. Summary of framework was presented in Figure 1.

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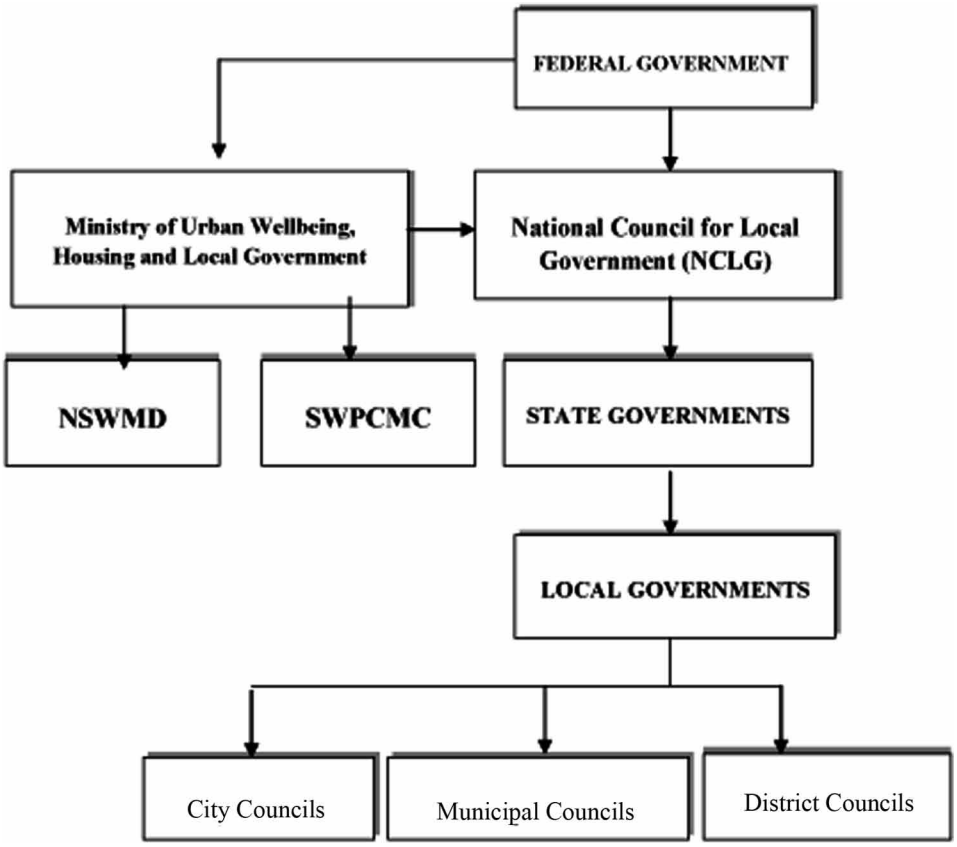
Figure 1. The Institutional Framework of the Malaysian Government
Sources from Razak A. A (2014)



National Solid Waste Management Department (NSWMD)

The NSWMD was established under the SWMPC Act of 2007 to integrate the solid waste management system at the national level. This Act provides executive authority to the Federal Government to carry out the responsibilities of solid waste and public cleansing management.

Before the establishment of NSWMD, the SWM function fell within the Engineering Division of Environmental Health and Project Implementation Division, Department of Local Government. When Act 672 and Act 673 were passed, this function was transferred to NSWMD and the Solid Waste and Public Cleansing Management Corporation (SWMPC). Such functions include:

- To propose policies, plans, and strategies for solid waste and public cleansing management;
- To formulate plans for solid waste management including location, type, and size of new treatment facilities, coverage areas of solid waste management facilities, solid waste management schemes to supply controlled solid waste to the solid waste management facilities, and the time-scale for the implementation of the plans;
- To set standards, specifications, and codes of practice relating to any aspect of solid waste and public cleansing management services;

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- To exercise the regulatory function specified in Act 672 and in any regulation made under the Act;
- To grant licenses and approvals under Act 672; and
- To carry out such other activities for the implementation of the Act.

Solid Waste and Public Cleansing Management Corporation (SWPCMC)

The SWPCMC was established to complement and ensure the successful implementation of the National Solid Waste Management Policy. In general, the policy aims to provide a comprehensive, integrated, cost-effective, and sustainable solid waste management system that caters to the demand for environmental conservation and public well-being.The Corporation was established under the Solid Waste Management and Public Cleansing Corporation Act of 2007 (Act 673) and commenced its operations on June 1, 2008 under the MHLG.

The Corporation has the power to administer and enforce solid waste and public cleansing management laws and matters related thereto. The role of the corporation is to ensure that solid waste and public cleansing management services are efficient and integrated and meet the expectations of consumers. The corporation's roles include the following:

- To recommend policies, plans, and strategies for solid waste management and public cleansing services to the National Solid Waste Management Department.
- To implement and promote public participation and awareness through various programs on solid waste management and public cleansing.
- To establish systematic recycling and waste segregation practices with an emphasis on sustainable development and incorporating economic, political, and social aspects.
- To process applications for new licenses and for renewal, including the revocation or suspension of solid waste management service provider licenses and submission of recommendations to the National Solid Waste Management Department.
- To monitor the performance of the concessionaires involved in providing solid waste management and public cleansing services.
- To identify environmentally friendly technologies that are safe and cost-efficient, and to conduct research on the development of solid waste management and public cleansing.
- To implement and enforce the laws and regulations on solid waste management and public cleansing.

Private Waste Manager

Privatization in Malaysia was initiated as a national policy in 1983 to address the economic problems at that time. The *Economic Times* defines privatization as a transfer of ownership, property, or business from the government to the private sector. In privatization, the government ceases to be the owner of the entity or business. This process involves three main areas; responsibility, assets, and personnel management. The Economic Planning Unit of Malaysia lists the objectives of the national privatization policy as follows:

1. To facilitate the economic growth of the country;
2. To reduce the financial and administrative burden on the Government;

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3. To reduce the presence of the Government in the economy;
4. To reduce the level and scope of public spending; and
5. To allow market forces to govern over economic activities and improve efficiency and productivity in line with the National Development Policy.

Privatization in the local government sector involves the delivery of public services such as sewerage, transportation, and solid waste management. In particular, the Malaysian government initiated the privatization of urban solid waste management in 1993. Such privatization included the storage, collection, transportation, processing, and disposal of solid waste. The objective was to provide an integrated, effective, efficient, and technologically advanced solid waste management system as part of Vision 2020. This move primarily aimed to reduce and recover waste and therefore, minimize the need for final waste disposal.

Furthermore, privatization was expected to restructure the existing solid waste management system of the LAs into a system that incorporates efficient recycling and environmental management measures. The privatization was also expected to address and resolve problems in solid waste management that were faced by the LAs such as finance, lack of expertise, illegal dumping, open burning, and the lack of proper solid waste sites (Abas & Seow, 2014).

The enforcement agency appointed by the government was the Solid Waste and Public Cleansing Management Corporation. Therefore, three private waste management consortiums were appointed for the entire country, namely:

1. Alam Flora Sdn Bhd, which is responsible for WP Kuala Lumpur, WP Putrajaya, and Pahang.
2. SWM Environment Sdn Bhd, which is responsible for Johor, Melaka, and Negeri Sembilan.
3. Environment Idaman Sdn Bhd, which is responsible for Kedah and Perlis.

However, several states such as Penang, Selangor, and Perak have refused the collection of the concessionaires. This crisis occurred because local authorities were not satisfied with the quality of services and costs of operation (Abas & Seow, 2014).

Non-Governmental Organizations (NGOs)

Non-governmental organizations such as Malaysian Environmental NGOs (MENGO), Treat Every Environment Special (TrEEs), Environmental Protection Society of Malaysia (EPSM), Lions Club, and the Rotary Club play an important role in the solid waste management process. These NGOs are often involved at the community level and organize activities such as recycling and environmental awareness programs that ultimately drive community participation in solid waste management.

INTERNATIONAL TRENDS

International trends in solid waste management provide a benchmark for the evaluation and future directions of integrated solid waste management in Malaysia (Victor, 2001). Other countries are more advanced than Malaysia in handling this particular issue. As such, the relevant development efforts, technologies, facilities, and initiatives can be modeled from the experiences of other countries. This chapter reviews some countries' relevant policies for benchmarking of solid waste management initiatives.

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US

The Congress passed the Solid Waste Disposal Act of 1965 to address the issue of growing solid waste volume in the US. Proper waste management is also ensured through this Act. The Act defined environmentally responsible methods to dispose trash of the household, municipal, commercial, and industrial levels. The Solid Waste Disposal Act of 1965 marked the beginning of a series of regulations that emphasized clean air and resource management. Significant amendments were made to the Act with the passage of the Resource Conservation and Recovery Act of 1976 (RCRA).

Resource Conservation and Recovery Act (1976)

The Resource Conservation and Recovery Act is commonly referred to as the RCRA, which is the US' primary law governing the disposal of solid, hazardous waste. The Congress approved RCRA on October 21, 1976 to address the increasing problems that the nation faced from the rising volume of municipal and industrial waste. RCRA, which amended the Solid Waste Disposal Act of 1965, set the national goals to achieve the following:

- Protection of human health and the environment from the potential hazards of waste disposal
- Conservation of energy and natural resources
- Reduction in the amount of waste generated
- Management of waste in an environmentally sound manner

Europe

Directive 2008/98/EC (2008)

Directive 2008/98/EC explained the basic concepts and definitions related to waste management, such as the waste management hierarchy (e.g., recycling and recovery).'Waste' means any substances or object which the holder discards or intends to discard or is required to discard (M.Gharfalkar et al., 2015). The waste hierarchy comprising of five measures; prevention, preparing for reuse, recycling, other recovery and disposal.

Sweden

The Ministry of Environment established the Swedish Environmental Protection Agency as the central government agency tasked to coordinate and implement environmental policies and protection (Tam, 2014). Under the Ministry of the Environment are county administrative boards and municipal executive boards that function as the respective regional and local authorities to conduct inspections and enforcement of environmental laws in Sweden. Local municipalities are also responsible for collecting and treating household waste, as well as setting their own sanitation plan and regulations for local waste management.

The waste management policy in Sweden is primarily governed by the Environmental Code and the Waste Ordinance. The Environmental Code sets out the framework for promoting sustainable development through the protection of human health and the environment, as well as the effective use of resources. It also contains specific provisions governing waste collection and disposal, resource management,

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permit system, supervising authority, and penalties for breaching relevant rules. The Waste Ordinance complements the Environmental Code by establishing general provisions for the regulation of waste management (Tam, 2014).

Tam (2014) explained that Sweden is also governed by the Industrial Emissions Directive issued by the EU, which commits its member states to controlling and reducing the impact of industrial emissions on the environment. The Directive is transposed into Swedish law through amendments to the Environmental Code and the implementation of six new regulations. Among the new regulations, waste incineration is primarily governed by the Regulation on Waste Incineration, the Environmental Regulation, and the Industrial Emissions Ordinance.

The Regulation on Waste Incineration establishes the emission limits of pollutants and the corresponding measurement requirements, whereas the Environmental Regulation sets the rules on the control, planning, and permission requirements for environmental activities, such as waste treatment. The Industrial Emissions Ordinance introduces the duty of operators to prepare a baseline report, as well as ensures the strict implementation of environmental inspections (Tam, 2014).

Japan

According to Borongan and Okumura (2010), the Waste Management and Public Cleansing Law, enacted in December 1970, stipulates that each municipality shall collect, transport, and dispose the municipal wastes generated within its area. The national government develops the fundamental policy for waste reduction and the development plan for waste treatment facilities, as well as provides technical and financial assistance to municipalities.

The Ministry of the Environment (MOE) is responsible for MSW management administration at the national level. The recycling of some types of municipal wastes is implemented in accordance with specific individual recycling laws, such as the following:

- Container and Packaging Recycling Law (enacted in June 1995, administered by the MOE and the Ministry of Economy, Trade and Industry (METI))
- Home Appliances Recycling Law (enacted in June 1998, administered by the MOE and the METI)
- Food Waste Recycling Law (enacted in June 2000, administered by the MOE and the Ministry of Agriculture, Forestry and Fishery)
- End-of-life Vehicle Recycling Law (enacted in July 2002, administered by the MOE and the METI)

In keeping with the "Mottainai" spirit, Japan exhibits good practices in the development of a sound material-cycle society through the 3R (reduce, reuse, and recycle) principle. Mottainai is a long-established Japanese concept, which means that something wasted without having made full use of its potential is a shame (Borongan and Okumura, 2010).

Singapore

Borongan and Okumura (2010) present in their report that Environmental Public Health Act (EPHA) developments are required to develop the necessary refuse storage and collection system, which will include refuse bin centers in premises for the proper management of refuse. The EPHA also provides

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the legislative framework for the licensing and regulation of waste collection and the establishment of approved waste disposal and recycling facilities. The EPHA includes several revisions to enforce sanctions for offenses on the illegal dumping of waste. The following regulations related to solid waste management supplement the EPHA:

- Environmental Public Health (General Waste Collection) Regulations
- Environmental Public Health (Public Cleansing) Regulations
- Code of Practice on Environmental Health
- Code of Practice for General Waste Collectors

Singapore has established an integrated solid waste management system that ensures all non-recycled wastes are collected and disposed of safely at waste-to-energy plants or at offshore sanitary landfills in the case of non-incinerable waste.

South Korea

Borongan and Okumura (2010) stated that all municipalities in South Korea know and practice the 3R principle. The ultimate goals of waste management in Korea are to ensure a clean environment for the people and the natural ecosystem by minimization of waste generation, optimization of waste recycling, and treatment of waste generated in an environmentally sound manner. A strategic approach to promote the 3R principle is ensured as the core measure to achieve the goals in the country. Therefore, all municipalities understand and try to practice this plan, despite their limited facilities for waste segregation/sorting, collection, and treatment in their respective areas. The regulations applied in South Korea include the following:

- Waste Control Act, 8 Mar, 1991
- Act on the Promotion of Saving and Reutilization of Resources, 8 Dec, 1992
- Act on the Promotion of Construction Waste Recycling, 21 Dec, 2003

CONCLUSION

Compared with other countries, Malaysia still has a long way to go in developing sustainable environmental principles for the Malaysian people. Several actions need to be taken, and these will start with the implementation and enforcement of existing waste management laws in the country and in all stages of waste created. The solid waste management challenges and issues that should be considered while framing solid waste policy include proper waste generation, segregation or separation at sources, collection, transportation, and disposal methods, landfill management, hazardous and other toxic material management, treatment, incineration, recycling and other technology standards, monitoring, evaluation, and continuous improvement methods. The most important challenge is on the change the mindset of the Malaysia community to reduce the waste at the sources. In addition to these issues, policy needs to address the short- and long-term economic, environmental, and social costs and benefits, funding methods, and roles of various stakeholders. The joint projects between municipalities and stakeholders bring

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Malaysia forward in terms of implementing recycling concepts. This initiative may reduce the amount of waste that goes to landfills. Partnerships and the continued cooperation of various stakeholders in municipal waste management efforts should be enhanced in the provision of resources for the effective implementation of waste management.

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Chapter 58
Giving Waste a Second Chance:
Public Awareness and Youth Empowerment

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ABSTRACT

Overpopulation is no doubt worldwide concern as it brings different problems to urbanization process as well as environment. Waste is number one side product of overpopulation. Waste generation is ever increasing in both urban and suburban area and has led to many environmental issues. Many of the waste generated have potential to be transformed into value added products. By recycling, reusing and re-purposing these wastes, we are actually reducing the amount of waste produced and at the same time helping to solve waste disposal problem as many of the wastes exhibit strong energy producing potential. Overpopulation may be an issue of its own; nonetheless, it also provides us an army of human power in tackling environmental issues. Population is a valuable asset. The potential of that amount of man power, especially youth, combining with various awareness campaigns and 3R campaigns introduced by government and NGO are important in targeting these problems.

INTRODUCTION

Disposal of high quantity of waste is an unparalleled environmental issue. Increase in population directly influences the waste generated per unit area as percentage of the population increases especially in urban areas. More and more people are moving into the city referable to economic activities, social

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activities and the quality of life available here. With increasing rate of population and urbanization, land available is not enough for proper waste disposal. This means the location of the residential area is getting closer to the vicinity of waste disposition area such as landfills and waste incinerators, which is in fact inevitable. Exposure to harmful pollutants around the area of waste disposal site especially waste incineration plants also raises health concerns.

There is no more doubt that increase in population translates to higher generation of waste (Agamuthu and Fauziah, 2011) and waste generation strongly varies depending on economic and geographical status of an area. Till 1993, waste generation in Malaysia was between 0.34-0.85kg per capita per day. However, at present, in Kuala Lumpur, capital of Malaysia, waste generation of household waste per capita is 0.80-1.30 kg per day (Abdul Jalil, 2010). In 2006, methods of waste disposition in Malaysia were:

- Recycling (5%),
- Composting (1%),
- Inert landfill (3.2%),
- Sanitary landfill (30.90%) and
- Other disposal sites (59.40%).

However, the government is targeting to increase recycling to 22% and composting to 8% by the year 2020 (Periathamby et al., 2009). Composition of waste in Malaysia is mainly composed of municipal solid waste (64%). A heavy percentage of the municipal solid wastes is recyclables (80%) and is disposed at landfills (Ministry of Housing and Local Government (MHLG), 2006). Landfill is still the most commonly used method of solid waste management in Malaysia due to its cost effectiveness (The Ingenieur, 2009). Nevertheless, landfill may soon give problem as it approaching its maximum capacity and simultaneously constructing a new landfill site is out of the question due to land scarcity with the increase in population (Latifah et al., 2009; Moh & Abd Manaf, 2014).

Recycling is the collection and processing of waste separation, the result being new consumer products. Recovery is the separation of mixed waste, with the final outcome of producing new raw materials for industries. Recently, waste-to-energy approach is emerging as a promising way of handing ever rising amount of waste especially in developing countries. Waste-to-energy (WTE) approach uses thermal and biological conversion technologies to release potential of usable energy contained in solid waste (Johri et al., 2011). Exceeding 800 thermal WTE plants are operating worldwide (Martin, 2012). Country such as Germany is using WTE to handle 35% of the total waste treatment (EU's average is 24%) and waste that was land filled comprises only 1% of the total waste (Eurostat, 2014). Population hike changes waste generation pattern and we are in need of more proficient waste handling methods and should not rely solely on one method. Malaysia has started the implementation of WTE mainly for agricultural waste and forestry residues in recent decades. It provides alternative for renewable energy for Malaysia (Tan et al. 2014). However, implementation of WTE on municipal solid waste is still not common. Nevertheless, agricultural industries in Malaysia are generating tonnes of waste that have massive potential as resource material for waste-to-energy approach.

Overpopulation may bring various challenges towards waste management. Nevertheless, for every nation to face this challenge, especially in urban areas provides infinite potential for handling the problems caused by overpopulation. Rules and regulations for waste management require manpower to implement them. Consequently, overpopulation does not solely bring negative impact towards the environment, but can however be seen as one of the most useful resources, in transforming the waste management situation.

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About nine out of ten people between ages 10 and 24 live in less developed countries. Total population in Malaysia in the year 2014 was 30.2 million, and population back in 1950s was 6.1 million (see figure 1). About 66.3% of population in Malaysia is between the ages of 15-59. In Malaysia, according to statistics, percentage of 10-24 years old is 20 to 29% in the year 2015 (UNFPA, 2014). This age group is the group of population that is more willing to accept and practice the concept of environmental friendly practices such as recycling, compared to the older generation.

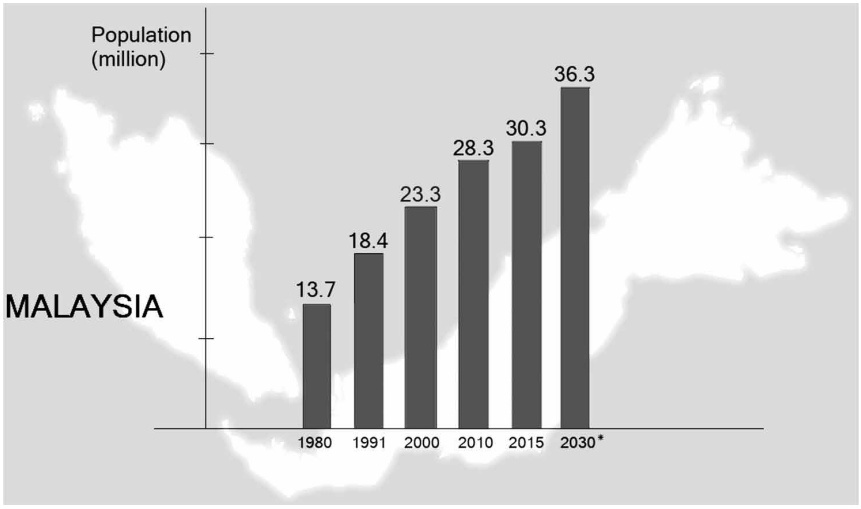
Today, many modernized cities which are highly populated such as Stockholm and Adelaide are endeavoring to adapt zero waste practice, a more cost effective and sustainable approach. "Zero waste city" has the perception of attaining 100% recycling rate and resources recovery from waste materials generated in the city (Zaman & Lehmann, 2011). The five waste management settings include:

- Social,
- Economic,
- Political,
- Technological and
- Environmental, and many stakeholders are involved.

They are interconnected and mutually dependent (Zaman & Lehmann, 2011). With human factor potential exhibiting from abundance of young population in the country, "zero waste city" may not only be a concept, but will become something that can be implemented.

Hence, overpopulation may not necessary be bringing only negative impact towards waste management in this modern era, particularly with proper awareness and technology.

Figure 1. Total population of Malaysia
Sources: Department of Statistics Malaysia (2010); United Nations (2015)



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SOURCES OF SOLID WASTE FOR SUSTAINABLE ENERGY

Waste generation rates are affected by socio-economic development, degree of industrialization, and climate. More often than not, the hike in the percentage of urban population induced by economic prosperity will lead to higher solid waste generation.

Generally, classifications of solid wastes are proposed as reported by its origin into four major types:

- Municipal solid waste (MSW),
- Agriculture solid waste (ASW),
- Industrial solid waste (ISW), and
- Healthcare solid waste (HW) (Sawalem et al., 2009; Eddine and Salah, 2012; Sadek et al., 2013).

Municipal Solid Waste (MSW)

Tonnes and tonnes of household waste are gathered every year and the main part comprises off disposal that ends in landfill such as food waste, cloth, paper waste, glass and et cetera. About 80% of the total municipal solid waste collected is biomass resource, such as putrescible waste and paper. These wastes have high potential in energy conversion via combustion, through by anaerobic digestion by the digester installed in landfill site. Gas obtained from the landfill site (50% methane and 50% carbon dioxide approximately) is derived from municipal solid waste that undergoes natural decomposition. It is scrubbed and cleaned and then fed into internal combustion engines or gas turbines for generating heat and power. The organic fraction of MSW is stabilized anaerobically by a high-rate digester with the intention of obtaining viable biogas for generating electricity and steam.

Agricultural Solid Waste (ASW)

Extensive amounts of crop residues are generated worldwide, and are undoubtedly not fully utilized. The most rampant agricultural residue is rice husks which is 25% of rice by mass. Other agricultural residues consist of"

- Sugar cane fibre,
- Cereal straw,
- Coconut husks and
- Shells.

In current farming practise, farmers either plough these agricultural residues back to the soil, burn the residues, left it for decomposition or grazed by cattle. Various studies on agricultural and biomass have clearly concluded that utilising portion of the crop residue for energy making is appropriate and viable as these residues hold the potential of being processed into liquid fuels for generating energy and heat.

Animal Waste

There are an extensive variety of animal wastes which can be utilised as biomass energy sources. The most extensively recognized sources are the animal and poultry manures. In the past this waste was

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recuperated and mostly sold as compost or just spread onto land, yet the announcing of new environmental control policy has resulted the requirement of certain level of waste management. This has then provided incentives for waste-to-energy approach. The common technique of converting these waste materials into value added product is via anaerobic digestion that produces biogas which can be used as fuel especially for internal combustion engines, for small gas turbines and even for space and water heating. Food processing and abattoir wastes are also exhibiting potential in anaerobic digestion feedstock (Eddine & Salah, 2012; Sadek et al., 2013)

Sugar Industry Wastes

Sugar cane industry creates extensive volumes of bagasse every year. Baggasse is a dominant source of biomass that has high potential to be employed as boiler feedstock for generating steam which can be utilized for processing heat and electricity production. Most of the sugar cane mills process their baggases to produce and supply the energy for their own needs and some sugar cane mills are capable to export significant amount of electricity to the power grid.

Forestry Residues

Forestry residues are created by operations for example, diminishing of plantations, clearing for logging roads and streets, separating stem-wood for mash and timber and natural attrition. Furthermore, wood processing also generates high amount of residues such as sawdust, off-cuts, bark and woodchip rejects. These wastes are often not utilized at all and are often disposed or left to decompose on site. Nevertheless, they are possible to be utilized after collection in biomass gasifier for producing hot gasses for steam production.

Industrial Solid Wastes (ISW)

Food industry is often the industry that generated a prominent number of residues on top of by-products that generally can be utilised as biomass energy sources. Waste materials are produced from every sectors of food industry; from meat production to confectionery is all producing waste that has potential as energy source. Other solid wastes in food industry include:

- Fruit and vegetables peelings and scraps,
- Food products that do not meet food control standards,
- Pulp and fibre from sugar and starch extraction,
- Filter sludge and
- Coffee grounds.

These wastes are usually not utilised and are often disposed of at the landfill.
Liquid wastes are also generated from:

- Washing of meat,
- Fruit and vegetables,
- Blanching of fruit and vegetables,

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- Pre-cooking meats,
- Poultry and fish,
- Cleaning and processing operations
- as well as wine making.

Content of starches, sugar and other dissolved and solid organic matter are high in these waste waters. These waste waters may be potentially processed via anaerobic digestion for producing biogas or to be fermented for ethanol production. Sadek et al. (2013), reported several industrial examples of waste-to-energy approaches that are already in existence.

Biomass

Biological material often termed as biomass can be used as a fuel source for energy generation. Technology to convert biomass to large amounts of electricity has been put in place by the Malaysian government. Simultaneously, small scale versions such as wooden stoves or furnaces are also being used. Biomass conversion also produces bio-fuels, such examples are ethanol, methanol, bio-oil, and bio-diesel. Among all domestic renewable energies, biomass energy is the greatest source. In Malaysia, the wood, rice, sugar and palm oil industries have been exploiting their biomass as fuel to offset (partially or fully) their energy needs. Malaysian oil palm biomass contributes about RM 6379 million of energy yearly. Even though it is already in practice, there is still a lot to done to optimize the usage of biomass for cogeneration in Malaysia (Sumathi et al 2008).

Steam is produced by the direct burning of feedstock which is used to power generators by the turbines. Empty fruit bunch (EFB) is most often used, among the other wastes of the oil palm industry for the generation of heat energy via combustion (Husin et al., 2005). Most palm mills burn oil palm fibre and shells as boiler fuel to generate steam for the extraction of crude palm oil and a small amount of electricity for internal use. EFB has a calorific value of about 18,838 kJ kg^{-1} and is able to produce an approximate of 7.65Mt (million tonnes) of power. The Chubu Electric Power in Sabah, Malaysia plans utilizes the empty palm bunches to generate the output of a 10,000 kW. This fulfils the EU standard guidelines (2002) for CO_2 emission and trading system for greenhouse gas emission allowances. Also proposed was the power plant in Pantai Remis, to generate 11.5 MW of electricity. It is to be fueled by EFB, supplying electricity to a distributor.

In the coming years, there is likelihood of depletion of oil and gas reserves, and in order to ensure the security of energy supply, the demand towards the establishment of hydrogen economy has come to the fore front. This has brought together scientists to seek for other means of extracting the energy from biomass. Studies in Malaysia are looking in to the production of hydrogen from POME using microflora isolated from POME sludge (Atif et al., 2005; Krishnan, 2006) The standard biogas hydrogen generation was observed to be of 57±2% with 7 d HRT. The generated biogas was free from methane which is a success.

POME can also be used to produce bio-gas via anaerobic digestion in which bacteria in organic matter decomposed without the presence of oxygen; resulting in extractable methane, a source of energy. 20 tonnes of FFB, generates 100 tonnes of POME, which yields about 400 m^3 of biogas and 10.8 MW of power (Sumathi et al 2008).

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OTHER LESS-FOCUSED POTENTIAL SOURCES OF BIOMASS FOR ENERGY GENERATION IN MALAYSIA

Paddy straw is found in large amount from paddy paddy field while rice husk is generated in great amount in the rice mill. Straw was utilized to produce biomass energy in China through direct combustion, anaerobic digestion and gasification. Utilization of crop straw via direct combustion was inefficient and at the same time has led to many ecological and environmental problems. However, with anaerobic digestion, the energy output in biogas contains the heat value of $2.5x10^4$ kJ m^{-3}, which is also equivalent to 0.76kg of standard coal. The amount of household biogas digesters has reached 7.64 million by the end of 2000 (Zheng et al., 2007). In gasification process, biogas produced using air and steam/air as gasifying agent was of low calorific value (CV) with an essential component of carbon monoxide (McKendry, 2002). Utilizing oxygen and steam as gasifying agent produces biogas with medium CV and the main elements are CH_4 and H_2 which can also be employed as fuels. Biogas with high CV can be produced via using hydrogen and hydrogenation as gasifying agent (Zheng et al., 2007).

The common practice in Malaysia was to send to landfill or open burning. However, lately, two rice mills in northern Malaysia have started to practice the usage of their residues to generate electricity (Shafie et al., 2012). Both of these mills were able to use up to 86,400t per year in generating power (700-1500kW). Cogeneration program of rice husk was initiated by European Commission (EC) and Association of South East Asian Nation (ASEAN). With the implementation of this program in rice mills, issues on rice husk management was solved and it has also provided the extra benefit of selling off the ash which can be used as construction materials (Karim Ghani et al., 2008) and electricity generated (Shafie et al., 2012).

Pineapple waste is also another main commodity in Malaysia as it is one of the oldest agro-based export-oriented industry dating back to the 19th century. Almost all of the pineapple waste is not utilized and the only mean of disposal is burning. Only 20% of the pineapple is processed into can food for consumption usage (Rosma & Ooi, 2006) and the residues (as much as 30-50% of total fruit weight) including the skin, core, base and crown are all directly disposed as waste during the canning process (Ong et al., 2014).

Potential of durian waste as raw material for second generation bioethanol production relies on its production and amount of waste generated. Considering that the durian production in Malaysia is showing an upward trend, tremendous amount of durian waste is foreseen to be left un-used. Amount of waste from durian seed and rind was reported to be 87,555.3 and 171,303.9 tonnes respectively in year the 2013 (Aditiya et al., 2015; Amid & Mirhosseini, 2012). If the potential of utilizing these wastes for energy production is made viable, significant improvement in waste management for sustainable environment, as well as renewable energy production are expected.

CURRENT ENERGY POLICY SCENARIO IN MALAYSIA

In Eighth Malaysia Plan, biomass, biogas, municipal waste, solar and mini-hydro were highlighted as valuable renewable resources and further promoted in Ninth Malaysian Plan (2005-2010) which has also underlined the focus on promoting the export of palm biodiesel (Abdul-Manan et al., 2014). We are in the era which is facing a pressing concern towards moving from heavily relying on fossil fuels to opening up new avenues for bio-based material. First Malaysia natural biofuel policy (NBP) was developed in

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Table 1. Energy potential of various agricultural biomass components in Malaysia

Biomass component	Calorific value (kJ/kg)	Potential energy generated (Mt)	References
Palm Empty fruit brunches (EFB)	18,838	7.65	Shuit et al., 2009
Palm Fiber	19,068	4.37	UNDP, 2007
Palm Shell	20,108	2.84	Sasaki et al., 2009
Palm Kernel	18,900	0.95	Asureira, 2002; Sumathi et al., 2008
Rice husk	15,324	0.17	Pütün et al., 2004; Aditya et al., 2015
Rice straw	13,620	0.28	Krishna & Babu, 1998

2006 and championed by the Ministry of Plantation Industries and Commodities Malaysia (MPIC). The Malaysia NBP anticipates the use of environmental friendly approach and sustainable resources derived energy to lessen the dependency of drastically depleting fossil fuels (Abdul-Maman et al., 2015). In 2009, National Renewable Energy Policy was introduced for rectifying the failure of attaining the target of 5% renewable energy in the energy mix. This policy also highlighted the applications of indigenous renewable energy resources through increased contributions of renewable energy for national power generation mix (KeTTHA, 2010). In 2005, National Biotechnology Policy was drafted in Malaysia with the aim of transforming Malaysian economy into a high-income, inclusive and sustainable one. This then lead to the launching of its very own bioeconomy program known as Bioeconomy Transformation Program (BTP) in year 2012. It works as a platform provided by government for private sector to maximize commercial opportunities. It is also designed specifically to benefit Malaysian society through cultivating commercialization of bio-based products from the industry (Bioeconomy Malaysia, 2014; Albrecht & Ettling, 2014).

With the abundance of agriculture residue, agricultural waste derived biofuel is the most promising form of renewable energy.

POPULATION INCREASE AND WASTE GENERATION SCENARIO IN MALAYSIA AND ASIA REGION

Increase in population used to be the key to economic growth and development. However, today, overpopulation has become a major problem especially in developed countries. Waste is typically population attributed. Depletion of resources and environmental destruction that come along with population growth are inevitable.

In West Asian countries; Nepal, Pakistan, India and Bangladesh the current and projected waste generation rates range from 0.12 -0.84 kg capita^{-1} day^{-1} in 2012 to 0.70 – 1.05 kg capita^{-1} day^{-1} in 2025. This is much lower as compared to East Asian countries; Thailand, Vietnam, Malaysia and Philippines as illustrated in Figure 2. China also contributes 1.02 kg capita^{-1} day^{-1} (2012) to an estimated 1.70 kg capita^{-1} day^{-1} in 2025. Malaysia is the second largest waste producers of the region (1.52 kg capita^{-1} day^{-1}) and is expected to increase by 20% in 2025. The expected increase in population in Malaysia (33.2 million) coupled with the increased pace of urbanization, would lead to large quantities of solid waste

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generated by 2025. It is obvious that, in near future, increase in waste generation is directly linked with the increase in populatio. Despite the effort in continuous research and development in waste derived energy, waste generation is still higher than the amount of waste that is being utilized.

With urbanization that is actively going on in all countries around the world, land scarcity is undoubtedly a fact. Land filling will soon become not viable despite its operation cost may still be lower if compared to other methods. Researchers worldwide are proactively looking for possible alternatives. Besides researching for alternatives, to face this issue, education and awareness campaigns have to play their roles with the intention of better handling the waste management crisis.

Figure 2. Current and projected waste generation rates (kg capita^{-1} day^{-1}) of selected countries
*Source: Hoornweg and Bhada-Tada (2012) *Projected value of year 2025.*

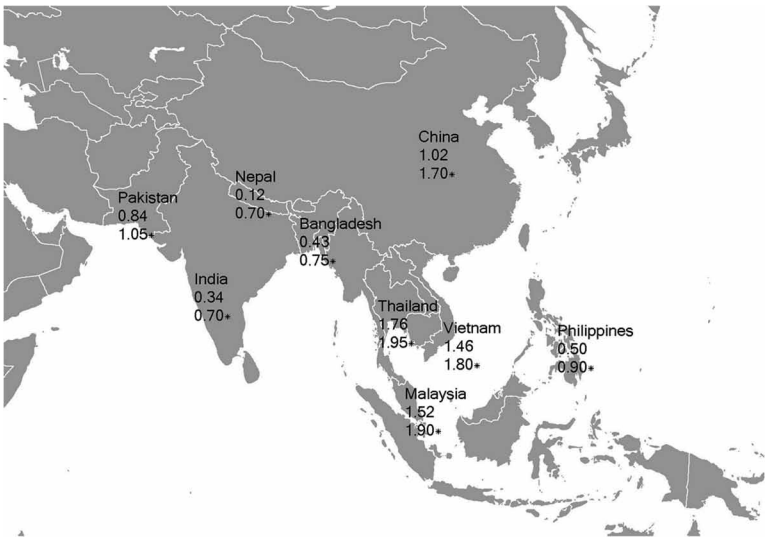

Table 2. Overview of urban population, waste generation and total energy use of selected countries in South East Asia

Current available data						2025	
Country	**Income level**	**Total urban population (thousand)**	**Population aged 10-24 in year 2014 (million) (UNFPA, 2014)**	**MSW per capita (kg capita^{-1} day^{-1})**	**Total energy use (kt of oil equivalent) (2011) (UN, 2015)**	**Projected urban population 2025 (thousand)**	**MSW per capita (kg capita^{-1} day^{-1})**
Malaysia	UMI	14,429	8.4	1.52	75,907	27,187	1.9
Thailand	LMI	22,453	13.5	1.76	119,147	29,063	1.95
Indonesia	LMI	117,456	66.1	0.52	209,009	178,731	0.85
Singapore	HIC	4,849	1.1	1.49	33,447	5,104	1.8
Vietnam	LI	24,001	23	1.46	61,210	40,505	1.8

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Malaysia is classified as upper middle income (UMI) country by World Bank (2012) with the total urban population of 14 million and waste generation (MSW) of 1.52 kg capita^{-1} day^{-1}. It is projected that by 2025, the MSW generated will increase to 1.9 kg capita^{-1} day^{-1} as shown in Table 2. If we are to look at total energy use, Malaysia, which has lower urban population compared to Vietnam, has higher energy consumption than Vietnam (United Nations, 2015). Hiking in waste generation per capita is also raising concern as Malaysia is showing ascending trend in both population and waste generation. Urban population in some countries in South East Asia (Malaysia, Thailand, Indonesia, Singapore and Vietnam) all indicate increment in year 2025 as projected by World Bank (2012).

In Tenth Malaysia Plan (2011-2015), the urgency of increasing public awareness and commitment for green technology application and adoption was highlighted as one of the key emphasis. Other than that, new mechanisms on renewable energy are also one of the areas of interest (Foo, 2015).

Commercial viability of renewable energy technologies especially the applicability of waste derived energy is receiving poor perception and awareness. This is also clearly reflected by limited numbers of research and development in both industrial and institutional research in Malaysia. In consequence, these possess significant drawbacks in government's effort in promoting renewable energy (Oh et al., 2010)

RECOMMENDATIONS

Increasing population, booming economy, urbanization and improvement in living standards have all contributed to solid waste generation (Guerrero et al., 2013). Many researchers have studied and looked into issues regarding overpopulation. However, the direct linkage between waste production and worldwide population growth is not commonly reviewed. With our current technology, waste symbolized misallocated resources. Waste management hierarchy (Figure 3) introduced by EPA has included management strategies and arranged according to environmental preference (US EPA, 2016). Reduction and reuse approaches are preferred over others. Treatment and disposal are the least favoured options. Local communities should have a role in carrying out reduction, reusing waste as well as recycling as they are the first tier in waste management. This will also allow public to be aware of their waste generation, including types of waste and amount of waste they generated. Rather than promoting waste reduction and recycling at community level, various schemes have been introduced by NGOs as well as industries to further strengthen the effort in a larger scale.

Youth Empowerment

Efforts in educating youth in sustainable waste management is utmost important as they are the group of population that are educated, and are more willing to accept the idea of sustainable approaches in waste management for better environment.

We are homing close to 1.8 billion of young people between ages of 10-24 and this group of population is the fastest growing of all (UNFPA, 2014). As part of the household, youth too contribute to waste problem. Youth are better equipped to reach their full potential when they are healthy and educated. Sadly, youth is also falls under the most vulnerable group towards the ill effects of improper waste management. Therefore, educating youth will definitely increase the practice of environment friendly approaches. Despite the advancement in technology that have granted us waste management technology such as landfill and waste to energy approach, the conventional 3R (Reduce, Reuse and Recycle)

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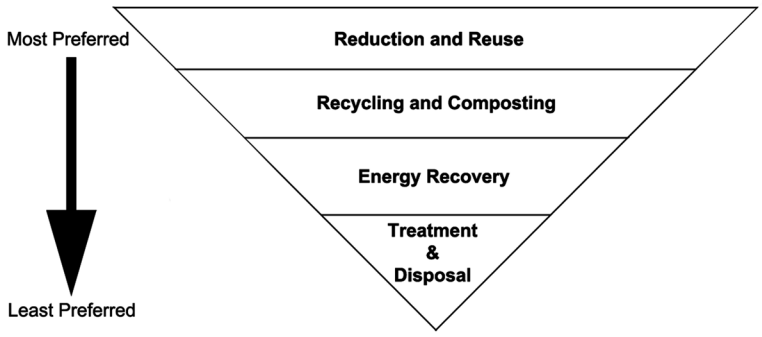
Figure 3. Waste management hierarchy
Modified from US EPA (2016)



is still the cornerstone of lots of waste disposal problem. Imagine this scenario, if majority of youth practise 3Rs and promote in their localities, we are indirectly having a green army that may turn the tide of environmental degradation. In Kenya, waste collection and a number of other public services was initiated by the Government in 2009. The Kazi Kwa Vijana (Work for Youth) programme was aimed at employing both urban and rural youth. We should not neglect youth in the battle against environmental degradation as a matter of fact, they are our strongest human force that are able to achieve the most.

Make a Difference Through Public Awareness

Environmental awareness allows us to better understand how delicate our environment is. Waste segregation, recycling programs and repurposing waste products and by-products may sound low-tech. However, these are the effort that may really bring drastic impact to our environment particularly in the long run.

Malaysia has recently introduced federal waste segregation programme based on the Solid Waste and Public Cleansing Management Act 2007 (Act 672) that was first approved by the Malaysian Parliament on July 17, 2007, and gazetted on Aug 30, 2007. Selected states and federal territories (Kuala Lumpur, Putrajaya, Pahang, Johor, Malacca, Negeri Sembilan, Perlis and Kedah) are involved in this new waste segregation program. However, if the waste segregation set up can be further developed, more waste, especially electronic waste can also be effectively segregated.

Various NGOs and companies have recently joined the forces of promoting the importance of recycling. The Emirates Environmental Group (EEG) has launched many community projects over the years especially waste collection campaign (neighbourhood recycling campaign) that reaches out to everyone categorised as households, schools, small organisations, hotels and factories. Certificates are given based on the largest collector in the different categories all over the UAE (green awards). Tax rebate from government is also given to encourage more participation (EEG, 2015).

Other than the conventional recyclable materials such as PET bottles, glass, aluminium can and papers, due to the ever growing fashion industry, several major clothing companies have started clothes recycling campaign. Fast-fashion, the clothing equivalent of fast food, has created sharp rise in amount of waste. The fast fashion's rapid-response production system which strongly relies on low-wage production in some of the poorest countries on earth has in a way, fueled the throwaway culture as the clothing is cheap (Ringstrom, 2015). A recent survey has revealed that most of the women's garments are worn only for seven times before being left out or tossed into the garbage (Cline, 2016).

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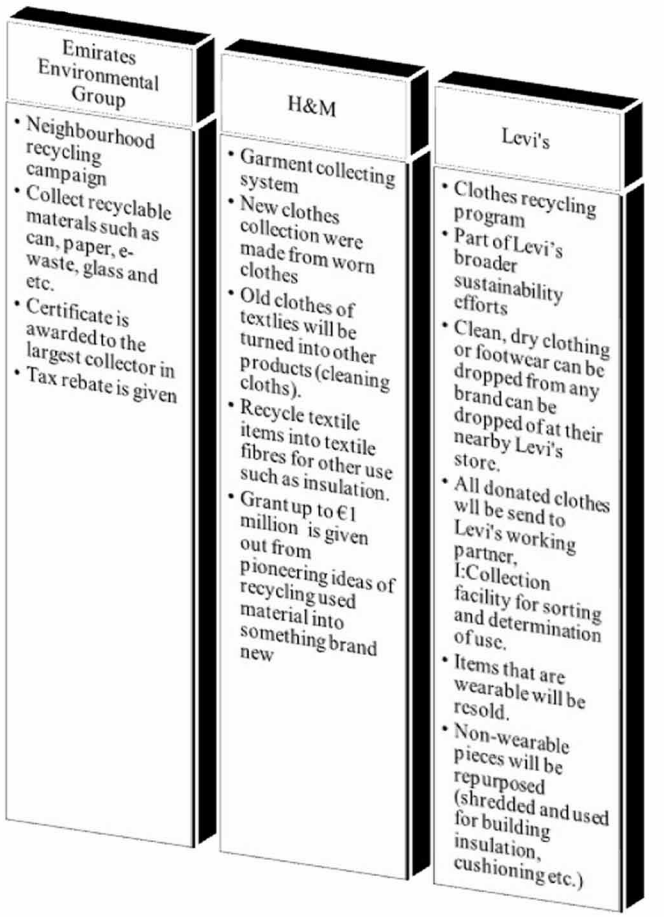
Studies revealed that an estimated 21% of annual clothing purchases stay in the home. This represents a potentially abundant of unseen waste that will gradually enter our solid waste stream. Meanwhile, according to the EPA office of Solid Waste, more than 68 pounds of clothing and textile per year per person are thrown away. Clothing and other textiles represent about 4% of the municipal solid waste and its showing rising trend (Claudio, 2007).

Sadly, recycling cotton clothes is not easy. Old cotton clothes will need to be chopped up and turned back into raw material which tends to lower the cotton's quality. However, several fashion industry tycoons have started several approaches on recycling clothing. Some efforts by NGOs and corporate are shown in the Figure 4.

Combining population as an asset and public awareness, improving waste management in all levels is not difficult. The potential of wastes generated should be fully utilized. Policy maker should learn from successful stories of other country and come up with proper plans and campaigns that are appropriate for their people. Increase in waste generation is a global problem, everyone is responsible. Through cooperation, everything can be made possible.

Figure 4. Examples of recycling program from non-government organisation and clothing companies



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CONCLUSION

With the progression of technology, life expectancy is now longer than previous. Increase in population is indeed a foreseen issue. It has become unavoidable for all countries in the world especially developing countries. The word population is always linked with environmental issues as waste is generally population attributed. Many countries such as Malaysia have the advantage of well-developed agriculture industry which generates high amount of agricultural waste that contains potential in generating energy through different technologies. With regard to environmental benefits, utilization of waste for energy generation is undoubtedly a good alternative in handling vast number of agricultural waste that exhibit promising energy potential. Despite the evidence that the waste derived energy may not be able to compete with the performance of fossil fuels, waste derived energy still deserve attention as the potential is massive. Technology advancement may be solving a lot of problems for us these days, however, please bear in mind that other efforts such as the 3R approaches and repurposing waste are playing a vital role too as they are the most direct method in addressing waste management problem that everyone can be involved in. After all, government policy, together with cooperation of public and other organization are utmost vital in effectively handling such issues. No single management approach is suitable in managing all types of waste. However, waste reducing and reuse are still the most effective ways of tackling the problem of increasing waste generation. Youth, as the most promising group with highest potential, should be encouraged in participating waste recycling and reusing program. By educating them, we shall have a group of people who are highly aware of the current environmental problems, and understand the effort they can provide in targeting these problems. Segregating waste for reduction in sending off waste to landfill, recycling the recyclable materials and composting biomass should be introduced into daily waste handling approach. Public should be aware of the current waste generation scenario in order to realize the hazard it brings.

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Chapter 59
Leachate Pollution and Impact to Environment

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ABSTRACT

Pollution prevention is a step towards obtaining a green environment, and no amount of effort in that direction should be considered too great. To this effect, the pollution by leachate and the resultant impact on the environment is discussed in this chapter. Types and sources of pollution, their transfer and effect have been discussed, so as to give a background understanding on pollution and hence provide a platform for its control. The age old waste disposal practice of open dumps and landfilling is discussed, highlighting the dangers of indiscriminate waste dumping and uncontrolled landfilling practices. Although other sources of leachate generation are highlighted, the chapter focuses on leachates from municipal landfills and the effect of its migration. Engineered landfills also known as sanitary landfills have performed better in curtailing the movement of leachates, hence the use of artificial liners or low permeability soils such as the well compacted clayey soils, to eliminate or minimize leachate migration.

INTRODUCTION

Generation and disposal of waste is considered absolutely normal and a part of everyday living, but the crux of the matter is the means by which the waste should be disposed safely to avoid pollution and ensure a healthy environment.

Open dumping of waste on land or in water bodies has been practiced from ancient times, but it is imperative that continuous awareness be made of the pollution effect, especially because some of the polluted water served various purposes including household uses and irrigation among others. Also, the indiscriminate dumping of waste on the ground constitute an eye sore and produces stenches which was offensive to human senses.

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Because of the aforementioned reasons, landfills are now more commonly used, in which wastes are buried in the ground. Unfortunately however, many so called landfills in the less civilized nations may just be regarded as 'glorified open dumps'. Landfills must be controlled to remove the demerits of uncontrolled landfills, especially regarding the generation of wastewater called leachates, bad odors and related problems that may lead to the pollution of the environment.

THE ENVIRONMENT AND SUSTAINABILITY

The environment may be considered in two primary forms; the natural and built environments. While the natural environment includes all the living and non-living things on the earth, existing in their natural state, the built environment is essentially a modified form of the natural environment. This may occur even from very simple and unbiased agricultural practices, construction exercises and mining, intended for human benefits. Therefore, it can be inferred that a natural environment hardly exists. Although, the building up of an environment may be with a noble intention, however, many of such practices may also lead to the pollution of the environment.

Environmental pollution is considered largely related to industrial revolution and urbanization (Xu, et al., 2014) with the emergence of many great factories; unprecedented air pollution and the discharges of very large volumes of industrial chemical waste.

Considering the plausible exposure of the built environment to contamination and degradation, all hands must be on deck towards achieving a sustainable environment. In essence, it should be possible to develop the environment for desired benefits without destroying the environment or negatively altering the natural state of the environment.

There are many types of pollution coming from various sources and of various consequences. A basic understanding of pollution would provide the awareness necessary to help individuals in the minimization of their contributions to the dangers of environmental pollution. Various pollution types and sources which may impact both the natural environment and human health negatively are discussed. However, the focus of this chapter is the effect of leachate pollution on soil, surface and ground waters, especially those located within the immediate environment of the site.

POLLUTION

Pollution is considered as the introduction of contaminants also called pollutants into any natural system thereby causing an adverse effect on the latter. In like manner, environmental pollution is the deterioration of the environment by the introduction of many factors occurring in forms such as chemical substances, and or energy sources including noise, heat, and light. The major forms of pollution and their specific contaminants are highlighted in Table 1.

Air Pollution

Air Pollution involves the contamination of the atmosphere by altering air chemistry and composition. Contaminants exist in the form of particulate matter like the dust, excess gases such as carbon dioxide (CO_2) and vapors that are not efficiently removed by natural cycles like the nitrogen cycle or carbon cycle.

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Table 1. Major forms of pollution, causes and their contaminants

Forms of Pollution	Causes	Contaminants
Air pollution	Release of chemicals and particulates into the atmosphere	carbon monoxide
Noise pollution	Excess noise or unpleasant sound causing temporary imbalance in nature	Aircraft, industrial, roadway, and high intensity sonar
Soil pollution	Release of chemicals due to spills or underground leakage	Hydrocarbons, heavy metals, MTBE, herbicides, pesticides
Thermal pollution	Human influence resulting in temperature change in water bodies	Use of water coolant in power plant & hot waste water discharges
Water Pollution	Discharges of waste water from commercial & industrial waste (including spills)	Chemical contaminants from industrial & domestic sewage

Although many sources of air pollution exist, the most abundant of them include the following:

A. Exhausts from vehicles and manufacturing processes (Bauer, et al., 2015; Reşitoğlu, et al., 2015; Zhang & Chen, 2015).
B. Natural sources such as volcanic eruptions, dry soil erosion and especially forest fires (Corlett, 2014; Rapport, et al., 1985).
C. Building and demolition of structures (Gadeke, et al., 2014; Gladstone & Martin, 2014).

The effect of air pollution is dependent on the type of pollutant and the extent of exposure. Common effects include increased smog, rain acidity, crop depletion due to insufficient oxygen and higher rates of asthma occurrence (Delfino, et al., 2014). They could also include Lung cancer, cardiopulmonary mortality (Kim, et al., 2015). Recently also, scientists have considered global warming as being related to an increased air pollution. And an investigation on how pollutants could affect mortality showed that the main pathway could be that fine particles can lead to systemic inflammatory and oxidative response (Beelen, et al., 2014).

Water Pollution

Water is deemed one of the most important resources and is very essential to life. 70% of the earth's surface is covered by water. Its pollution involves contamination by particulate matter, chemicals, and bacteria matter that deteriorate the purity of water and its other qualities.

The spread of water pollution is possible because the different sources of water (e.g. rivers, lakes, oceans and underground reservoir) flow together and a possible pollution of any of the sources may eventually spread during their flow.

Possible causes of water pollution include the following:

A. Sedimentation due to soil erosion (Alexandridis, et al., 2015; Carkovic, et al., 2015; Rickson, 2014; Ryken, et al., 2015)
B. Inappropriate disposal of waste (Flanagan, 2015; Mahmood & Malik, 2014; Mudhoo, et al., 2015; Yang, 2015)

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C. Leaching of soil pollution (Dudar, et al., 2015; Minhas & Yadav, 2015; Nassar, 2015).
D. Decayed organic matter in and related to agricultural activities (Li, et al., 2014; Wesström, et al., 2014).

Water pollution has far reaching effects which includes the following:

A. It diminishes the quantity and availability of potable water.
B. It lowers the supply of water required for agricultural purposes such as crop irrigation, fish farming, wildlife, etc.

Land Pollution

Land pollution also referred to as soil pollution involves the contamination of the soil from habitation, land cultivation or wildlife and game reserves. Land use pattern such as mining and agriculture may also be sources of exposure to soil or land pollution (Xu, et al., 2014).

Land pollution generally inhibits the natural growth and creates an imbalance in the land structure. Pollution can be deliberate such as landfills, or they may be unintentional, in which case they are more able to spread widely and their effects are also far reaching.

Pollution sources that may not be peculiar to only the land include the following:

A. Spills from sewers and hazardous waste (Ali, et al., 2015; Gavrilescu, et al., 2015).
B. Occasional use of inorganic pesticides and other temporary farming practices (Boison & Turnipseed, 2015; Donati, 2015; Gomiero, 2015; Teló, et al., 2015).
C. Destructive land practices such as strip mining and deforestation (Ncube-Phiri, et al., 2015; Ravi & Priyadarsanan, 2015).
D. Dumps and litters from the households (George, 2015; Musingafi, et al., 2015; Wachirawongsakorn, 2015).

The effects of land pollution include the following:

A. Deficient growth and lower crop yields.
B. Depletion of wildlife.
C. Possibility of water pollution.
D. Visual pollution.
E. Soil erosion and desertification.

Noise Pollution

Noise pollution refers to any undesirable level of sounds resulting from human activities that may interrupt the normal living standards. Urban noise pollution is considered to be associated with urban development (Bhave & Shaikh, 2014).

Sources of noise pollution include the following:

A. Manufacturing mills (Chakraborty, et al., 2014; Noweir, et al., 2014).

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B. Construction and demolition exercises (Arthur-Aidoo, et al., 2014; Emmanuel, et al., 2014).
C. Traffic (Abbaspour, et al., 2015; Al-Mutairi & Al-Rukaibi, 2014).
D. Aircrafts (Ozkurt, et al., 2014).
E. Moving Trains (Kirillov, et al., 2014; Monazzam, et al., 2014).
F. Entertainment activities including cinemas and parties(Archibald, 2014; Sari, et al., 2014)

Noise pollution may be either of temporary or permanent sources. Effects of noise pollution include the following:

A. Impairment of hearing (Hammer, et al., 2014).
B. Interferences with wildlife existence.
C. A general degeneration of lifestyles and standards.

Radioactive Pollution

Although exceedingly hazardous, radioactive pollution is a highly uncommon type of pollution. However, very strict environmental regulations have been instituted by the government as a control and preventive measure to avoid the dangers of its occurrence. Although rare, there are yet occurrences of natural radioactivity (Krishnamoorthy, et al., 2014).

Sources of radioactive pollution include:

A. Accidental leakages from nuclear power plants.
B. Improper disposal of nuclear water.
C. Mining operations for radioactive substances like Uranium.
D. Radionuclides from rock phosphates used in industrial manufacture of fertilizers (Ajmal, et al, 2014).

The Effects of radioactive pollution include the following:

A. Possible birth defects.
B. Soil sterilization which may result in both air and water pollution.
C. Cancers and other related issues in both the wildlife and in humans.

Thermal Pollution

This is mostly a result of excessive heat which generates unpleasant consequences over a long period of time but having long term effects. Thermal pollution may be a frequent occurrence because of the earths' natural thermal cycles which regulate the atmospheric temperatures. Thermal pollution is often times confined to the immediate areas of pollution but may have a wider effect over a large geographic area.

Sources of thermal pollution include the following:

A. Power plants and refineries (Hanna & Oliva, 2014).
B. Particulates trapping heat.
C. Urban sprawl.

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D. Deforestation.
E. Temperature loss in moderating water supplies.

Possible effects of thermal pollution from increases in temperature include the following:

A. Mild climatic changes.
B. Swift changes may affect the wildlife.

Light Pollution

Any over illumination that obstruct visibility is considered to be a light pollution. Excessive artificial lighting may be a source of light pollution that degrades the environment (Gaston, et al., 2014; Pun, et al., 2014).

Sources of light pollution include:

A. Lighting from large cities (Pun, et al., 2014).
B. Advertisements and billboards (Pun, et al., 2014).
C. Cinemas, sports and other night time activities.

Effects of light pollution:

A. Light pollution may render the stars to be near invisible which may interfere with astronomical observations.
B. Light pollution around residential areas may affect the quality of life for residents.

Visual Pollution

These are primarily the things which constitute an eyesore. They are unappealing and also wanted. The sources of visual pollution include the following:

A. Billboards and advertisement.
B. Power lines.
C. Construction sites.
D. Polluted and neglected land area.

Although visual pollution has a fewer environmental and immediate health effects, the pollutants may have detrimental effects such as;

A. They may reduce the value of properties.
B. They may affect personal senses.
C. To lower the quality of life in affected areas.

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Personal/Private Pollution

This pollution may not be easily felt or identified as it affects the individual body and lifestyles. The pollution of this sort may be caused by voluntary or involuntary actions such as:

A. Abuse of alcohol, drugs and smoking habits.
B. Physical and emotional abuse.
C. A poor habit and living conditions.
D. Poor personal attitudes.

It is worth noting that there is a connection of a chain type between all the types of pollution e.g. the electric plants have to burn more fossil fuels to generate the energy needed before light and the resulting pollution. Pollution from fossil fuel in air pollution may also be washed down to the earth as acid rain to increase water pollution. The pollution cycle may be indefinite; hence very deliberate efforts must be made at the management.

SOLID WASTES, OPEN DUMPS, AND LANDFILLS

Literally, solid waste may refer to any discarded solid materially. But technically, it encompasses the refuse, garbage or sludge resulting from any water and wastewater treatment or pollution control. They include any disposed solid, liquid or semi-solid material that may also contain gases. Essentially, solid waste may thus consist of solid, liquid and gaseous substances. The classification of solid waste based on the source of generation includes municipal, agricultural, industrial, construction and demolition, etc. For treatment purposes and to make sorting prior treatment to be easier, disposed wastes are categorized as listed in Table 2. But the percentage composition of each category differs from households to communities. Also, an attempt has been made by Omari, et.al. (Omari, et al., 2014) to distinguish the percentage composition of each category by nations and re-categorizing by the standard of living of the various nations as low, medium and high income.

Table 2. Classification solid wastes

S/No.	Characterization	Reference
1	Food	(Casado et al., 2015; Edjabou et al., 2015; Forbid & Busch, 2015; Gu et al., 2015; J. Kinobe, Gebresenbet, Niwagaba, & Vinnerås, 2015; J. R. Kinobe, Niwagaba, Gebresenbet, Komakech, & Vinnerås, 2015; Lin, Wang, Chi, Huang, & Yan, 2015; Otchere, Anan, & Bio, 2015; Roberts, 2015; Suthar & Singh, 2015; Yay, 2015; Zorpas, Lasaridi, Voukkali, Loizia, & Chroni, 2015; Zuberi & Ali, 2015)
2	Plastic	
3	Paper	
4	Metals	
5	Glass	
6	Textile	
7	Cardboard	
8	Combustible	
9	Others	

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The most common method of solid waste management include; prevention, minimization, re-use and re-cycle, energy recovery and landfill disposal, (UNDP, 2008). The open dumps were of course the earliest.

Open Dumps

Open dumping of waste has been in practice since ages past and is still very common in undeveloped and developing nations(Jayaweera & Bandara, 2014), but the attendant risk of pollution has necessitated the use of safer waste disposal techniques to avoid pollution and ensure a healthy environment. Figure 1 shows an open dump site.

Open, unmanaged and or uncontrolled waste dumps may have the following resultant effects:

A. Produce liquid waste (leachate) and gaseous emissions (landfill gas) that are potential environmental pollutants.
B. Disposal sites may become a breeding ground for many disease-bearing pests and micro-organisms.

Landfills

Landfills are considered the oldest form of treating waste in a method of disposal by burying in designated sites, (Singh & Ramanathan, 2010). Although not properly covered, Figure 2 shows a landfill site. Sanitary landfills are sites for the isolation and disposal of waste, either by burying underground or in large piles to be monitored very closely to prevent environmental pollution as much as possible.

It is very important that a landfill be managed properly, otherwise it may pose serious environmental hazard through the discharge of polluted wastewater as leachate and air pollution from stenches and release of poisonous and flammable gases. In view of these, advances in landfills have included the construction, operation and strict technical supervision to minimize environmental effects thereof.

Figure 1. An open dump site

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Figure 2. Landfill site in Matang, Taiping, Perak, Malaysia

Sanitary landfilling thus provides the means of a controlled waste disposal on land, hence, a properly managed sanitary landfill provides a control for the exposure of the environment and human to the harmful effects of waste dumps and landfills.

Sanitary landfill has been considered suitable for solid waste disposal in developing nations, because of their relative simplicity, flexibly of operation and relative cost effectiveness. It may be practical for industrialized nations to meet all the conditions of a sanitary landfill while it may be technologically and economically impractical for several developing nations. However, all possible efforts must be made to meet the most important criteria within the available set of technical and financial situations.

Although almost all waste can be disposed via landfill, the European Union, EU landfill sites must now be categorized as either; hazardous non-hazardous and or inert. Wastes are therefore checked and weighed to ensure compliance with landfilling operation permit. Minimal sorting may be of assistance where necessary. The waste is tipped into the landfill, compacted and covered to prevent littering, odor and pest infestations while the waste is gradually decomposed by microbes. Water infiltration, biological degradation of organic matter present in the waste, movement of dissolved or suspended material within the waste dump are to mention a few intricacies.

Although the sanitary landfill is more environmental friendly, the Southeast Asian countries and many less developed nations use more of the open landfills because of the inability to cope with the high volumes of waste generated and disposed each day (Ngoc & Schnitzer, 2009). Landfills may be classified on the basis of structure as highlighted in Table 3.

Stages of Solid Waste Decomposition

Solid waste decomposition that generates leachate within a landfill involves a series of complex physical, chemical and biological reactions which begins right after placement of waste and continue through the entire lifespan of the landfill. The rate of decomposition is dependent on the physical, chemical and microbiological conditions developed within the fill over the time considered (Andreottola & Cannas, 1992; Barlaz, 2006), as shown in Table 4. Landfill decomposition is divided into five phases as itemized in Table 5. The rate and characteristics of leachate produced from a landfill vary from one phase to another, and reflect the microbial mediated processes taking place inside the landfill.

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Table 3. Categorization of landfill sites

S/No.	Category of landfill	Method of waste decomposition
i	Aerobic	Have leachate collection pipes and air flow pipes to make more aerobic than the semi-aerobic.
ii	Semi-aerobic	Have bigger leachate collection pipes than the improved sanitary. It has lower moisture content and air flow ducts are provided.
iii	Anaerobic	Wastes are tipped in excavated sites or valleys. Under anaerobic conditions, wastes are filled with water to decompose.
iv	Anaerobic sanitary	Wastes are sandwiched between soils.
v	Improved anaerobic sanitary	Similar to anaerobic except for the bottom laid leachate collection system and a lesser moisture content than the aerobic.

Source: Environmental Pollution Control Centre, Osaka Prefecture, 2009.

Table 4. Methods solid waste decomposition

Method	Process	Characteristics	Reference
Physical	Segregation, mechanical size and volume reduction	It excludes phase changes.	(Demirbas, 2011; Laner, Crest, Scharff, Morris, & Barlaz, 2012; Liu, Xu, Li, & Xu, 2011; Poznyak, Bautista, Chaírez, Córdova, & Ríos, 2008; Sarkar, Ghosh, Bannerjee, & Aikat, 2012)
Chemical	Include; combustion, pyrolysis and gasification	It involves phase changes of waste with a reduction in volume.	
Biological	Include; aerobic and anaerobic degradation	Phase changes, reduced BOD, increased pH.	

Table 5. Stages of landfill decomposition

Stage	Decomposition type	Characteristics	Reference
I	Initial adjustment	Involves the initial placement of waste and the buildup of moisture within the landfills.	(Ermolaev, 2015; He & Shen, 2006; Liao, Yang, Shen, & Long, 2013; Niemietz, 2008; A. Zaman, 2012; A. U. Zaman, 2010)
Ii	Transition	Increase in leachate generation, with measurable concentrations of chemical oxygen demand (COD) and intermediates such as volatile fatty acids (VFA).	
iii	Acidification	Continuous hydrolysis and fermentation of waste decrease in pH with dominant VFA.	
Iv	Methane fermentation	Decreased organic strength while the intermediate acids utilized by methane-forming consortia (methanogen bacteria) and converted into methane and carbon dioxide. Leachate pH is elevated to the level of biocarbonate buffering system.	
v	Maturation	Low concentrations of leachate	

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LANDFILLING AND LEACHATE

Leachate

Leachate refers to water or liquid flowing either vertically or laterally through the soil, landfill, etc. while collecting soluble and suspended materials along. It is the water and other soluble materials that have drained out of a deposit or tipped material. Figure 3 shows the leachate from a landfill site.

Leachate is generated during the decomposition of waste and drained or leached from land or any stockpiled organic waste material. Its composition is largely affected by the age of fill and type of waste. The liquid consists of both suspended and dissolved material. A breakdown of carbonaceous materials produces additional water and several other materials such as:

A. Methane gas.
B. Carbon dioxide.
C. Complex organic acids.
D. Aldehydes.
E. Alcohols.
F. Simple sugars.

Important factors influencing leachate generation are:

A. The rainfall, washing down the waste at dump sites.
B. Liquid wastewater produced from the breakdown of waste.

Figure 3. Landfill Leachate in a concrete tank

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There is no standard or consistent chemical and microbiological composition of any landfill leachate and the factors influencing leachate composition include the following:

A. Physical composition of dumped wastes.
B. Environmental conditions.
C. Landfill operational management.
D. Waste decomposition dynamics.

Leachates can be classified on the basis of waste degradation as:

A. Acetogenic leachates are also referred to as young leachates. They are leachates from a young landfill. These are characterized by a high COD, BOD, and BOD/COD.
B. Methanogenic leachates are also referred to as old leachate derived from the older landfill. They are more extensively degraded than the acetogenic leachates and are characterized by lower COD, BOD and BOD/COD.

Leachate Pollution Problem

On the basis of the above definition and understanding, leachate may be from various sources such as farming areas, feedlots, cemeteries (Spongberg & Becks, 2000; Zychowski & Bryndal, 2014) and landfills. The most common is the leachate from the landfill (see Figure 3) which is the focus of this chapter. Potential leachate Pollution from beneath and around the landfill site is also considered. The indiscriminate dumping of refuse or dumping in uncontrolled landfills may adversely affect both human health and the environment (Kumar & Alappat, 2005; Lo, 1996). Landfill leachate is characteristically concentrated, variable in quantity and quality hence difficult to treat (Milke, 1995). A variety of pollutants contained in landfill leachate are potential contaminants that are able to affect the quality of both ground and surface waters (Christensen, et.al., 1994).

Also, methane gas released during the breakdown and decomposition of waste may be dangerous if it is allowed to build up. Landfill sites and the leachate produced are odorous with the potential to pollute the air. Associated problems include the following:

A. Odors from landfill sites.
B. Offensive and unsightly sites.
C. Possible air pollution from methane gas released during the breakdown and decomposition of waste.
D. Methane gas is flammable, hence the danger of explosion if it builds up in the landfill.
E. Possible water pollution in the event of a punctured landfill lining or a break or leak of the leachate which could migrate from the landfill to contaminate the surrounding soil and exposed water systems.
F. The problem of finding an appropriate site for the location of sanitary landfills as most people would not agree to have a site too close to their properties for obvious reasons. Landfills are therefore remotely located from the public.
G. Difficulties with transporting waste to landfill sites.
H. The need for many landfills because decomposition is slow and potentially incomplete due to their designs.

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I. Fear of a possible ground instability due to soil shifts during waste decomposition.

Characteristics of Landfill Leachate

Leachate characterization is an important factor to establish an effective management strategy for a Landfill (El-Fadel, et al., 2002). Landfill leachate characteristics may be grouped into four types of pollutant (Greenman, et al., 2009; Huang, et al., 2009; Modin, Persson, et al., 2011), namely:

A. Dissolved organic matter.
B. Inorganic macro-components.
C. Heavy metals.
D. Xenobiotic organic compounds.

Further characterization includes the following;

A. Dark colored
B. Odors
C. High organic and inorganic load.
D. High dissolved organic matter, including volatile fatty acid; refractory organic matter, humic substances .
E. Macro inorganics compounds (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH^{4+}, Fe^{2+})
F. Heavy metals (Cd^{2+}, Cr^{3+}, Cu^{2+})
G. Microorganisms from total and thermo tolerant coliform
H. High biochemical oxygen demand (BOD) (4,000-13,000mg/L)
I. High chemical oxygen demand (COD) (30,000-60,000mg/L)
J. High strength ammonium nitrogen (500-2000mg/L)
K. High BOD/COD (0.4-0.7)
L. pH of 4-8.5

Landfilling Processes Producing Leachate

Processes by which leachates are generated in a landfill are in three categories, namely;

1. **Physical Processes:** The physical processes involved in landfilling include:
    a. **Compaction and Settlement:** This is the compression of waste to obtain a reduction in size by the use of a compacting machinery and the efforts from the wastes and soil cover (burden). The settling so achieved is also partly from the loss of mass due to biological and chemical decomposition.
    b. **Dissolution and Transport:** The physical reaction of dissolution is greatly affected by the quantity of water entering the fill. Also, as water acts as the medium of dissolution of soluble material, it also serves as the medium for the transportation of both dissolved and un-decomposed materials.
    c. **Adsorption and Absorption:** These are both physical processes in a fill for the immobilization of living, non-living and dissolved pollutants.

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2. **Chemical Processes:** Oxidation and typical acid-metal reactions such as organic acids and dissolved carbon dioxide (CO_2) produced in the biological processes.
3. **Biological Processes:** The importance of biological reactions cannot be overemphasized. Its' most importance is in the following;
    a. It stabilizes the organic fractions.
    b. It converts large portions of the carbonaceous and proteins substances into gas, thereby reducing the volume of organic wastes. Biological processes are achieved by various means including the following:
        i. **Aerobic Decomposition:** This is responsible for most of the decomposition within a fill. It starts right after the waste is buried. The biological processes seem to be the most important but it is however greatly affected by both the physical and chemical processes.
        ii. **Anaerobic Decomposition:** Most biodegradable organic matter in a fill is decomposed anaerobically because the oxygen within the landfill gets depleted very fast.

Regrettably, the products of anaerobic decomposition in a landfill can be environmentally unfriendly if not properly monitored. Volatile Organic acids and gases are the principal products.

The principal gases formed are:

a. Methane (CH_4)
b. Carbon dioxide (CO_2)

Gaseous products in trace amounts are:

a. Hydrogen Sulphide (H_2S)
b. Hydrogen (H_2)
c. Nitrogen (N_2)

4. **Environmental Factors:** Main factors of influence in biological decomposition in a conventional fill include:
    a. Moisture.
    b. Temperature.
    c. Microbial content.
    d. Degree of waste resistance to microbial activities.

Factors Influencing Leachate Composition

The factors influencing leachate composition includes the following:

A. Designation of landfill for a particular waste type.
B. Composition of waste.
C. Moisture content.
D. Particle size of waste.
E. Degree of compaction.
F. Site hydrology.

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G. Climatic conditions such as rainfall, temperature, humidity etc.
H. Age of the fill/ Landfill age.
I. Design of landfill.
J. Type of liners used.
K. Waste pretreatment such as segregation or sorting, shredding, bailing of the waste.

Leachate and Soil Pollution

Quite a number of works have been conducted to investigate and determine the extent of soil contamination due to migration of leachate from uncontrolled or unlined landfill sites using geophysical and physicochemical studies (Ayolabi, et al., 2014; Kabala, et al., 2014). The extent of leachate migration and effectual soil contamination from a 17year old uncontrolled landfill in Southeastern China was assessed in a clayey soil of about 9m depth. Cutting sub-sections and analyzing soil samples for Total nitrogen, soil organic matter, chloride, sodium, and COD in the pore water. Leachate related Chloride was found in the soil up to the 3m depth, nitrogen in up to 2m depth, while sodium and COD up to between 3 –5m and 2-3m respectively (Zhan, et al., 2014). A related investigation found pollution to be a result of contaminant migration and has suggested the use of a liner under the storage basin to stop or reduce its migration (Bouzayani, et al., 2014).

Leachate and Water Pollution

Several more studies have been carried out to determine the effect of leachate pollution on water systems (Melnyk, et al., 2014). Geophysical studies for the assessment of ground water contamination by leachate from an uncontrolled landfill located in the city of Guadalupe Victoria, Mexico was conducted. Results showed a leachate contaminant plume which extended up to 20m SE and 40m NW of the landfill investigated. Although unlike the practice of using a site with low-permeability soils, the study area was of a silty sandy soil which is able to encourage the flow of leachate. Also, geochemical data of the water samples showed a characteristic sodium sulfate, sodium chloride, high ionic and organic matter (Reyes-López, et al., 2008).

(Fernández, et al., 2014), investigated both surface and ground water samples for pollution due to a leachate plume transport from a municipal landfill in Pacara Pintado, northwestern Argentina. The plume showed high concentrations of Fe, Mn, NH_4^+, Cl^-, Cr, and organic matter up to a 900m depth.

An investigation of ground water pollution due to leachate from an uncontrolled municipal landfill identified total dissolved solids (TDS), chlorine, ammonia, iron (Fe), and manganese (Mn) as to be the indicators of landfill leachate migration.(Han, et al., 2014). More data on soil and water pollution from leachates is presented in Table 6.

Leachate Pollution Index (LPI)

Leachate pollution Index (LPI) is the tool used to evaluate the leachate pollution potential of landfill sites. It is used to monitor the pollution potential due to the movement of leachate from the landfill into ground (soil) and surface waters within a given geographical location.

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Table 6. Typical leachate pollution data for both soil and water

Pollutant	Medium	Variation	Baseline	Reference
Mercury (Hg)	Soils within the mine	3.8-11µg/g (300m away from the mine)	0.03-0.05 µg/g (24km away from the mine)	(Gray, Theodorakos, Fey, & Krabbenhoft, 2015)
	Mine water run-off	7.9-14ng/L	0.05-3.1 ng/L	
Fluorescent dissolved organic matter (FDOM)	Groundwater	40% photo degradation	8% photo degradation	(Graham, Baker, Andersen, & Acworth, 2015)
Copper (Cu), from pig manure	Soil	32-164 µg/L	50µg/L	(Ostermann et al., 2015)
Cd, Pb	Soil	Highly contaminated	NA	(Wu, Leung, Pérez, Huang, & Wang, 2015)
TI		Considerably Contaminated		
PBDEs and metals	paddy soils and river sediments	Decreased PSII, affected photosynthesis, inhibited algal growth.	NA	(Nie et al., 2015)

A practical application of the concept of LPI was used to rate two active and two closed landfill sites in Hong Kong (Kumar & Alappat, 2005). It compared the leachate contamination potential of the two active and two closed sites and found that the closed sites had an equal or more contamination potential than the active sites. It is thus advised that post-closure monitoring is taking very seriously until the leachate generated is well stabilized. Also, it reported that leachate characteristics may differ greatly over time, even within a single municipal landfill site.

Because the greatest concern with leachate is the fear of a possible pollution due to uncontrolled leachate movement into the surrounding surface water and ground water or the sea. The Leachate pollution Index (LPI) is therefore a technique using a comparative scale to measure the leachate pollution potential (LPP) of individual landfill in a geographical area, over a period of time, (Kumar & Alappat, 2005). Other works have also been done using the LPI to evaluate the pollution potential of leachates especially from unlined landfill sites in relation to a resultant degradation and health hazards due to ground water pollution (Muralidhar, et al., 2014). In a related study, (Guerrero-Rodríguez, et al., 2014) found that leachates of higher LPIs were likely to exert more damaging effect than those of lower LPIs on to life. The tool was again used to determine the levels, variability and degree of heavy metal pollution in a municipal solid waste dump site in comparison with adjoining area and the waste dump site to be of higher heavy metal pollution (Essien & Hanson, 2014).

With the aid of the LPI, the following has been made possible;

A. Assessment and classification of landfill sites based on their leachate pollution potential.
B. Allocation of resources for management and control of landfill sites.
C. A continuous monitoring over a period of time using the LPI can provide the pattern of leachate pollution which can be employed in trend analysis.
D. It helps in the enforcement of standards and regulations for engineering and environmental control.
E. It provides information for scientific research and public awareness.

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The LPI has been applied in various assessment of landfill on the basis of their leachate contamination potential.

The LPI is a hazard identification tool while the other factors that need consideration include the following:

A. Dose response effect is important for consideration although it depends on the leachate receiving environment.
B. The generated volume of leachate.
C. The type of soil strata.
D. Depth of water aquifer.
E. Effective and affected population.

Leachate Management

The management of leachate essentially involves the means by which to prevent the migration of leachate beyond the site. It focuses on the containment or prevention of leachate spread so as to avoid a possible contamination of soil and water.

However, a common practice is to use an effective impermeable liner collection system. Also, leachate collection pipes are entrenched near the bottom of the liner layers and are connected to a main pipe that leads to a leachate holding tank (see Figure 4-6). The use of low-permeability soils is to minimize the convective flux of contaminants.

Figure 4. Concrete tank connected with underground pipes to receive Leachate from adjacent landfill

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Figure 5. Concrete tank connected with underground pipes to receive Leachate from adjacent landfill

Figure 6. Concrete tank connected with underground pipes to receive Leachate from adjacent landfill

Essential Features of Landfill Sites

Wastes are dumped in organized layers, alternating between waste and soil to prevent odors and allow a faster decomposition. The landfill is sealed and covered with clay.

A least of four basic conditions to be met by any standard sanitary landfill in its design and operation include:

A. A full or partial hydrogeological isolation to be provided artificially using an impervious soil layer of clay or a synthetic liner, if it does not exists naturally as clay or rock bed. This is to lower leakages of leachates from the base of the site and hence lower the contamination of surrounding soil and ground water. A system of leachate collection should be provided below the base.

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B. A proper design and preparations from local geological and hydrogeological investigations to include also a plan for waste disposal and a final restoration of the site.
C. Provision for trained staff to take control of the site supervision through the design, construction, waste deposition, regular operation and maintenance.
D. Planning and execution for waste dumping and compaction in layers to be covered with soil above each layer of waste.

CONCLUSION

Having discussed the pollution types, sources, effect and narrowing down to leachate generation, the leachate migration has been shown to pollute the soil, surface and ground waters particularly within the immediate geographical location of the landfill site. Characterization of the different types of leachate both old and young have shown a high content of contaminants which should be prevented from infiltrating both soil and water bodies particularly within the very immediate environment. It is therefore necessary to make a conscious and consistent effort towards controlling or preventing the migration of leachate. The generation of waste is obviously unavoidable, but a more decisive and collective efforts must be made by all, to reduce the volumes generated as this would mean a lesser volume to be available for treatment and hence a lesser leachate generation from landfills. Environmental authorities, especially those of the underdeveloped and developing nations, must make efforts to abolish the open dumps and uncovered landfills. They must bring on a system where the sanitary landfill is used if the landfill is desired for waste management. There must be provision to immediately cover any tipped waste to exclude unwanted scavengers and make the condition favorable for either of the means of waste decomposition within the fills, as desired. An engineered landfill, with a close, constant and continuous monitoring is advised.

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Chapter 60
Socio-Economic and Environmental Impacts of Poor Paper Management at Higher Education Institutions in Ethiopia:
Evidence From Hawassa University

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ABSTRACT

Currently there are 34 universities in Ethiopia which enrolled hundreds of thousands of students which generated large volume of waste paper a year. Therefore, this article has an objective of assessing the socio-economic and environmental impacts of poor paper management at higher education institutions of Ethiopia with a particular focus on Hawassa University. The findings of the study revealed that a large volume of paper is consumed for different academic purposes. Due to the poor management of paper consumption as well as poor waste management practices, the university faced socio-economic and environmental problems. By 2015/16 academic year a total of 94,025 reams of paper were used at Hawassa University. This has created a large volume of waste paper at offices, which resulted in un-pleasant working environment. Incineration is the only means of waste paper disposal, which created environmental pollution and health risks to the university community. Moreover, the university also lost a significant amount of money which would have been gained from selling to paper recycling industries.

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INTRODUCTION

Increases in literacy, GNP and population in developing countries results in continued growth of paper and paperboard consumption, at a faster rate than in developed countries. Following this consumption level, the waste paper generation is increasing highly, so do the economic and environmental impacts. Hence, the demand for recycling and reduction of the volume of waste paper generated increases as well (Van Beukering and Bouman, 2001).

As it is indicated by Rutgers (2004) cited in Randall (2005), the amount of paper printed in a University with a campus population of ten thousand students is more than one million sheets of paper per month. Correspondingly, paper products make up a large proportion of the solid waste generated by universities, due to their educational and academic endeavours (Modzelewski, 2007).

Paper that does not contain any recycled material is produced from timber (Modzelewski, 2007). A sheet of paper made from wood consumed seventeen watts per hour of electricity (Randall, 2005). It asserts that paper production leads to forest depletion and consumption of energy. Moreover, it has a significant negative impact on biodiversity (Armstrong et al., 1998). However, paper and paper products are regarded as cheap products, often undervalued, and much paper is wasted with no or minimal re-use.

In addition, paper consumption does not only refer to the paper used either for printing or photocopying but also the costs of printing, storage, transporting, disposal and recycling (Randall, 2005). Considering this, formulating comprehensive solid waste management policy and programs in the university based on the generating source are imperative (Armijo de Vega et al., 2008).

Like many developing countries, there is an increasing consumption of paper in Ethiopia. When we compare the consumption level, the education sector especially universities and colleges are the primarily users of papers. This can be explained by the rising number of students who are enrolled every year in these sectors. Currently, Ethiopia has thirty-four public universities. The government has also planned to build eleven additional universities in the second growth and transformational Plan (GTP-II) of 2015/2016-2019/2020. This expansion brings high paper consumption as well as large volume of waste paper generation which leads to environmental problems if there is no proper consumption and waste paper management. Though it is very difficult to find a study conducted on paper consumption and waste paper generation of these universities, one can estimate that every year the consumption and waste paper generation can increase at an alarming rate due to the increasing number of students.

Therefore, this study is aimed at assessing the socio-economic and environmental impacts of poor paper management by taking Hawassa University as a case study.

The Case Study Institution, Hawassa University

Hawassa University is one of the public higher education institutions in Ethiopia located at Hawassa City in Southern Nations, Nationalities and Peoples Regional State. Hawassa is 273 km south of Addis Ababa. The University is among the first-generation universities in Ethiopia and has 5 campuses (The university main campus, the College of Medicine and Health Science, the College of Agriculture, the College of Forestry and Natural Resource, the College of Business and Economics). Hawassa University offers programs at bachelor degrees, master degrees and doctoral degrees levels in several areas of study. According to data from Planning Directorate of Hawassa University (2016), the university had 1393 academic staffs of which 377 were on study leave, and 55 were expatriates. It had also 176 technical assistants, 4998 administrative staffs, 680 health officers, and 91 contractual workers. There was a total

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of 39660 students (at masters and under graduate level in different programs) (interview with Planning Directorate of Hawassa University, 2016).

Like any other academic institutions, Hawassa University has educational and academic endeavor, and hence it has high consumption of papers for preparing exams, course outlines, handouts and other miscellaneous activities. This makes paper products to be a large proportion of the solid waste to be generated by the University.

The university has no a recycling practice and/or linkage with companies which recycle paper, which makes incineration a widely used practice of waste paper management, which again creates environmental pollution as well as health risks. The university has also no effective environmental policy regarding waste management that in turn leads the university not to properly carry out its responsibility for sustainable protection of the environment and wise use of resources.

In this University, the mismanagement of papers at different offices is quite common. There are a collection of undistributed course outlines, exam papers, students' assignment papers, handouts, letters, and the like which are hoarded for many years. This shows the improper and ineffective handling mechanism of different used papers. Due to this, it is common to listen complains of many students due to loss of their exam papers and grades.

REVIEW OF RELATED LITERATURES

Solid Waste Management

A solid waste is any discarded material which is abandoned and inherently waste-like. An abandoned material is something which is being disposed and incinerated. It is the unwanted or useless solid materials generated from combined residential, industrial and commercial activities in a given area. It may be categorized according to its origin (domestic, industrial, commercial, construction or institutional); according to its contents (organic material, glass, metal, plastic, paper, etc.); or according to hazard potential (toxic, non-toxin, flammable, radioactive, infectious, etc.) (Ajith, 2014). As indicated in Ministry of Urban Development and Construction of Ethiopia (2012), solid waste includes any garbage, refuse, and sludge, and other discarded material including solid and semi-solid wastes.

Waste management is control of waste related activities which ultimately aimed at conserving and protecting human health and the environment (Pongracz et al., 2004). Solid waste management is the discipline associated with the control of generation, storage, collection, transfer, and transport, processing and disposal of solid waste by considering issues of socio-economic and environment (Ministry of Urban Development and Construction of Ethiopia, 2012). Management of solid waste reduces or eliminates adverse impacts on the environment and human health and supports economic development and improves quality of life (Thompson and Wilson, 1994).

Comprehensive solid waste management programs are one of the greatest means to achieve institutional sustainability. Effective solid waste management requires a complete understanding of the composition of a waste stream as well as the activities that determine its generation (Farmer *et al*., 1997). Armijo de Vega and his colleagues stated that tailoring solid waste management programs is important which considers the ground reality than mimicking it from somewhere else (Armijo de Vega et al., 2008).

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Methods of Waste Paper Management

Methods of waste management include 3Rs; reduce, reuse, and recycle (Ajith, 2014; Mohanty, 2011; Peprah et al., 2015). There are many environmental benefits that can be derived from the use of these methods. They reduce or prevent greenhouse gas emissions, reduce the release of pollutants, conserve resources, save energy and reduce the demand for waste treatment technology and landfill space.

Reduction

Waste reduction and reuse of products are both methods of waste prevention. They eliminate the production of waste at the source of usual generation and reduce the demands for large scale treatment and disposal facilities. Reducing the amount of the product to be purchased is the most significant of all the options to manage waste. The key is to only purchase goods that we need and in the right amount (Abdul-Rahman, 2014).

As indicated in Clean Up (2009), principles of reducing paper consumption include double-side printing, write notes and notices on a communal whiteboard, taking notes on a laptop or tablet instead of paper; distributing memos via email or post one copy to a bulletin board; sending, requesting, storing, circulating, editing and filing electronic copies of documents and assignments instead of paper versions, creating an electronic mailing list for newsletters and notices, copy texts as many times as possible per sheet, submit your work by email or electronic delivery systems like Google docs, Dropbox, Moddole, and the like.

Reuse

Reuse refers to using materials repeatedly. According to Abdul-Rahman (2014:3), the process of reusing starts with the assumption that the used materials that flow through our lives can be a resource rather than refuse. "Waste, after all, is in the eye of the beholder. One person's trash is another person's treasure…" As stated in Peprah et al. (2015), reuse involves secondary and subsequent uses of waste materials either in part or whole which is achieved through sorting done at source rather than disposal site and, through detailed processes of checking, cleaning, refurbishing, repairing whole items or spare parts.

Reusing paper is another important principle which includes purchasing paper with 100 percent recycled content that is third party certified, using printed paper as scrap or packing material, sharing print copies of documents, manuals or directories, keeping pieces of paper that have been printed or written on and write notes or print drafts on the blank side (Clean-Up, 2009).

Recycling

Recycling is a practice which is applied for waste materials which cannot be reused directly but can be converted to new products or raw materials (Peprah et al., 2015). Recycling is important to save energy, reduce raw material extraction and combat climate change. Recycling our rubbish is better for the environment rather than incinerating or land-filling it (Friends of the Earth, 2008; DECCW, 2010). Soil and water pollution increases as practices of incineration and landfill increases.

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Paper recycling saves the natural wood, decreases the operation and capital cost to produce virgin paper, and decrease water consumption. It also gives rise the environmental conservation (Cabalova, *et al*., 2011).

Benefits of Paper Recycling

Paper recycling has various benefits which include environmental, social, and economical.

Environmental Benefits

Recycling is well-known for its environmental benefits, which include resource conservation, energy conservation, and reductions in water and air pollution, including reductions in greenhouse gas generation (New Jersey Waste Wise Business Network, 2013; Clean Up, 2009; Department of Ecology State of Washington, 2015).

It reduces the demand for wood, requires less total energy to manufacture than virgin paper, and reduces solid waste and greenhouse emissions created by disposing paper in landfill (Clean Up, 2009). Department of Ecology State of Washington (2015) also stated that recycling is also important to save raw materials.

Socio-Economic Benefits

Recycling is an important segment of the national economy; creates jobs and saves money for generators of waste. It helps local industries to grow and to create employment opportunities. As far as energy is concerned, there is 28 -70 percent less energy consumption in producing recycled paper compared to virgin paper. Every tone of recycled paper saves approximately 4 barrels of oil, 4200 KW house of energy (New Jersey Waste Wise Business Network, 2013). Paper recycling also helps to create job opportunities (Bekiroglu and Elmas, 2017; European Environment Agency, 2011). According to European Environment Agency (2011) recycling creates employment opportunities in terms of collection, materials handling and processing to manufacturing products, particularly for low skilled workers.

Paper Production and Its Impacts

Despite predictions that the digital revolution would make paper as obsolete as the type writer, paper remains central to our lives. Instead, global paper consumption has increased dramatically over the last decade, and will continue to rise, especially in developing countries. Paper is one of the most important and widely used consumer materials with an endless ability to be transformed. Paper products are ubiquitous in a society which used for newspapers, magazines, catalogs, office paper, packaging and tissue products (Robert, 2007; Clean Up, 2009).

The primary raw material for paper production is pulps fibers obtaining by complicated chemical processes from natural materials mainly from wood. This fibers production is very energy demanding and it uses many of chemicals which are very problematic for environmental protection. Modern paper production involves mechanical, chemical - or a combination of both - pulping to convert raw materials

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into various paper products. These processes consume large amounts of energy and use valuable natural resources, including trees and water. Certain processing techniques such as bleaching are also known to be environmentally harmful (Bajpai, 2015).

One of the most significant impacts of the paper industry is climate change. Every phase of paper's lifecycle contributes to global warming, from harvesting trees to production of pulp and paper to eventual disposal. It is estimated that 42% of the industrial wood harvest is used to make paper (Robert, 2007). As stated in Clean Up (2009), paper production consumes trees and water, release CO2, and generate landfill. Trees are the main resource in the paper production, a tone of paper consumes approximately 20 full-grown trees while recycling 1 tone of paper saves 13 trees. Moreover, to make just one tone of paper out of virgin material over 90,000 liters of water are used which will fill 450 rain barrels. Each tone of paper that is recycled saves: almost 13 trees, 2.5 barrels of oil, 4100 kWh of electricity, 4 cubic meters of landfill and 31, 780 liters of water.

Sustainability at Higher Education

Sustainable University is defined as:

…a whole or as a part, that addresses, involves and promotes, on a regional or a global level, the minimization of negative environmental, economic, societal, and health effects generated in the use of their resources in order to fulfill its functions of teaching, research, outreach and partnership, and stewardship in ways to help society make the transition to sustainable lifestyles… (Velazquez et al., 2006, p. 812)

Sustainability in relation to HEIs is associated with carrying out activities that are ecologically sound, socially and economically viable, and that they will continue to be so for future generations. Universities have a moral and ethical obligation to act responsibly for the environment (Armijo de Vega et al., 2008) and its inhabitants (Armijo de Vega et al., 2003). Alshuwaikhat and Abubakar (2008) claim that HEIs should not only educate, but also demonstrate environmental principles and stewardship by taking action to understand and reduce impacts that result from their activities.

HEIs' role in promoting sustainability is of paramount importance for various reasons. In the first place, HEI can take the advantage of professional with wide range of field of study that is vital for achieving the objectives of sustainable development (Forrant and Pyle, 2002). Secondly, they are places where students who are forerunners in achieving sustainable development are found in large number (Thompson and Green, 2005). Thirdly, it is also expected that they can be role models for the society thereby influence the actions of the society (Stephens et al., 2008).

Waste characterization studies at colleges and universities identify campus specific and regionally relevant opportunities for waste reduction and recycling, representing an essential step towards greening the campus (Creighton, 1998). When carefully planned, campus waste characterization studies are relatively inexpensive and can generate administrative support, cooperation among students, faculty and staff and inspire further involvement in campus sustainability issues (Beringer et al., 2008). In addition to the overall desire to become green, rising campus waste disposal costs and shrinking landfill space often demand waste minimization approaches at IHE (Noeke, 2000).

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MATERIALS AND METHODS

The study employed both quantitative and qualitative approaches. A descriptive research design based on cross-sectional survey was applied. The design is appropriate to assess the current status of paper use and waste paper management at Hawassa University. Moreover, this method could yield rich data that can be inferred about other universities in Ethiopia. The qualitative approach helps to gather data about how academic staffs in particular and the university in general consume paper and manage waste papers. Besides, it helps to understand how waste paper management affects the socio-economic and environmental conditions in the university.

For this study, a total of 144 respondents were supposed to be selected randomly from the total academic staff list of 72 schools (2 respondents from each school/department) found in different colleges and Institute of Technology at Hawassa University as shown in Table 1. However, questionnaires distributed to 6 departments/schools (12 questionnaires) were incomplete and hence discarded, and the remaining 22 questionnaires distributed to 10 schools/departments were not returned. Hence, the analysis is made using 110 respondents.

In addition, a total of 35 key informants and one focus group discussion with instructors (one from each college/institute); which consists of 8 members were incorporated from Hawassa University. These respondents were selected purposively based on their exposure with regard to paper consumption and waste paper management (see Table 2).

Quantitative data was collected using questionnaires which were distributed to 110 respondents. The type of questionnaires was dominantly close-ended. Before the actual administration of the data collection process, questionnaires were pretested and corrections were made accordingly. Moreover, qualitative data was collected using key informant interview, observation, FGD, and document analysis. To do this a semi-structured key informant interview questions were developed to the relevant respondents from respective units of the university. Observation was made in order to understand the management of used papers in office of the academic staffs, students dormitory and within the compound in general, the time and the means of waste paper disposal. Data from secondary sources was collected from different articles, and other published and unpublished sources.

Table 1. Sample size selected from colleges and Institute of Technology

College/Institute	No. of Schools	Total Sample From Each College/ Institute
Institute of Technology	10	19
College of Natural and Computational Science	7	13
College of Medicine and Heath Science	4	7
Hawassa College of Agriculture	9	15
Wondogenet College of Forestry and Natural Resource	9	18
College of Business and Economics	8	16
College of Social Science and Humanity	9	18
College of Law and Governance	2	4
Total	**58**	**110**

Source: Fieldwork, 2016

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Table 2. List of key informants from Hawassa University

Key Informants	No.	Description
Heads of schools	16	Two from each college/Institute
Instructors	8	One from each college/Institute
Duplication Centers	5	One from each campus
Campus Beautification Directors	5	One from each campus
Continuing Education Program (CEP) coordinator of the university	1	
Total	35	

Source: Fieldwork, 2016

Besides Campus Beautification and Facility Management Directorate Directors of other 32 Ethiopian Public Universities were interviewed via phone call in order to understand their waste paper management practices.

Quantitative data is analyzed by using descriptive statistics like percentage and frequency. Moreover, the qualitative data was narrated and summarized to support the quantitative data.

RESULTS

Paper Use at Hawassa University

In Hawassa University, paper is used for both academic and administrative purposes (i.e. writing letters, notice, duplicating cost-sharing forms, training manuals, evaluation forms etc). However, this study focused only on paper used for academic purpose. Accordingly, Table 3 shows that Papers are used for printing and copying exams, handouts, course outlines, worksheets, and the like. Among the different purpose of paper in the academic division, exams (53.6%) consume more sheets of papers followed by handouts (39.1 percent).

Table 3. The purpose of paper consumption at Hawassa University

No.	Purpose	No.	%
1	For exam	59	53.6
2	For handout	43	39.1
3	For exam and handout	3	2.7
4	For exam and course outline	2	1.8
5	For exam, course outline and handout	3	2.7
	Total	**110**	**100.0**

Source: Fieldwork, 2016

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Consumption Level of Paper at Hawassa University

Consumption level of the university is computed by taking the total number of courses of a program, the responses of instructors about their consumption level for course outlines, quizzes, mid exams, final exams, and assignments in each program, and the number of students in that program.

Table 4 shows the average amount of paper consumption at Hawassa University by 2015/16 academic year. Accordingly, for 16225 regular students, 3520 reams of paper were used for duplication of course outlines, 9872 reams for quizzes, 2793 reams to duplicate worksheets, and 8129 reams to duplicate final examinations. The table also shows that for its extension programs (both weekend and evening), the university used 975 reams to duplicate course outlines, 1848 reams to duplicate mid exams, and 2981 reams to duplicate final exams for 7411 students. For 7830 students who attend summer education program, the university consumed 1323 reams of paper to duplicate course outlines, 1662 reams to duplicate mid exams, and 2440 reams to duplicate final examinations. That means, the university used 13550 reams of paper to duplicate final exams, 9872 reams of paper to duplicate quizzes, 5818 reams of paper to duplicate course outlines, 3510 to duplicate mid exams, and 2793 reams of paper to duplicate worksheets for 31466 students. Generally, 35543 reams of paper were used by Hawassa University for academic purposes for 31466 students by the 2015/16 academic year.

Beyond this, large volume of paper is also consumed by the students to duplicate handouts and to write assignments. As indicated in Table 5, regular students used 52256 reams of paper to duplicating handouts, to write individual assignments (437 reams), and group assignments (122 reams).

Table 4. Paper consumption level at Hawassa University by 2015/16

Program	No. of Students	Average Consumption					
		Course Outline	Quizzes	Mid Exam	Work Sheet	Final Exam	Total
Regular	16225	3520	9872	*	2793	8129	24,314
Extension (Weekend + Evening)	7411	975	*	1848	*	2981	5804
Summer	7830	1323	*	1662	*	2440	5425
Total	31,466	5,818	9,872	3,510	2,793	13,550	35,543

Source: (Fieldwork, 2016)

*: refers to modes of assessments which are not applicable to the respective programs.

Table 5. Paper taken into the university

Program	Handout	Ind. Assignment	Gr. Assignment	Total
Regular	52,256	437	122	52, 815
Extension	*	1898	760	2,658
Summer	*	1640	1229	2,869
Total	**52,256**	**3975**	**2111**	**58,342**

Source: Fieldwork, 2016

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Generally, 52815 reams of paper are consumed by the regular students for the aforementioned purposes. Extension students in both weekend and evening programs consumed 1898 reams of paper to write individual assignments and 760 reams to write groups assignments. Similarly, summer students also consumed 1640 reams of paper to write individual assignments and 1229 reams of paper to write group assignments. Generally, Table 5 shows that total of 583342 reams of paper are used by the students (all regular, extension, summer) for the purposes of handout duplication[1], and write-up of assignments. As shown in Table 4 and 5 a total of 93,885 reams of paper become waste at Hawassa University by 2015/16.

Paper Management Practice at Hawassa University

In this section, paper management refers to practice of duplicating exams and course outlines, habit of printing and duplicating double-side, using back side of papers for different purposes, proper management of paper outside offices, the proper management of modules administered by CEP, and waste paper management.

Duplication of Exams and Course Outlines

In order to use papers efficiently, duplicating exams and course outlines based on the exact number of students is vital. As shown in Table 6, 68.1 percent of respondents replied that they know the number of students they teach by counting them in class. Key informant interview made with teachers reveals that attendance sheets also helps to count the number of students in a class. However, such means are not effective to know the exact number of students:

Attendance sheets and counting students in class are not effective ways to know the number of students since some students do not regularly attend the class. There are also some students who add some courses but not attend the classes. (Interview with an instructor from Technology Institute, 2016)

The major problem is the registrar doesn't send the list of students to each school and respective staff immediately after their registration. Sometimes, we [Instructors] voluntarily go to the registrar to get the list of our students. Unless it is based on our estimation that we duplicate exams and course outlines. (Interview with an instructor from College of Law and Governance, 2016)

Key informant interviews with teachers and school heads revealed that sometimes departments and schools might not have the data about students of each batch:

The school doesn't get the list of students of each batch at the beginning of academic years. The registrar sends the grade submission which contains the list of students at the end of each semester. (Interview with Head of School of Governance and Development Studies, 2016)

This leads teachers to duplicate some more course outlines and exams. It is only 18.2 percent of the respondents who might know the exact number of student by taking data from the registrar (15.5%), and from the school (2.7%).

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Table 6. Means to know the number of students before duplicating course outlines and exams

No.	Ways to Know No. of Students to Duplicate Materials	No.	%
1	By counting their numbers in the class	75	68.1
2	By taking the data from the registrar	17	15.5
3	By estimation	13	11.8
4	By asking other instructors who teach in that program	2	1.8
5	By taking data from the school	3	2.7
	Total	**110**	**100.0**

Source: Fieldwork, 2016

Habit of Instructors to Use Duplex and the Back Side of Papers

In order to reduce paper use at campus, it would be necessary to get much information on each page as possible and also users should always print and copy double sided (EAUC, 2010). As indicated in Sarantis (2002), many organizations have had savings of thousands or even millions of dollars through their paper use reduction efforts. Heather Sarantis further stated that approaches such as double-side copying or printing, may address the ways that people use paper every day. However, as it is depicted from Table 7, it is only when teachers print and duplicate course outlines that they do have often a good habit of using double-side of the paper (76.4 percent). Data from focus group discussants revealed that double side duplication of course outlines is not to have proper consumption of paper:

We don't have an issue of wise use of paper, because the university doesn't have shortage of papers. Hence, we use double side particularly to duplicate exams for large number of students. This is not to save paper but for easily handling and stapling. For example, if you have 8 pages of an exam, then you can staple only four sheets of papers. It is good particularly for common courses. (Summery from FGD, 2016)

The above anecdote shows that instructors do not have attention to wise use of paper. Paper is seen as a cheap resource within the university. However, this study found out that Wondogenet College of Forestry and Natural Resource forced its staffs to print as well as duplicate duplex:

The duplication center doesn't have its own paper. Instructor should bring papers from their respective school/department based on the number of students. we force instructors to bring the number of students as well as the total number of pages to be duplicated before providing sheet of papers. Even the duplication center doesn't make one-side duplication. (Interview with Head of School of Wondogenet Natural Resource Management, 2016)

This study also found that Wondogent college of Forestry and Natural Resource is the only College of Hawassa University which uses paper efficiently.

Table 7 also shows that there are instructors who never or rarely use double-side while they are printing and duplicating course outlines (5.6 percent), worksheets (17.6 percent), exam papers (21.8 percent), and handouts (40 percent).

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Table 7. Habit of using double-side of the paper

Frequency of Distribution	Exam Papers		Handouts		Course Outlines		Worksheets	
	Freq.	%	Freq	%	Freq.	%	Freq.	%
Always	60	54.5	46	41.8	84	76.4	47	51.6
Mostly	9	8.2	8	7.3	6	5.5	15	16.7
Sometimes	17	15.5	12	10.9	13	11.8	13	14.3
Rarely	13	11.8	37	33.6	6	5.5	14	15.4
Never	11	10.0	7	6.4	1	.09	2	2.2
Total	**110**	**100**	**110**	**100**	**110**	**100.0**	**91**	**100.0**

Source: Fieldwork, 2016

Unable to print and duplicate double side refers that the back side of the paper becomes empty. Proper management of paper includes using this back side of used papers for different purposes. As indicated in Table 8 it is only 20 percent of the respondents who do have a good habit of using the back side of used papers:

I use the back side of used paper for write short notes, to take attendance of students, and to print drafts of research proposals. (Interview with an Instructor from school of Mathematics and Statistics, 2016)

However, 28.2 percent of respondents infrequently use the backside of used papers, and 20 percent have never had such experience. Table 8, hence, portrays that in addition to having weak experience of using-double side to print and duplicate materials, poor management of paper use is exacerbated by poor experience of instructors to use the back side of a used paper which again creates high paper consumption.

Management of Leftover Course Outlines and Exams

As shown in Table 9, 61.8 percent of the respondents replied that there are occasions in which duplicated exams and course outlines are left undistributed. Data from key informants and FGD revealed that exams are left undistributed when questions are stolen as well as when there are extra exam papers

Table 8. Experience of instructors to use backside of used papers

Regularity	Use of Back Side of Used Papers	
	Freq.	%
Always	6	5.5
Mostly	16	14.5
Sometimes	35	31.8
Rarely	31	28.2
Never	22	20.0
Total	**110**	**100.0**

Source: Fieldwork, 2016

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duplicated. This is particularly common in common courses (like Communicative English, Civic and Ethical Education, Logic and Reasoning skill).

As it can be observed from Table 9, 41.8 percent of respondents replied that they put undistributed exam papers somewhere in the office. Some instructors tear it and put into the dustbin (27.5 percent) followed by those who give it to office cleaners for incineration (12.7 percent).

Duplicated course outlines are left when all students are not available in the day-one-class one time. Key informants further replied that instructors often do not distribute the remaining course outlines for absent students in the next class:

In the day-one-class-one time, it is few students who appear in the class. Hence, many course outlines are not distributed. In the next-day class, I don't want to carry the left course outlines. Just I put it in my office. (Interview with an instructor from school of behavioral science, 2016)

Table 9. Course outlines and/or exams left undistributed and measures taken

	Situation of undistributed exams and course outlines	**Response**	
		Freq.	%
Item 1	Always	4	3.6
	Mostly	24	21.8
	Sometimes	40	36.4
	Rarely	35	31.8
	Never	7	6.4
	Total	**110**	**100.0**
Item 2	**Measures taken to undistributed course outline**	**Response**	
		Freq.	%
	Keep the course outlines for next semester	32	29.1
	Tearing and put it into the dust bin	13	11.8
	Put it somewhere in the office	48	43.6
	Give papers for office cleaners to incinerate it	14	12.7
	Use it to write some short notes	2	1.8
	No left over	1	0.9
	Total	**110**	**100.0**
Item 3	**Measurers taken for left exams/quizzes *left undistributed***	**Response**	
		Freq.	%
	Tearing and put into the dustbin	30	27.3
	Put it somewhere in the office	46	41.8
	Give papers for office cleaners to incinerate it	28	25.5
	There is no left exam/quizzes	6	5.4
	Total	**110**	**100.0**

Source: Fieldwork, 2017

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It is clear that leftover papers at office increase the volume of waste paper which makes proper management of waste papers challenging. Significant number of respondents (43.6 percent) replied that undistributed exams and course outlines are put somewhere in the office without any use. However, 29.1 percent of the respondents replied that they keep undistributed course outlines for another semester.

Duration of Keeping Used Papers at Office

Proper management of used papers is partly subject to the period of keeping used papers at office among other things. Table 10 shows instructors' experience of how long they keep exam papers at office. 52.7 percent of the respondents replied that they keep it for less than a year. While 25.5 percent of them replied that they keep exam papers from one to two years. The remaining 21.8 percent of the respondents keep exams for more than two years.

Regarding the periods of keeping exam papers, Hawassa University Senate Legislation 2015 Article 83(5) stated that *'Copies of all exams, tests and quizzes.... shall be kept with the instructor for at least one year*'. This statement doesn't tell the maximum period of keeping exam papers. This has its own repercussion on the mismanagement of papers at staff offices since it creates fear among the staff to dispose exam papers and hence keep it for more than one year. Coupled with absence of enough shelves, this creates unsuitable working environment at offices.

Used Paper Management at Offices

Table 11 shows that the overall management of used paper at offices. Accordingly, 56.3 percent of respondent replied that there is not proper management of used papers at offices. Interviews with instructors revealed that this poor management has results paper mess at offices, loss of students records and other relevant files.

Data from observation, FGD, and key informant interviews revealed that poor management of used papers at offices is caused by absence of mechanisms to dispose waste papers timely, absence of centers to amass waste papers, lack of adequate shelves at offices, presence of exam and assignment papers kept for long periods, lack of adequate and sufficient dustbins, and collection of MA/Msc Thesis and senior essays for many years (see Figure 1):

Table 10. Periods of keeping exam papers at office

Period of Keeping	Freq.	%
Less than six month	14	12.7
seven month-12months	44	40.0
13 months-24 months	28	25.5
More than 24 months	24	21.8
Total	**110**	**100.0**

Source: Fieldwork, 2016

Table 11. Management of used papers at offices

Management Level	Freq.	%
Very good	10	9.1
Good	38	34.5
Poor	47	42.7
Very poor	15	13.6
Total	**110**	**100.0**

Source: Fieldwork, 2016

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Figure 1. Mismanagement of papers at office of instructors (Fieldwork, 2016)

Where do I put my used papers? Nowhere! Look at my desk; it is full of used papers. It doesn't looks like an office. I fell that this affects my personal and professional image. Sometimes, I left some relevant documents including students' exam papers. I do have many complaints from students due to loss of their exam papers. (Interview with an instructor from school of Business and Economics, 2016)

Paper Management by CEP

As part of the curriculum of summer program, students are expected to take modules back home and read the modules during the winter time. Nonetheless, there are problems associated with duplication, storage and distribution of these modules. This is due to untimely duplication and distribution of modules by CEP which contribute for wastage of papers. According to the interview with coordinator of the duplication center and CEP coordinator, it is associated with shortage of papers to duplicate modules resulted from the delay of paper purchase. Even in some cases modules are duplicated by estimation. This is the result of absence of clear communication between the registrar and CEP unit. It is also associated with lack of adequate and qualified workers in the duplication center. Despite summer students are supposed to collect modules for the coming winter tutorials, modules are duplicated after summer students left the campus; hence many of copies are left uncollected.

Moreover, modules which are left from the past year or before are not counted properly. As a result, every year CEP orders duplication of modules without taking into account the number of uncollected modules from the previous years. Figure 2 shows some undistributed modules for summer students.

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Figure 2. Mismanagement of undistributed modules (Source: Fieldwork, 2017)

Means of Disposing Waste Papers at Hawassa University

Interviews with the directors of facility and campus beatification centers of the five campuses of the university reveals that the university does not have a practice of waste characterization. Different wastes are collected and taken into incinerating sites of the respective campuses. Office cleaners collect the papers every morning and whenever there is demand from offices to incinerate used papers (see Figure 3). Incineration sites are not far from staff offices which would have serious health risks. Outside offices, there are no dustbins. From our personal observation and interviews with proctors, students left their course outlines, handouts, exercise books and other paper products within their dormitories and around, particularly at the end of each semester. At the end of each semester, janitors collect left exercise books, text books, and handouts of students and incinerate it. This shows the university does not have clear environmental policy for appropriate use or disposal of wastes in general and waste paper in particular.

According to data from phone interviews with Campus Beautification and Facility Management Directorate Directors of 32 Ethiopian public universities, incineration is the only means of disposal of waste papers. It is only Adama University which has a link with Ethiopian Pulp and Paper S.C (EPPSC) that recycles waste papers. The university has established a system to supply waste papers to EPPSC with a price of 1.75 birr per Kg of waste paper. Annually, the university supplies around 3700kg of waste papers to the industry and earns 6, 475 Birr. According to interview data from Adama University, creating such a link with paper recycling companies has different socio-economic and environmental benefits which include income generation, reducing incineration practice that reduces air pollution and associated health risks, creating conducive working environment, and employment creation.

Paper Recycling Practice in Ethiopia is in an infant stage. During the time of this study, there were only two recycling companies which are found at national level. These are Anmol product Ethiopia PLC, and Ethiopian Pulp and Paper S.C which are located in Addis Ababa. These companies purchase used papers from different organizations and recycle it. The outputs of recycled papers from these companies include papers used to duplicate national exams, cartons, classer, hard papers used as patients' card in hospitals and clinics, and exercise books.

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Figure 3. Mess of papers around the building of teachers' offices and incineration (Source: Fieldwork, 2016)

DISCUSSION

Wise management of papers would have immense contribution to the socio-economic and environmental development at university and country level. It can reduce consumption and waste generation. Recycling is one of the 3Rs of waste management which saves energy, reduce raw material extraction and combat climate change (Friends of Earth, 2008). However, incineration which is the only mechanism of waste paper disposal at Hawassa University in particular and other Ethiopian public universities in general, has many socio-economic and environmental impacts.

As indicated in ID2 Communications (2009), producing one sheet of A4 size paper consumes 0.012 percent of a tree and 122 ml of water. Likewise, 6.8 g of CO2 is released into the atmosphere, and 0.5 g of land waste is generated. That means to produce 93885 reams of paper (See Table 4 and 5), 5631.3 trees, and 5725155 liters of water are required, 319.1tones of CO_2 released to the atmosphere, and 23463.75 kg land waste is created. Since 2012/13, a national harmonized modular curriculum was implemented in all public universities. Moreover, the number of students enrolled each year at these universities is more or less similar. This makes the level of paper consumption is relatively similar across universities. This has an implication that Ethiopian higher education institutions demand large amount of paper per year which contribute environmental degradation at large. Hence, practicing wise use of paper at universities which consumed large amount of paper can reduces the consumption level which again reduces the required tree and water, CO_2 and land waste produced, and other chemicals.

As stated in Sarantis (2002), reducing paper consumption can improve efficiency and reduce costs. Heather Sarabtis further stated that beyond being efficient and effective, organizations also would get reputation for being environmentally conscious. However, as shown in Table 4 and 5, a total of 93855 reams of paper are used at Hawassa University each year. This volume of waste paper would have been reduced if the university had had the habit of waste paper management practices of reducing and reusing waste papers.

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Recycling is the last option of the 3RS of waste management hierarchy. However, as discussed above, incineration is the only means of disposal at Hawassa University and other Ethiopian public universities. Selling the above mentioned volume of paper to industries that recycle paper would have generated money to the university. According to Ethiopian Pulp and Paper Share Company, the company can pay 2.50 to 3.00 Ethiopian Birr to purchase 1 kg of waste paper. Hence, Hawassa university has lost economic gain of 586,593.75 to 703, 912.50 Ethiopian Birr by 2015/16 since it incinerates its waste paper. Considering this case, Ethiopia lost large amount of money due to absence of practicing recycling waste papers across its public universities.

In addition to the aforementioned environmental and economic impacts, poor management of papers has resulted different social impacts like regular student complaints due to loss of their exam papers, poor working environment, and poor professional image to instructors. Lack of a center to collect waste papers each year has created unpleasant working environment to instructors, and other university community. It is common to see loss of exam papers of students at offices due to hoard of waste papers for many years.

CONCLUSION

This study had an overarching objective of assessing the socio-economic and environmental impacts of poor paper management at Hawassa University. The findings of this study revealed that paper is used for different academic purposes in Hawassa University. Quizzes and final exams consume large volume of paper in the University followed by duplicating course outlines.

Proper management of paper is vital particularly for academic institutions. Nevertheless, in Hawassa University, there is no proper management of used and waste papers due to lack of organized system which resulted in different socio-economic and environmental impacts.

Paper recycling practice in Ethiopia is very infant. Except Adama University, other public universities did not have linkage with companies which recycle waste papers. This makes incineration as the only means of waste paper disposal. Moreover, used exam papers are also kept for three and more years at offices partly due to vague statement of the university legislation; exam papers should be kept for 'at least one year.' This creates unpleasant working environment at offices.

The study also revealed that there are slight experiences of printing and/or duplicating materials duplex. However, this study explored that the main reasons behind double side printing and duplicating is to reduce time and energy spent for stapling, and to minimize the number of papers for easy handling. This makes the practice of duplex to be subject to the volume of paper to be printed and duplicated. Beyond this, instructors did not have good habit of using the blank side of used papers. This shows that application of the principles of 'reduce' and 'reuse' of waste are not applied in the university.

The paper use, the volume of waste paper generated and the management practice in the other public universities is not different from Hawassa University. Therefore, the findings of this study entail the need for integrating waste paper management issues in legislations of universities to reduce socio-economic and environmental impacts of poor waste paper management.

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ENDNOTE

[1] We do not have data about the volume of reams of paper required to duplicate handouts by summer and extension students.

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Chapter 61
Long-Term Performance Evaluation of Groundwater Chlorinated Solvents Remediation Using Nanoscale Emulsified Zerovalent Iron at a Superfund Site

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ABSTRACT

This chapter addresses a case study of long-term assessment of a field application of environmental nanotechnology. Dense Non-Aqueous Phase Liquid (DNAPL) contaminants such as Tetrachloroethene (PCE) and Trichloroethene (TCE) are a type of recalcitrant compounds commonly found at contaminated sites. Recent research has focused on their remediation using environmental nanotechnology in which nanomaterials such as nanoscale Emulsified Zerovalent Iron (EZVI) are added to the subsurface environment to enhance contaminant degradation. Such nanoremediation approach may be mostly applicable

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to the source zone where the contaminant mass is the greatest and source removal is a critical step in controlling the further spreading of the groundwater plume. Compared to micro-scale and granular counterparts, NZVI exhibits greater degradation rates due to its greater surface area and reactivity from its faster corrosion. While NZVI shows promise in both laboratory and field tests, limited information is available about the long-term effectiveness of nanoremediation because previous field tests are mostly less than two years. Here an update is provided for a six-year performance evaluation of EZVI for treating PCE and its daughter products at a Superfund site at Parris Island, South Carolina, USA. The field test consisted of two side-by-side treatment plots to remedy a shallow PCE source zone (less than 6 m below ground surface) using pneumatic injection and direct injection, separately in October 2006. For the pneumatic injections, a two-step injection procedure was used. First, the formation was fluidized by the injection of nitrogen gas alone, followed by injection of the EZVI with nitrogen gas as the carrier. In the pneumatic injection plot, 2,180 liters of EZVI containing 225 kg of iron (Toda RNIP-10DS), 856 kg of corn oil, and 22.5 kg of surfactant were injected to remedy an estimated 38 kg of chlorinated volatile compounds (CVOC)s. Direct injections were performed using a direct push rig. In the direct injection plot, 572 liters of EZVI were injected to treat an estimated 0.155 kg of CVOCs. Visual inspection of collected soil cores before and after EZVI injections shows that the travel distance of EZVI was dependent on the method of delivery with pneumatic injection achieving a greater distance of 2.1 m than did direct injection reaching a distance of 0.89 m. Significant decreases in PCE and TCE concentrations were observed in downgradient wells with corresponding increases in degradation products including significant increases in ethene. In the pneumatic injection plot, there were significant reductions in the downgradient groundwater mass flux values for chlorinated ethenes (>58%) and a significant increase in the mass flux of ethene (628%). There were significant reductions in total CVOCs mass (78%), which was less than an estimated 86% decrease in total CVOCs made at 2.5 years due to variations in soil cores collected for CVOCs extraction and determination; an estimated reduction of 23% (vs.63% at 2.5 years) in the sorbed and dissolved phases and 95% (vs. 93% at 2.5 years) reduction in the PCE DNAPL mass. Significant increases in dissolved sulfide, volatile fatty acids (VFA), and total organic carbon (TOC) were observed and dissolved sulfate and pH decreased in many monitoring wells. The apparent effective destruction of CVOC was accomplished by a combination of abiotic dechlorination by nanoiron and biological reductive dechlorination stimulated by the oil in the emulsion. No adverse effects of EZVI were observed for the microbes. In contrast, populations of dehalococcoides showed an increase up to 10,000 fold after EZVI injection. The dechlorination reactions were sustained for the six-year period from a single EZVI delivery. Repeated EZVI injections four to six years apart may be cost-effective to more completely remove the source zone contaminant mass. Overall, the advantages of the EZVI technology include an effective "one-two punch" of rapid abiotic dechlorination followed by a sustained biodegradation; contaminants are destroyed rather than transferred to another medium; ability to treat both DNAPL source zones and dissolved-phase contaminants to contain plume migration; ability to deliver reactants to targeted zones not readily accessible by conventional permeable reactive barriers; and potential for lower overall costs relative to alternative technologies such as groundwater pump-and-treat with high operation and maintenance costs or thermal technologies with high capital costs. The main limitations of the EZVI technology are difficulty in effectively distributing the viscous EZVI to all areas impacted with DNAPL; potential decrease in hydraulic conductivity due to iron corrosion products buildup or biofouling; potential to adversely impact secondary groundwater quality through mobilization of metals and production of sulfides or methane; injection of EZVI may displace DNAPL away from the injection point; and repeated injections may be required to completely destroy the contaminants.

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INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) such as tetrachloroethene (PCE) and trichloroethene (TCE) are dense non-aqueous phase liquid (DNAPL) contaminants widely found in groundwater at Superfund sites in the U.S. They have very low maximum contaminant levels (MCL) for drinking water set up by the US Environmental Protection Agency (EPA) (0.005 mg L^{-1} for both PCE and TCE). There is an urgent need to develop and verify cost-effective methods for groundwater remediation. During the past decade, a novel approach called nanoremediation has gained support from both environmental research and application communities. Nanoremediation is an environmental nanotechnology that uses nanomaterials for environmental cleanup. It has the potential to decrease the overall costs of site remediation, reduce cleanup time, eliminate excavation and disposal of contaminated soil, and reduce contaminant concentration, and it can be done *in situ* (Karn et al., 2009). Of the nanomaterials explored for remediation, nanoscale zerovalent iron (NZVI) has been the most widely used in both laboratory and field studies for groundwater and hazardous waste treatment (Zhang, 2003; Li et al., 2006; Zhan et al., 2011; Tang and Lo, 2013; Guo et al., 2015). A pioneer field test showed potential applications of the nanoscale Fe/Pd bimetallic particles for treating groundwater chlorinated ethenes such as TCE (Elliott and Zhang, 2001). A latter field study conducted in Taiwan confirmed the effectiveness of Pd/Fe bimetallic particles for dechlorination of vinyl chloride (Wei et al., 2009). Other field studies have tested uncoated NZVI (Lacina et al., 2015) and a variety of stabilized and composite NZVI nanomaterials such as palladium-catalyzed and polymer-coated NZVI (Henn and Waddill, 2006) and carboxymethyl cellulose stabilized NZVI (Bennett et al., 2010; He et al., 2010) for groundwater remediation of chlorinated solvents with promising results.

Recent progress has been made in several key areas that has deepened our understanding of the merits and uncertainties of NZVI-based remediation applications. These areas include the materials chemistry of NZVI in its simple and modified forms, the NZVI reactivity with a wide spectrum of contaminants in addition to the well-documented chlorinated solvents, methods to enhance the colloidal stability and transport properties of NZVI in porous media, and the effects of NZVI amendment on the biogeochemical environment (Yan et al., 2013, O'Carroll et al., 2013). Nevertheless, concerns about the safety (the long-term fate, transformation, and ecotoxicity of NZVI in environmental systems) and efficiency of the NZVI technology have limited its applications (Crane and Scott, 2012). The extent and type of NZVI technology applications differ between Europe and the USA (Mueller et al., 2012). Europeans have been more conservative and only three full-scale remediations with NZVI had been carried out up to year 2012, while NZVI has become an established treatment method in the USA. Bimetallic particles and emulsified NZVI, which are extensively used in the USA, have not yet been applied in Europe. Economic constraints and the precautionary attitude in Europe raise questions regarding whether NZVI is a cost-effective method for aquifer remediation. Challenges to the commercialization of NZVI include mainly non-technical aspects such as the possibility of a public backlash, the fact that the technology is largely unknown to consultants, governments and site owners as well as the lack of long-term experiences (Mueller et al., 2012). A more recent review shows that nanotechnology is more effective for removing emerging contaminants and treatment cost of some nanotechnology is comparable to that of conventional methods (Adeleye et al., 2016).

A special formulation of ZVI, namely emulsified zerovalent iron (EZVI) was developed using a surfactant, biodegradable vegetable oil, water, and nanoscale or microscale zero valent iron (ZVI) particles in an emulsion (Geiger et al., 2003; Quinn et al., 2005). The emulsion droplets enhance contact between

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the ZVI and the DNAPL. The ZVI provides rapid abiotic degradation of the DNAPL constituents and the oil provides an immediate sequestration of the DNAPL constituents as well as a long-term electron donor source to enhance further biodegradation. The EZVI was field tested and monitored for up to two years to treat source-zone CVOCs dominated by TCE at a site in the Cape Canaveral Air Force Station, FL (Quinn et al., 2005; O'Hara et al., 2006). Results showed that EZVI injection into a source area containing TCE using pressure pulse technology had decreased the mass flux of dissolved phase TCE from the DNAPL source zone, and decreased the amount of free-phase DNAPL mass over time. Most of the field tests involving NZVI have been monitored in a short-term fashion (several months to two years) and long-term monitoring is lacking. There is a continuing need for long-term assessments of groundwater remedial systems and some efforts have been made to meet such needs. One example is a field test of permeable reactive barrier of ZVI for treating groundwater hexavalent chromium [Cr(VI)] and TCE that had been continually monitored for 14 years (Wilkin et al., 2014) and is still being monitored today.

Built on previous EZVI success, Su et al. (2012, 2013) further tested EZVI injection using pneumatic fracturing injection and direct injection methods for treating source-zone PCE contamination at Parris Island, South Carolina, USA, and reported a two-and-a-half-year performance evaluation. Here we present an update on the treatment efficiency after six years of operation. Such long-term performance evaluation will help fill the knowledge gaps of such technology and help design cost-effective strategies for site remediation and closure.

BACKGROUND

Groundwater contamination to depths of approximately 5.8 m below ground surface (bgs) by PCE occurred from a 1994 spill at the Marine Corps Recruit Depot (MCRD), Parris Island, South Carolina, superfund site (Vroblesky et al., 2011; Su et al., 2012). A PCE DNAPL source area was delineated in field investigations conducted in 2005 and 2006 (Figure 1a). Groundwater table is about 1.3 m bgs with small seasonal variations. Groundwater flow follows a northwest-southeast path with very slow velocity at about 0.046–0.055 m day^{-1}. Containment and treatment of the source zone was critical in controlling the migration of the contaminant plume. EZVI technology was chosen due to its previous success at the National Aeronautical and Space Administration (NASA)'s Launch Complex 34 (LC34) located on the 45th Space Wing's Cape Canaveral Air Force Station, FL (Quinn et al., 2005; O'Hara, et al., 2006). EZVI was injected using pressure pulse technology in that study resulting in uneven distribution of the injected EZVI although a decrease in TCE mass flux and TCE DNAPL mass were achieved. Following that study NASA tested four techniques (pneumatic fracturing, direct injection, hydraulic fracturing, pressure pulsing) for separately delivering 379 liters of EZVI to depths of 4.9 to 5.8 m below ground surface (bgs) in an open field near the original injection location. NASA concluded that pneumatic injection and direct injection methods allowed for more controlled injection without loss of EZVI above or below the target depth interval. In the present study, an additional field test was conducted to provide more field demonstration data to improve the EZVI delivery approach and to confirm and validate the technology for widespread use for DNAPL source zone treatment.

Two types of performance monitoring wells (six fully screened and seven multilevel monitoring wells) were installed in two test plots at the site in June 2006 (Figure 1b). Five 5.79-m deep and 5.08-cm diameter monitoring wells (PMW-2, PMW-3, PMW-4, PMW-5, and PMW-6) were installed, screened from 1.22 to 5.79 m bgs in the pneumatic injection plot where an estimated 38 kg of CVOCs was pres-

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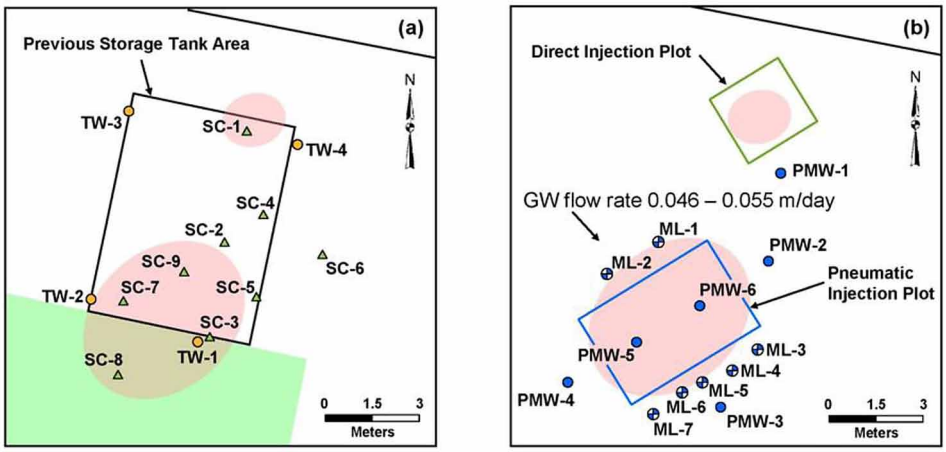
Figure 1. Left panel (a) shows locations of soil cores (green triangles) and temporary wells (orange circles) collected in June 2005 and June 2006 to further evaluate contaminant distribution. The demolished building is shown by the green area. Right panel (b) shows locations of fully screened monitoring wells (blue circles) and multilevel monitoring wells (quartered circles) installed in June 2006 to target the source areas shaded by pink color.



ent. Additionally, seven multilevel monitoring wells (1.27-cm diameter) were installed, with each well screened at seven depth intervals (mid-screen depths at 1.22, 1.98, 2.74, 3.51, 4.27, 5.03, and 5.79 m bgs for ML3, ML4, ML5, and ML6; mid-screen depth at 1.07, 1.83, 2.59, 3.35, 4.11, 4.88, and 5.64 m bgs for ML2 and ML7). In the direct injection plot where an estimated 155 g of CVOCs were present, one 4.11-m deep and 5.08-cm diameter monitoring well (PMW-1) was installed, screened from 1.07 to 4.11 m bgs.

Baseline soil core and groundwater sampling and analyses were conducted before EZVI injection. Eight soil cores (SC-1 through SC-8, Figure. 1a) were collected from ground surface to a depth of 6.10 m bgs at the site during the June 2005 site investigation to evaluate the CVOC mass distribution following the procedures as described by Quinn et al. (2005). An additional soil core (SC-9) was collected from within the pneumatic injection test plot in June 2006 to complete the baseline CVOC mass evaluation. Soil cores were sub-sampled in 0.61-m long sections and CVOCs were extracted and preserved on-site from each section using methanol. The 200 to 300 g wet soil sample was collected and placed in a pre-weighed 500 mL glass container. After capping, the container was reweighed to determine the wet weight of the soil. The container was then filled with 250 mL of reagent grade methanol. The container was then weighed a third time to determine the weight of the methanol added. After the container was filled with methanol and the soil sample, it was agitated by hand for approximately 10 minutes. After shaking, the container was re-weighed to ensure that no methanol was lost during the agitation period. The container was then placed upright and suspended soil matter was allowed to settle for at least 30 minutes. Following the settling period, methanol extract was decanted into glass VOA vials using disposable pipettes. The vials were then capped and stored in a cooler on ice at 4°C until they were shipped on ice to an analytical laboratory. The dry weight of each of the soil samples was determined by sending a subset of the core to the laboratory for moisture content analysis. The final concentrations of VOCs were calculated per the dry weight (105 °C dry basis) of the soil.

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Test plot dimensions of 4.57 m wide, 3.05 m long, and 3.66 m in vertical thickness (1.83 to 5.49 m bgs) were used for the VOC mass estimate calculations in the Pneumatic Injection test plot (these are the same test plot dimensions used for VOC mass estimate calculations during the Environmental Security Technology Certification Program or ESTCP demonstration). PCE DNAPL mass was estimated from threshold PCE soil concentrations using equation (1) below to evaluate the presence of DNAPL:

$$C_t = C_{water} (K_d \rho_b + n)/\rho_b \quad (1)$$

where:

C_t = maximum PCE concentration in the dissolved and adsorbed phases (mg Kg^{-1})
C_{water} = PCE Solubility; 240 mg L^{-1}) at 20°C
ρ_b = bulk density of soil (g cm^{-3}): clay/silty clay = 0.98; sand = 1.55; peat = 0.3 (from soil core SC-9)
n = porosity (unitless): clay/silty clay = 0.625; sand = 0.281; peat = 0.844 (from soil core SC-9)
K_d = partitioning coefficient of PCE in soil (mg Kg^{-1}) = $K_{oc} f_{oc}$
K_{oc} = organic carbon partition coefficient for PCE (L Kg^{-1}): clay/silty clay = 447; sand = 355; peat = 631 (Montgomery, 2000)
f_{oc} = fraction organic carbon (unitless): clay/silty clay = 0.045; sand = 0.00088; peat = 0.25 (from soil core SC-9)

Measurements of soil porosity, bulk density, and fraction of organic carbon were performed on select soil samples from soil core SC-9 to further refine CVOC mass estimates.

CVOC and ethene mass flux estimation was made using groundwater concentrations in the upgradient (ML-1 and ML-2) and downgradient (ML-3 through ML-7) multilevel well transects by assuming an effective cross sectional area (perpendicular to groundwater flow) for each multilevel well screen. CVOC and ethene mass flux was also made using the integral pump tests (IPTs) performed downgradient of the pneumatic injection test plot in well PMW-3 prior to EZVI injection in October 2006, March 2009, and at the end of the performance monitoring period in September 2012.

Groundwater samples were analyzed off-site within the limits of sample holding times for CVOCs [PCE, TCE, cis-1,2-dichloroethene (cDCE), trans-1,2-dichloroethene (tDCE), 1,1-Dichloroethene, and vinyl chloride (VC)], dissolved hydrocarbon gases (DHGs) (acetylene, methane, ethene, and ethane), and volatile fatty acids (VFAs) (acetic, CH_3-COOH; butyric, CH_3-CH_2-CH_2-COOH; lactic, CH_3-CHOH-COOH; propionic, CH_3-CH_2-COOH; and pyruvic acids, CH_3-CO-COOH). For CVOCs, groundwater samples (preserved by acidification using concentrated H_2SO_4 to pH less than 2 and cooled to 4 °C on ice) were analyzed by EPA Method 8260B using gas chromatography-mass spectrometry. For DHGs, groundwater samples were measured by gas chromatography (Kampbell and Vandegrift, 1998). For VFA analysis, groundwater samples were collected in 250-mL amber glass jars and preserved by adding concentrated H_3PO_3 to achieve pH 2 and refrigerated to 4 °C. Samples were filtered through a 0.45-µm membrane and a subsample of 50-mL aliquot was injected directly into the high-pressure liquid chromatography (HPLC), separated by a chromatography column, and the eluting compounds were measured with a UV detector. Total organic carbon (TOC) and total inorganic carbon (TIC) in groundwater samples were determined using a carbon analyzer (Dohrmann DC-80). Dissolved anions (chloride, sulfate, and fluoride) were measured using capillary ion electrophoresis (CE, Waters Quanta 4000E). Samples were collected, filtered with a 0.45-µm filter (Gelman Aquaprep) and acidified to pH less than 2 with HNO_3 (Optima,

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Fisher Scientific) for total dissolved metals plus Si and S. Analyte concentrations were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkineElmer Optima 3300DV). Analytical quality assurance was practiced during sample collection, storage, and analyses. Detailed information about detection limits, recovery rates, and standard materials was provided in the standard operation procedures for each analyte, for example, method detection limit was 0.17 mg L^{-1} for PCE, 0.20 mg L^{-1} for ethene, 0.39 mg L^{-1} for acetic acid, and 0.263 mg L^{-1} for chloride. The percentage of recovery ranged generally between 95% and 105%. For evaluating reproducibility of groundwater analysis, one replicate groundwater sample was collected and analyzed for every 10 samples.

The EZVI was synthesized on-site by combining 10% by weight NZVI (RNIP-10DS from Toda Kogyo Corporation, 35–140 nm, and a composition of 66% Fe^0 and 34% Fe_3O_4), 51% tap water, 38% corn oil and 1% surfactant (Span 85). The EZVI injections were carried out between October 14 and 18, 2006. Detailed injections were described previously (Su et al., 2012, 2013). Briefly, in the pneumatic injection plot, 2180 liters of EZVI containing 225 kg of iron (Toda RNIP-10DS), 856 kg of corn oil, and 22.5 kg of surfactant were injected to remedy an estimated 38 kg of CVOCs. In the direct injection plot, 572 liters of EZVI were injected to treat an estimated 0.155 kg of CVOCs. The CVOC total mass change was estimated from pro- and post-demonstration soil cores. Daylighting of injected EZVI occurred at several locations but the total amount of daylight was less than 10%.

Groundwater sampling and analyses after EZVI injection were conducted in November/December 2006; January, March, and July 2007; January and July 2008; March 2009; September 2010; and October 2012. For each sampling event, groundwater samples were collected from select fully screened and multilevel monitoring wells and analyzed for either some or all of the parameters initially tested during baseline sampling activities. All of the monitoring wells were sampled for the October 2012, last event.

In October 2012, four post-demonstration soil cores was also collected in the pneumatic injection test plot from locations adjacent to the baseline soil cores (less than 0.3 m away), and cores were analyzed for CVOC concentrations to determine post-demonstration CVOC mass estimates. As was done during baseline sampling, post-demonstration CVOC concentrations from wells PMW-5 and PMW-6 were used to calculate estimates of dissolved phase CVOC mass in the southwestern and northeastern halves of the pneumatic injection test plot, respectively and the estimate of the sorbed and DNAPL mass was determined using the soil cores.

EZVI PERFORMANCE EVALUATION

Concentrations of CVOCs and Ethene in Relation to Geochemical Parameters

Baseline data show that PCE and *c*DCE were the predominant CVOCs in downgradient well PMW-3 in the pneumatic injection plot (Figure 2a). The presence of *c*DCE indicates reductive dechlorination of PCE through natural attenuation processes had been occurring. After EZVI injection, concentrations of PCE and TCE temporarily increased but quickly decreased; whereas, *c*DCE showed an increase then decrease after 21 months (Figure 2a). Concentrations of VC were mostly lower than those of *c*DCE. Concentration of *c*DCE was the lowest four years after EZVI injection then it bounced up after that. The rebound of *c*DCE may be a result of near exhaustion of added carbon sources for microbial dechlorination since the NZVI had corroded completely about three months after injection (Su et al., 2013). This also indicates that one single EZVI injection was able to maintain the activity of dechlorination for as

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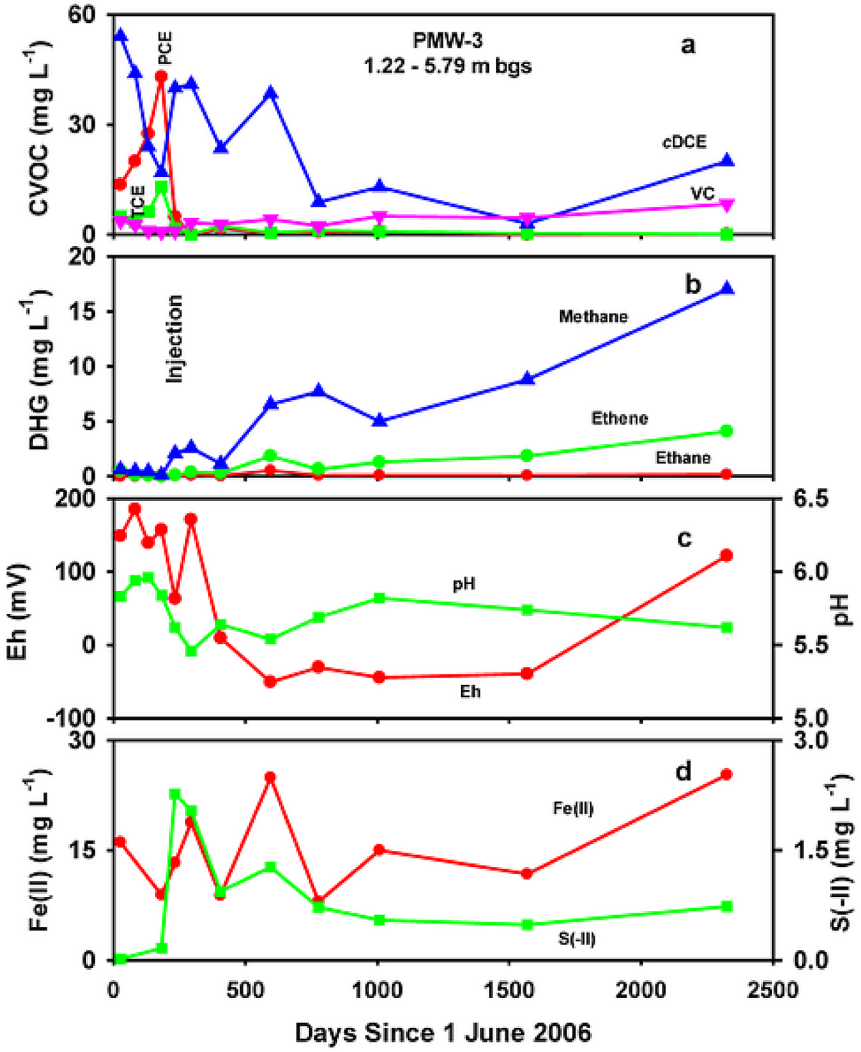
long as four years. Dissolved ethene and methane also increased after injection (Figure 2b). Dissolved DHGs were in the order: methane > ethene > ethane > acetylene (not shown but less than 0.12 mg L^{-1}). Eh values showed steady decrease from about 150 mV to -45 mV then rebounded after four years; whereas, pH values showed a minimum of 5.46 five months after injection and then rebounded to 5.82 thirty months after injection followed by a slight decrease afterwards (Figure 2c). Dissolved Fe(II) was variable and sulfide concentrations showed a spike three months following injection and then slowly decreased (Figure 2d). Dissolved sulfate concentrations decreased after injection likely as a result of microbial reduction (data not shown). TOC showed a spike after EZVI injection (data not shown) likely due to organics released by the breakdown of the corn oil and surfactant components of the EZVI. DO levels were between 0 and 1.5 mg L^{-1}.

Figure 2. Temporal changes in monitoring well PMW-3 (1.22–5.79 m bgs, downgradient of the pneumatic injection test plot) of VCOC (a), DHG (b), Eh and pH (c), and dissolved ferrous iron and sulfide (d) before and after EZVI injection.



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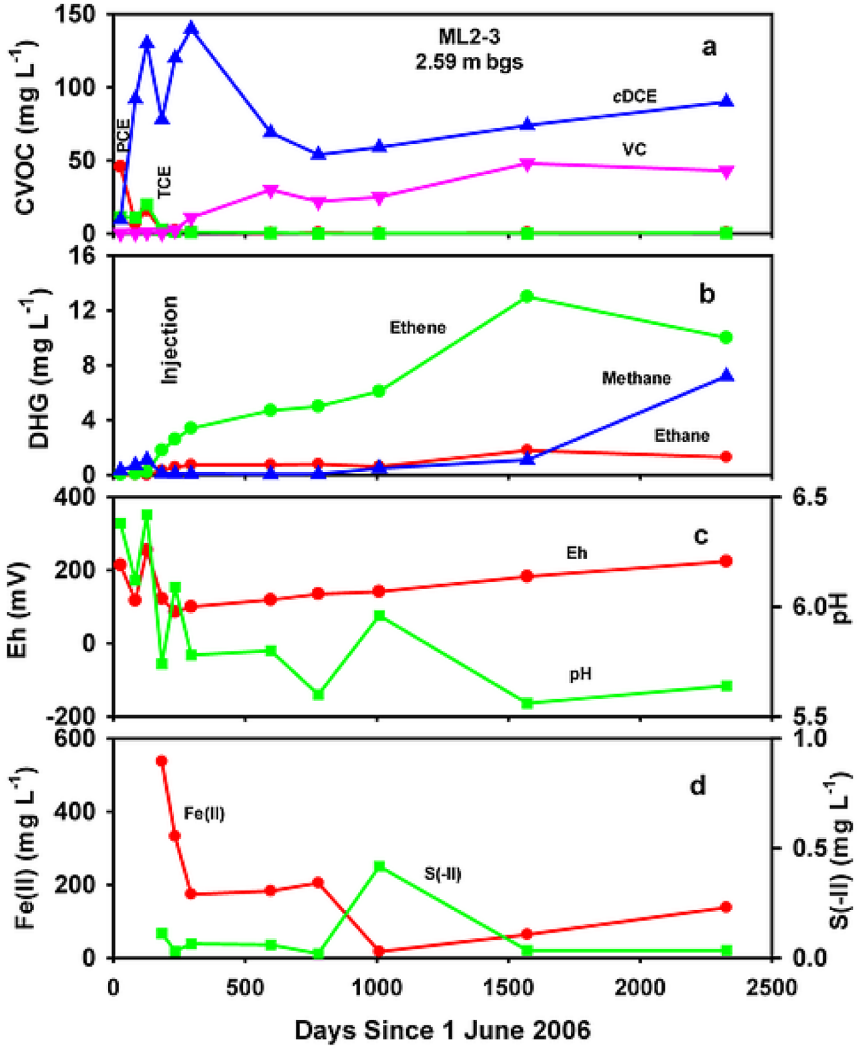
Prior to EZVI injection, *c*DCE and PCE showed the highest CVOCs concentrations in the upgradient multilevel monitoring well ML2-3 in the pneumatic injection plot, which was similar to other upgradient wells (Figure 3a). Natural attenuation of PCE was occurring by the presence of PCE degradation products of TCE, *c*DCE, and vinyl chloride (VC). After injection, concentrations of PCE and TCE decreased to low levels, and *c*DCE peaked then decreased before rebounding; whereas, VC increased over time to reach steady state (Figure 3a). The DHGs especially ethene increased dramatically after injection (Figure 3b) indicating enhanced dechlorination of CVOCs upon EZVI addition.

Slightly different trends were observed in the downgradient well ML7-5. Concentrations of *c*DCE increased after injection, reached a plateau from year three to year four, and finally declined thereafter (Figure 4a). Dissolved DHGs increased after injection and were in the order: methane > ethene > eth-

Figure 3. Temporal changes in monitoring well ML2-3 (2.59 m bgs, upgradient of the pneumatic injection test plot) of VCOC (a), DHG (b), Eh and pH (c), and dissolved ferrous iron and sulfide (d) before and after EZVI injection.



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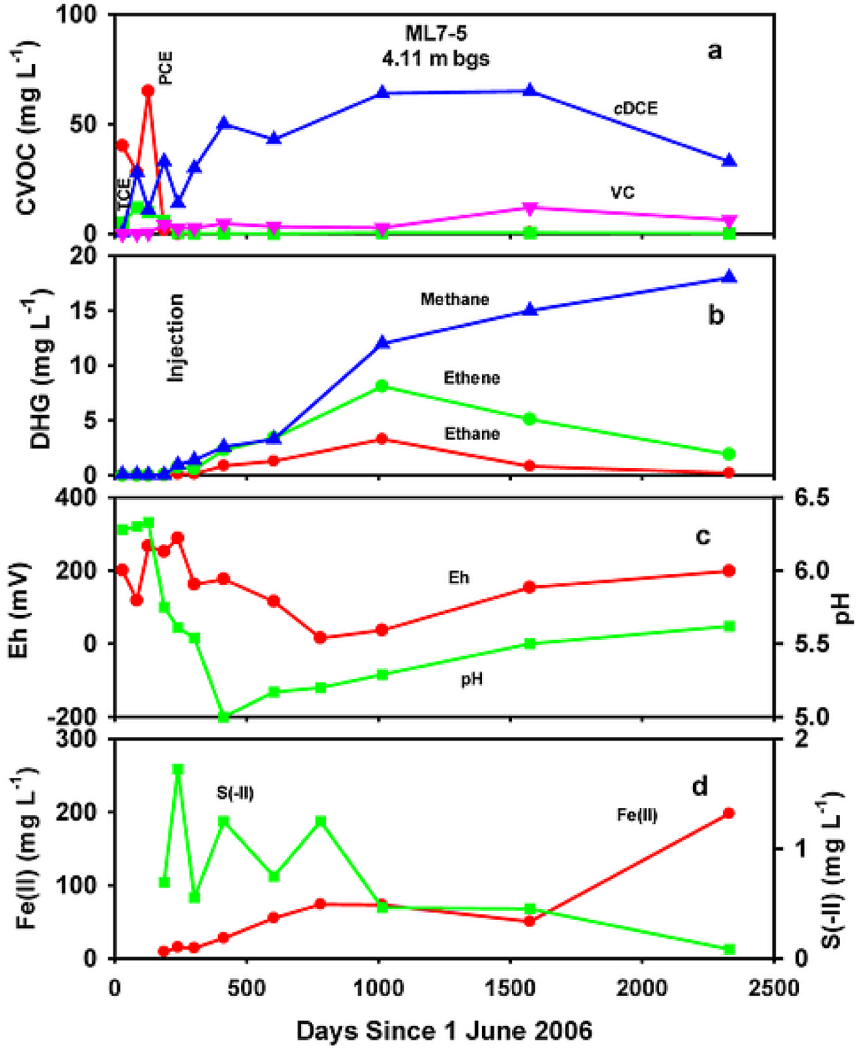
ane > acetylene (not shown but less than 0.12 mg L^{-1} (Figure 4b). Greater decreases in CVOCs were observed in downgradient well PMW-1 in the direct injection plot (data not shown) and PMW-3 in the pneumatic injection plot. Redox potential in the upgradient well ML2-3 decreased right after EZVI injection (Figure 3c); whereas, Eh values in downgradient well ML7-5 showed a slower (time lag) but smaller decrease over time (Figure 4c). The pH values decreased from 6.4 to the lowest value of 5.6 for ML2-3, and to the lowest value of 5.0 for ML7-5 (Figure 4c) before rebounding back.

Dissolved Fe(II) concentrations was estimated to be from 2 to 21 mg/L from total dissolved Fe measurement assuming all the dissolved Fe is ferrous iron in monitoring well ML2-3. Dissolved Fe(II) reached 538 mg L^{-1} after injection then decreased over time (Figure 3d). Dissolved sulfide was low pos-

Figure 4. Temporal changes in monitoring well ML7-5 (4.11 m bgs, downgradient of the pneumatic injection test plot in the direct injection test plot) of CVOC (a), DHG (b), Eh and pH (c), and dissolved ferrous iron and sulfide (d) before and after EZVI injection.



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sibly due to precipitation with Fe(II) to form iron sulfides. Dissolved Fe(II) increased over time after EZVI injection reaching 200 mg L^{-1} at year six. Changes in geochemical parameters generally agreed with other field studies (for example, Wei et al., 2010).

Significance of pH Changes

The pH is a master variable in biogeochemistry that is controlled by a combination of multiple reactions and vice versa. The aquifer at the site is slightly acidic before EZVI injection. It became even more acidic after injection. Such decrease in pH after injection could be a result of several biogeochemical processes simultaneously taking place. The fermentation of organic compounds in the corn oil produces VFAs that generates H^+ ions. PCE undergoes abiotic dechlorination by NZVI to produce ethene, magnetite, HCl, and hydrogen gas as indicated in Eq. (2).

$$3C_2Cl_4 + 12Fe^0 + 16H_2O \rightarrow 3C_2H_4 + 4Fe_3O_4 + 12\ HCl + 4H_2\ (g) \quad (2)$$

X-ray diffraction results for the iron corrosions products collected from purging water in monitoring wells and from soil cores showed that magnetite was a major NZVI corrosion product identified in this field study (Su et al., 2013) although other minerals such as green rust and siderite cannot be ruled out. Bacterial reductive dechlorination using H_2 gas (McCarty, 1997; Smidt and de Vos, 2004) derived from iron corrosion could also generate HCl as shown in Eq. (3).

$$C_2Cl_4 + 4H_2\ (g) \rightarrow C_2H_4 + 4HCl \quad (3)$$

The VFAs such as acetic acid can be used by microbes in biological dechlorination to produce HCl and CO_2 (gas) that lower the groundwater pH (Borden, 2007) as shown in Eq. (4).

$$C_2Cl_4 + CH_3\text{-}COOH + 2H_2O \rightarrow C_2H_4 + 4HCl + 2CO_2\ (g) \quad (4)$$

The pH decrease and concentrations of chloride ions increase in monitoring wells are additional evidence of the active dechlorination of CVOCs taking place in groundwter at the site due to EZVI injection. An optimal pH of 4.9 was reported for abiotic TCE degradation by zerovalent iron (Chen et al., 2001); whereas, the optimum pH values of 6.8 to 7.6 were reported for the maximum microbial reductive dechlorination (Zhuang and Pavlostathis, 1995). The pH values observed in the source area were mostly above pH 4.9 and below pH 6.8. Nevertheless, microbial reductive degradation was not prohibited under the lower-than-optimum pH conditions in the source area. There was no need to artificially adjust the pH of the aquifer for the optimal performance of EZVI at this site. The pH values in most monitoring wells showed an increasing trend between 2.5 and six years after injection due to soil buffering effect as shown in an example for ML7-5 (Figure 4c). This rebound in pH should provide a more favorable environment for the dechlorinating microbes to do their work over long periods of time after EZVI injection.

Dissolved VFAs

Typical distribution of dissolved VFAs is shown for downgradient multilevel cluster ML-7 wells at three depths (Figure 5). VFAs were negligible before EZVI injection and were dramatically increased

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for three of the five VFAs measured. Dissolved propionic acid, acetic acid, and butyric acid were the dominant acids with lactic acid and pyruvic acid showing only trace amounts. The acid concentrations were highest at the shallow depth than at the bottom depth, probably because the lighter corn oil (relative to water) from disintegrated EZVI emulsions tended to migrate (float) towards the top portion of the saturated subsurface where it was used most by microbes as a food source. Corn oil as a component in the EZVI formulation seemed to supply a variety of electron donors such as VFAs that persisted in the source area subsurface over a prolonged period of time up to six years due to the very slow groundwater velocity (0.046 – 0.055 m day^{-1}). An earlier study showed similar VFA distribution trends when emulsified soybean oil was used in a study to enhance anaerobic bioremediation of a TCE source area (Borden et al., 2007). In that study, no NZVI was used. Although vegetable oil itself is a good carbon source for the dechlorinating bacteria, vegetable oil alone may not be as effective as a combined vegetable oil and NZVI. NZVI helps a rapid establishment of reducing conditions that is favorable to the microbial dechlorination. In addition, NZVI provides additional iron that can be transformed to form iron sulfides. Iron sulfides can abiotically degrade CVOCs (He et al., 2015).

Mass Flux

Results of pre-injection and post-demonstration mass flux estimates calculated using CVOC concentrations from the five multilevel wells ML-3 through ML-7 on the downgradient side of the test plot revealed significant reductions in mass flux of the parent compounds PCE and TCE, and of the degradation product *c*DCE (data not shown). In contrast, the mass flux of the degradation products VC and ethene increased significantly over the test period. The increase in ethene mass flux indicates that the reduction in PCE, TCE, and *c*DCE concentrations were due to degradation and not just displacement of water or DNAPL out of the plot.

Total CVOC Mass Reduction

It was estimated from the baseline groundwater and soil sampling events that the total mass of target CVOCs in the pneumatic injection test plot was approximately 38 kg, of which roughly 29 kg (or ~76%) is attributed to PCE DNAPL (Table 1). Post-demonstration sampling results were used to calculate a CVOC total mass of approximately 8.3 kg (Table 1) in the pneumatic injection test plot, of which roughly 1.4 kg (or ~17%) is attributed to PCE DNAPL. Injection of EZVI into the pneumatic injection test plot resulted in approximately 95% reduction in the estimated mass of PCE DNAPL, and approximately 78% reduction in the total mass of target CVOCs. This is lower than an estimated 86% reduction in the total mass of target CVOCs made two and a half years after EZVI injection as reported by Su et al. (2012). Variability of soil cores collected for CVOCs extraction and determination may have contributed to the difference. Nevertheless such reduction is significant from a single EZVI injection event. Repeated EZVI injections could have been used to more completely degrade CVOCs in the source zone but this was not an objective of this field test. Because a single injection was able to maintain active removal of CVOCs for at least four years (Figure 2a), repeated injections may be arranged four years apart to achieve a more cost-effective injection schedule for complete source remediation.

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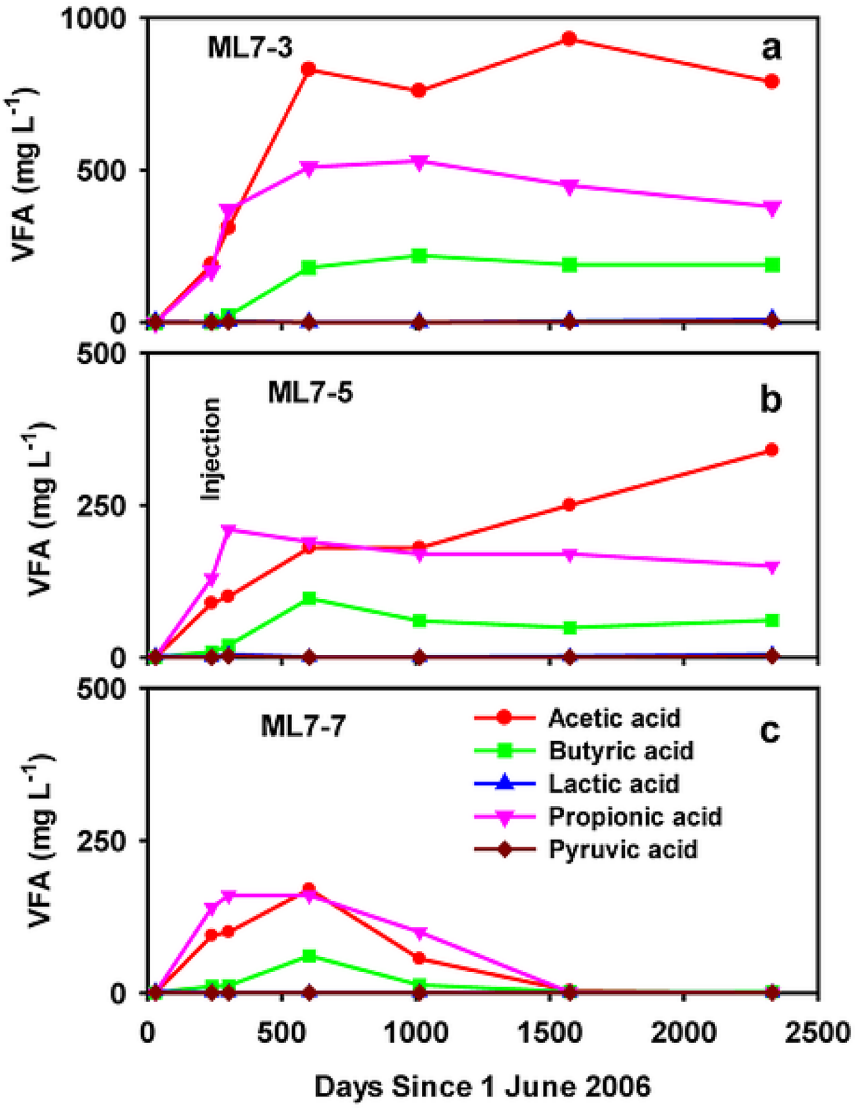
Figure 5. Temporal changes in dissolved volatile fatty acids in monitoring well ML7-3 (2.59 m bgs) (a), ML7-5 (4.11 m bgs) (b), and ML7-7 (5.64 m bgs) (c) downgradient of the pneumatic injection test plot before and after EZVI injection.



PROCESSES OF DECHLORINATION IN THE SOURCE AREA

Mechanisms and pathways of dechlorination in the source area involve several processes that were likely responsible for the accelerated CVOC degradation in the present study. This field test further shows that the EZVI provided multiple reactions for reduction in CVOC mass including rapid abiotic dechlorination resulting from the NZVI and a slower biological dechlorination resulting from the presence of the vegetable oil that was sustained for a more prolonged period of time; however, it is difficult to assess how much contributions of CVOC degradation are from abiotic and biotic pathways. The injected NZVI creates reducing conditions that result in immediate abiotic dechlorination of CVOCs and these condi-

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Table 1. Pre- (year 2006) and post-demonstration (year 2012) CVOC mass estimates in the pneumatic injection plot

Media	VOC	Pre-Injection Mass (g)			Post-demonstration Mass (g)		
		Sorbed/Dissolved	DNAPL	Total	Sorbed/Dissolved	DNAPL	Total
Soil	PCE	2,760	29,028	31,788	3,116	1,384	4,500
	TCE	1,317	0	1,317	672	0	672
	Cis-DCE	1,254	0	1,254	1,542	0	1,542
	VC	2,214	0	2,214	204	0	204
Groundwater	PCE	577	0	577	48	0	48
	TCE	267	0	267	50	0	50
	Cis-DCE	588	0	588	1,226	0	1,226
	VC	12	0	12	103	0	103
Total Mass (g)		8,990	29,028	38,018	6,962	1,384	8,346
% Reduction					23%	95%	78%

tions are consistent with the reduced redox required for biological reductive dechlorination processes. Anaerobic and aerobic corrosions of NZVI also causes a small increase in pH (Eqs. (5) and (6)) that can be beneficial in buffering the production of acid that can be associated with biological processes such as fermentation producing VFAs and other biological reactions (e.g., Eqs. (3) and (4)).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \text{ anaerobic corrosion} \quad (5)$$

$$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \text{ aerobic corrosion} \quad (6)$$

The influence of the NZVI on the redox conditions in the bulk fluid in the vicinity of the injected EZVI will be less significant than if the NZVI was injected in the absence of the emulsion but as the corn oil and surfactant components of the EZVI breakdown and the NZVI is no longer shielded within the emulsion, the beneficial impact of the NZVI will become more significant. In general, there is strong indication that biological dechlorination is significant at both test plots. This generalization is supported by: (1) presence of daughter products of PCE (TCE, *c*DCE, and VC) at elevated concentrations prior to EZVI injection; and (2) *c*DCE and VC as major dechlorination products after EZVI injection. Similar biological processes also have been shown in a previous field test using Pd-catalyzed and polymer-coated nanoiron suspension to treat TCE, *c*DCE, and VC (Henn and Waddill, 2006). Microbial analysis was performed using soil cores collected from the source area, and in agreement with another study in the southern groundwater plume area (Vroblesky et al., 2009), the results revealed the presence of microbes (*Dehalococcoides* sp. and *Dehalobacter* sp.) known to degrade chlorinated solvents. A variety of microbes can degrade PCE and TCE, but only microbes related to the genus *Dehalococcoides* are known to degrade *c*DCE and VC to ethene (He et al., 2003 a, b; Schmidt and de Vos, 2004). Complete sequential dechlorination of PCE to ethene has been observed for *Dehalococcoides etheneogenes* (Maymo-Gatell et al., 1997). Microcosm studies show no deleterious effect on total bacterial abundance from NZVI (Kirschling et al., 2010). There is no evidence of adverse impact to microbial communities

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after EZVI injection; in contrast, population of dehalococcoides was increased from less than 10^3 cells per g of fresh soil in the saturated zone to up to 10^7 cells per g of fresh soil with a 10,000 fold increase after injection in this study, in agreement with an earlier field study (Kirschling et al., 2010). It is likely that a collection of dechlorinators are involved in the degradation of PCE and its chlorinated daughter products in the source area.

ADVANTAGES AND DISADVANTAGES OF THE EZVI TECHNOLOGY

EZVI holds promise in remediating sites cost effectively and addressing challenging site conditions, such as the presence of DNAPL. Based on the previous and present work, the following general statements can be made with regard to the pros and cons, or strengths and weaknesses of the EZVI technology. The main advantages of the EZVI technology over other treatment technologies (pump-and-treat, thermal, conventional PRBs) include:

- An effective "one-two punch" of rapid abiotic degradation followed by slower biological degradation;
- Contaminants are destroyed rather than transferred to another medium;
- Ability to treat both DNAPL source zones and dissolved-phase contaminants to contain plume migration;
- Due to the enhanced reactivity and fast corrosion potential of NZVI, EZVI is most suitable for treating the source-zone DNAPL where the greatest economic benefits can be made;
- Ability to deliver reactants to targeted zones not readily accessible by conventional PRBs; and
- Potential for lower overall costs relative to alternative technologies such as groundwater pump-and-treat with high operation and maintenance costs or thermal technologies with high capital costs.

The main disadvantages of the EZVI technology are:

- Difficulty in effectively distributing the viscous EZVI to all areas impacted with DNAPL;
- Potential decrease in hydraulic conductivity due to iron oxide buildup or biofouling;
- Potential to adversely impact secondary groundwater quality through mobilization of metals and production of sulfides or methane if excess electron donor, in the form of the vegetable oil, is added;
- Injection of EZVI may displace DNAPL away from the injection point; and
- Repeated injections of EZVI may be required to completely destroy the contaminants.

FUTURE RESEARCH DIRECTIONS

It is still a challenge to deliver NZVI to a targeted subsurface zone in a uniform fashion. EZVI injection may be more applicable to deeper aquifers than the shallow aquifers that may help minimize daylighting. Research is needed to explore more effective injection technologies to minimize preferential flow and daylighting at sites with varying lithological and hydrogeological conditions. Formulation of NZVI

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to make it injectable while maintaining its reactivity can be further improved. Injected nanoiron was shown to transform to iron oxides (with greater particle size) mostly within three months (Su et al., 2013). Fate and transport of NZVI in the subsurface during expanded periods up to many years are still poorly understood. Corrosion products of NZVI such as green rusts, iron sulfides, and magnetite may offer additional benefits for CVOC degradation – such abiotic pathways and their relative contributions to the overall contaminant contamination need to be evaluated in detail in both laboratory and field studies. Being consistent with other field studies, the results of the current field applications with respect to contaminant reduction are promising, and no major adverse impacts on the environment have been observed so far. It is thus expected that these tests will contribute to promoting the technology in other geographical places such as Europe (Mueller et al., 2012).

CONCLUSION

Positive results have been obtained from a six-year field test using a single EZVI injection event for source zone remediation at a Superfund site contaminated with DNAPL PCE. Addition of EZVI resulted in more reducing conditions that stimulated dechlorinating bacteria (dehalococcoides); there is no evidence of adverse effect to the microbial communities. High dissolved VFA concentrations were sustained in the shallow monitoring wells even after six years of EZVI injection, indicating the excellent sustainability of the EZVI technology at this site where groundwater flow is slow. There were significant reductions in the downgradient groundwater mass flux. There were significant reduction in total VOC and DNAPL. A combination of abiotic (from NZVI and its corrosion products) and biotic (from bacteria) pathways lead to contaminant degradation through dechlorination reactions. EZVI technology can be successfully applied to treat source zone DNAPL.

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KEY TERMS AND DEFINITIONS

Abiotic Dechlorination: Dechlorination by inorganic reactants such as elemental iron and sulfides.

Biotic Dechlorination: Dechlorination by microbes such as *Dehalococcoides* sp. and *Dehalobacter* sp.

Chlorinated Volatile Organic Compounds: Compounds that contain chlorine atoms and are volatile. Examples include tetrachloroethene or perchloroethene (PCE) and trichloroethene (TCE).

Dense Non-Aqueous Phase Liquid: A denser-than-water NAPL, i.e. a liquid that is both denser than water and is immiscible in or does not dissolve in water.

Groundwater: Liquid water that seeps through the soil or rocks underground.

Groundwater Remediation: The process that is used to treat polluted groundwater by removing the pollutants or converting them into harmless products.

Mass Flux: The rate of mass flow per unit area.

Maximum Contaminant Levels: Standards that are set by the United States Environmental Protection Agency (EPA) for drinking water quality. An MCL is the legal threshold limit on the amount of a substance that is allowed in public water systems under the Safe Drinking Water Act.

Non-Aqueous Phase Liquids or NAPLs: Liquid solution contaminants that do not dissolve in or easily mix with the water. Examples are oil, gasoline, and petroleum products.

Nanoremediation: An environmental nanotechnology that uses nanomaterials for environmental cleanup.

National Priorities List (NPL): The list of national priorities among the known releases or threatened releases of hazardous substances, pollutants, or contaminants throughout the United States and its territories. The NPL is intended primarily to guide the EPA in determining which sites warrant further investigation.

Superfund Site: An uncontrolled or abandoned place where hazardous waste is located, possibly affecting local ecosystems or people. Sites are listed on the National Priorities List (NPL) upon completion of Hazard Ranking System (HRS) screening, public solicitation of comments about the proposed site, and after all comments have been addressed.

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Chapter 62
Government's Role in Setting Optimal Policies for Green Supply Chain

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ABSTRACT

In the last two decades lot of research was done in the area of Green design and Green supply chain management. But very few researchers have really tried to study the government's role in the implementation of Green designs and Green supply chain in any nation. In this paper simple general equilibrium model is used to analyze the benefits from taxes, and subsidies by government for green disposal efforts such as waste reduction, waste recycle, remanufacturing, and disposal on both the manufacturers and household consumers.

INTRODUCTION

In every year since 1993 has been in the top 20 warmest years on record[1]. Environmental degradation and increasing resource depletion has compelled the governments across the globe to set policies on green practices such as Green design, Green procurement, Green manufacturing, Green packaging, Green distribution and Green disposal for all the manufacturing companies. Furthermore, with a global concern to environmental issues, various countries have framed stringent laws on disposal of goods, and are imposing green barriers while importing commodities from the global markets.

Fullerton and Wu (1998) in the paper "Policies for green design" initiated the discussion on how the government can use different mix of policy instruments to deal with various organizational and market failures in managing household waste. They suggested in the absence of a market for recycled goods, the mix of consumption tax, packaging tax and recyclability subsidy on producers of different industrial and household products can lead to minimizing the amount of waste generated and maximization of reuse and recycling of material. Similarly, if household and industrial waste is collected free of charge, then the

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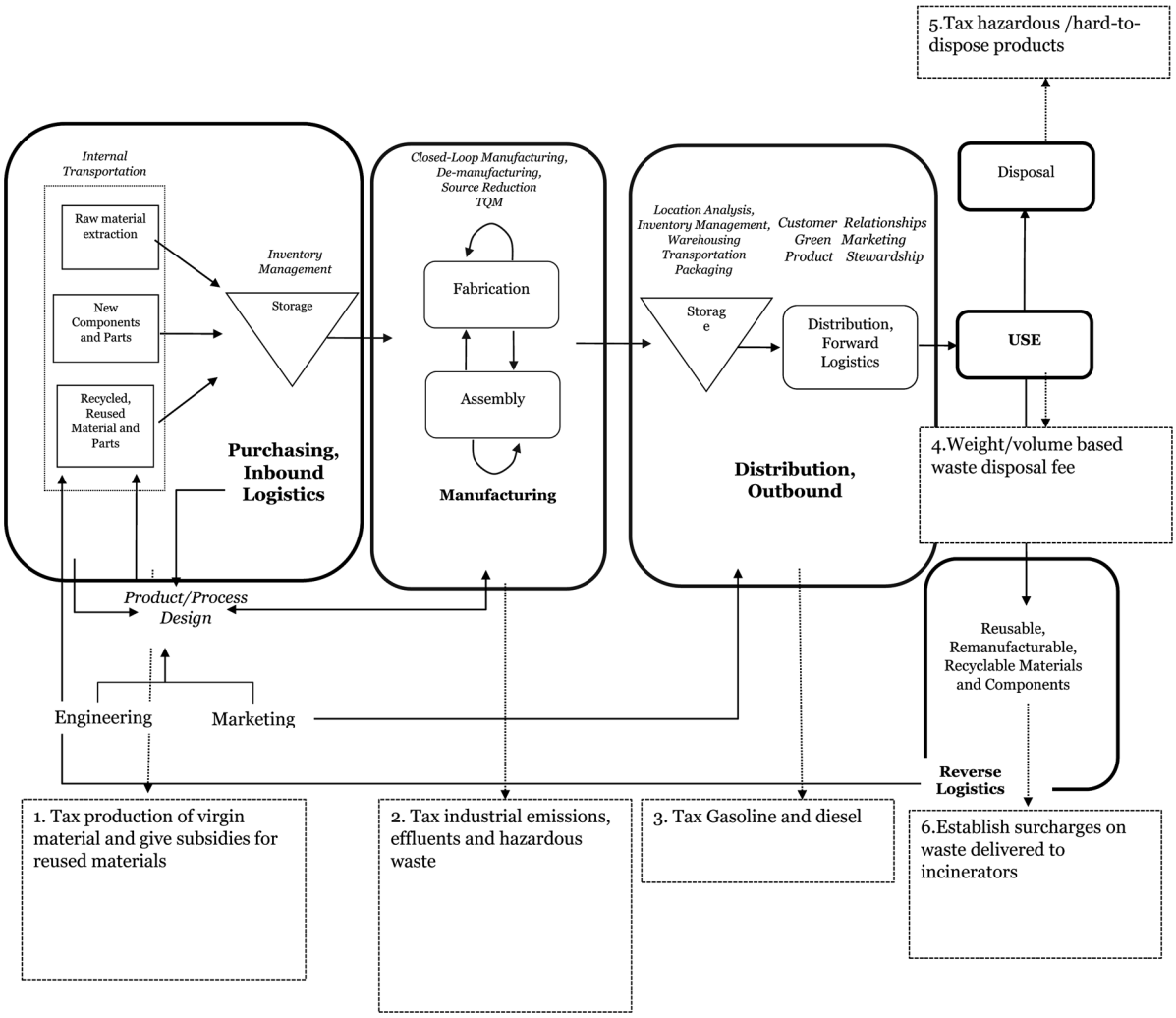
Figure 1. Government policies for manufacturers and consumers at different stages of supply chain



combined effect of consumption tax, packaging tax and recyclability subsidy on producers may lead to optimize the amount of waste in the entire product-life-cycle starting from design, to production, packaging, sales, use and disposal. Figure-1 shows how the government policies can target different stages in the product life cycle. Policies that affect product design will also affect product disposal and vice versa.

BACKGROUND

The concept of Green Supply chain Management was first put forward in US Michigan State University in 1996 (Zhou, 2009). Since then the scholarly interest in the area of Green Supply chain Management has rapidly developed across the world. Benita M. Beamon, (1999), in her Paper "Designing the green supply chain, Logistics Information Management", gave a new aspect to the Supply chain management by taking environmental challenges to production and manufacturing into thought. She insisted on re-

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ducing waste and minimizing the use of resources at each stage of the supply chain. Also to lower the environmental damage all the supply chain members should examine their "ecological footprint" and make Green supply chain as a practice for lowering the ecologic footprint of supply chains (van Hoek, 1999).

Organizations have started viewing many of these environmental programs like technological and organizational development projects, as possible alternatives for gaining a competitive advantage (Sarkis, 2002). Subhajit Mazumder and Anand Chatterjee in the paper "Green Supply Chain as a competitive advantage enabler in the FMCG sector" have said that cost strategy (low cost) and Evolving strategy (focus) are now out dated and for sustaining in the aggressive market they need to improve the supply chain efficiency and should become more environmentally conscious. A number of green practices were suggested by Srivastava (2007) likes green design, reverse logistics, product recovery, logistic design, solid waste management and so on. Sanjeev Swami and Janat Shah (2011) in the paper "Channel Coordination in Green Supply Chain Management: The Case of Package Size and Shelf-Space Allocation" addressed the benefits of vertical coordination in a green supply chain between the players at the upstream and downstream levels of the chain and to reduce the pack size of products that helps in saving environmentally costly transportation cost.

Aref A. Hervani, Marilyn M. Helms, Joseph Sarkis, (2005), in their paper "Performance measurement for green supply chain management", tried to design a Performance measuring system for GrSCM. In the paper they said in supply chains with numerous vendors, producers, distributors, and retailers the Green performance measurement is very challenging because it is difficult to attribute performance results to any one particular entity within the chain. And the problem gets amplified if the member organizations don't follow any standardized data, poor technological Integration among partners, cultural dissimilarities, lack of understanding of organizational plan, differences upon metrics, or unclear understanding of the needs for inter-organizational performance Measurement, etc. They suggested Environmental performance indicators can be used in evaluating the environmental performance of activities, processes, hardware and services.

GREEN INITIATIVES BY DIFFERENT GOVERNMENTS

As part of its commitment to improve the environment and the quality of life of its citizens, the Canadian government on April 1, 2006 made the policy of green procurement mandatory for all its government purchases.[2] On November 26, 2008 United kingdom (UK) government enacted the climate change act to improve carbon management and help the transition towards a low carbon economy in the UK.[3] The Japanese government is planning to introduce a new tax to curb carbon emissions from fiscal year 2016. Similarly in 2012 china announced increases in resource taxes on six minerals, such as tin, iron ore, and in February 2013, the US Department of Energy announced USD150 million in Advanced Energy Manufacturing Tax Credits for clean energy and energy efficiency manufacturing projects across the US.[4] Also the European Union (EU) too has waste management policies with aim to reduce the environmental and health impacts of waste and improve Europe's resource efficiency.[5] With most governments from the developed nations actively trying different green practices, the impacts from their efforts need to be evaluated.

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A SIMPLE MODEL FOR ANALYSING WASTE REDUCTION AND WASTE REUSES EFFORT

The model is derived from the model suggested by Fullerton and Wu (1998) with the assumption that household consumer can also dynamically support the government's efforts in reducing waste. It is assumed that all the different manufacturers produce identical goods and all the household consumption is identical. A representative firm produces a consumable goods with the cost function $c(q, e)$, where $q \geq 0$ is the quantity of goods produced and $e \geq 0$ is the effort put by the firm to reduce waste at the source, such as reduced use of virgin toxic materials, minimizing material use for production, economic packaging, reverse logistics, etc. Any household in a nation has the utility function $u(q, a) – (m + d)$, where $q \geq 0$ is the quantity of goods produced and $a \geq 0$ is the amount of effort by the household in reducing waste, and 'm' is the monetary cost incurred in the consumption of q and 'd' is the cost incurred while disposing the waste. Household cost incurred in the disposal of waste (d) may include reuse, remanufacture, and recycle of products.

The amount of waste needed to be disposed after consumption will depend on $q, e, a,$ and may be denoted by $w(q, e, a)$. Disposing waste may incurs two different types of cost. The first is the tangible cost of collecting, transporting, shorting, recycling and reuse of waste, denoted by "T" per unit of waste. The second type of cost is the intangible cost on environment and society, and is denoted by "I" per unit of waste. All the above functions are twice differentiable, so as to satisfy $cq > 0$, $ce > 0$, $uq > 0$, $ue < 0$, $wq > 0$, $we < 0$, $wa < 0$ and guarantying an unique solution to the problem.

The policy instruments available to the government are 1) unit consumption tax (t) 2) unit subsidy on waste disposal (λ), 3) unit subsidy on manufacturers waste reduction effort (γ), and 4) Governments direct investment for waste reduction and recycling facilities (θ).

Optimized Social Impact and Decentralizing Efforts

Due to quasi-liner preferences, the first optimal solution for the above model is maximizing household utility, less the cost of production, and cost of waste disposal by household, manufacturer, and the government. Then the objective function becomes $u(q, a) - c(q, e) - (T + I)\, w(q, e, a)$ and the first order condition for interior maximum are

$$uq – cq - (T + I)wq = 0, \tag{1}$$

$$- c_e - (T + I)we = 0, \tag{2}$$

$$ua – (T + I)wa = 0 \tag{3}$$

Each of the above conditions equates marginal social costs to marginal social benefits.

The following are the outcomes from decentralized market efforts. Let's assume the price for a unit consumable good is 'p' and the price of waste disposal per unit waste is 'χ'. If the above mentioned subsidies and taxes are implemented on household consumers, the objective function becomes $u(q, a) - (p + t)q - (\chi + \lambda)\, w(q, e, a)$. The first order conditions for maximum household consumer's utility are

$$u_q - (p + t) - (\chi + \lambda)w_q = 0 \tag{4}$$

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$$u_a - (\chi + \lambda)w_a = 0 \quad (5)$$

From the given price and government policy variables, the producer's profit function may be derived as $pq - c(q, e) + (\gamma + \theta)e$ and then the first order conditions for profit maximization are

$$p - c_q = 0 \quad (6)$$

$$- c_e + \gamma + \theta = 0 \quad (7)$$

If Optimal Policies for Passive Household Waste Reduction Effort – a = 0

If the household consumers are not pro-active with respect to waste reduction effort, then the equations *(3)* and *(5)* are not applicable. Now if we compare the remaining equations for social optimal results and decentralized outcomes, we can easily find that they are equal if and only if $t + (\chi + \lambda)\, w_q = (T + I)\, w_q$ and $\gamma + \theta = - (T + I)\, w_e$. These conditions may lead to a series of optimal policies as the three parameters to be considered, $t, \lambda, \gamma + \theta$ are needed to be calculated using two equations.

One of the possible optimal government policy may be obtained by setting $t = 0, \lambda = T + I - \chi$ and $\gamma + \theta = - (T + I)w_e$. In this case the combined effort of unit subsidy on household waste disposal and a unit subsidy on the manufacturers and governments waste reduction effort can achieve the social optimal. If the waste disposal service to the household is provided at marginal cost so as $\chi = T$, then the unit tax for household waste disposal will be equal to the pre unit social and environmental cost of waste, ie., Pigouvian tax[6]. Instead suppose the household waste disposal is provided free of charge then, $\chi + \lambda = 0$, is possible because the problem of illegal waste disposal which is very common in most of the counties can be controlled. Once the illegal waste disposal problem is curbed then the remaining policy instruments can be implemented to achieve social optimum. That is, $t = (T + I)w_q$, $\gamma + \theta = - (T + I)w_e$ along with $\lambda = - \chi$ may also lead to social optimal. Again we can use consumption tax and waste reduction subsidy on manufacturers in the Pigouvian way.

If Optimal Policies for Passive Household Waste Reduction Effort - $a \geq 0$

Once the household start active waste reduction efforts, then the comparison for social optimal conditions in the *equations (1-3)* and the decentralized efforts in the *equations (4-7)* will lead to three equations:

$$t + (\chi + \lambda)w_q = (T + I)\, w_q \quad (8)$$

$$\gamma + \theta = - (T + I)\, w_e \quad (9)$$

$$(\chi + \lambda)w_a = (T + I)\, w_a \quad (10)$$

Now there will be only one unique combination of policy devices that implement the social optimal: $t = 0, \lambda = T + I - \chi$, *and* $\gamma + \theta = - (T + I)\, w_e$. The reason for such uniqueness in the optimal policy is purely because government has only three policy devices to control the three private variables.

The optimality of the above policy can be automatically explained. Free waste disposal (or a fixed payment for waste disposal) does not provide the household or manufacturer any incentives to make any

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waste reduction effort. Everyone in the society (manufacturer, households, institutions, etc.) expect some kind of return on investment (ROI) from their efforts for reducing or safe disposing the waste. This is why most governments are charging taxes at Pigouvian rates.

CONCLUSION

From the above discussions we can conclude that even in the absence of active involvement from household consumers on waste reduction efforts, the governments are capable in setting policy procedure. The reasons behind governments' flexibility in setting policy is the availability of three policy instruments *(t, λ, γ+θ)* to target the two private variable *(q,e).* The role of the waste disposal tax and subsidies becomes more significant only when the household consumers and the manufacturers actively start reducing waste, and reusing/ remanufacturing/ recycling materials.

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5. Being wise with waste: the EU's approach to waste management, available at http://ec.europa.eu/environment/waste/pdf/WASTE%20BROCHURE.pdf
6. Pigouvian taxes are named after economist Arthur Pigou. William Baumol was instrumental in framing Pigou's work in modern economics. It's a special tax that is often levied on companies that pollute the environment or create excess social costs through business practices. In a true market economy, a Pigovian tax is the most efficient and effective way to correct excess social cost.

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Chapter 63
Green IT Adoption Practices in Education Sector:
A Developing Country Perspective

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ABSTRACT

Green IT is a resource efficient and effective consumption to reduce organizations processes impacts to the environment using information technology. This article aims to explore GIT practices of higher education institutions in the Philippines, where a qualitative multiple-case study is used. The study found that higher education institutions Green IT adoption covers the use of paperless and digital archiving systems, resource efficient IT equipment, responsible electronic waste disposal, recycling and reuse, and initiated awareness programs to educate the employees about Green IT and sustainability. The study also found that these practices are in its early stage of adoption in higher education institutions in the Philippines. This article also presents practical and research implications to further the uptake of Green IT in higher education institutions.

1. INTRODUCTION

Green IT (GIT) is a resource efficient and effective consumption through the use of IT infrastructure and systems. It also involves managerial and individual's practices towards sustainable environment (Lei and Ngai, 2013). It is an approach to encourage stakeholders' participation in solving environmental problems, and strategic focus for organizations to achieve sustainability (Loeser et al., 2017). Essentially, this approach is expected to reduce business operations cost, wastes and emissions of carbon footprint, thus, minimizing the overall impact of IT usage in the environment (Gholami et al., 2013).

Although there are different approaches to achieve GIT benefits, both for organizations and environment (Asadi and Dahlan, 2017), a handful of studies explored on GIT practices in organizations, more specifically, the education sector. First, the education sector researchers are actively involved in the

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growing literature of GIT exploring private and public organizations. To date, limited studies have been published on exploring the practices of GIT in higher education institutions (HEI). Second, there is a growing appreciation of GIT adoption in higher education institutions in developed countries. However, there is an inadequate investigation of evidence of GIT in developing countries. Third, higher education institutions have started offering programs on sustainability and environment. It presents a challenge of how universities adopt to GIT as a way to foster environmentally sustainable efforts. Thus, this study is motivated by these concerns that the literature lacks in-depth investigation of the GIT practices, issues, and challenges faced by higher education institutions. Hence, this study fills the gap of understanding Green IT adoption practices in higher education institutions.

This study contributes to growing literature on GIT adoption in higher education institutions, more specifically, in a developing country perspective, the Philippines. Also, it offers new insights on the state of Green IT adoption covering the practices and potential challenges faced by higher education institutions, and approaches to achieve sustainability. Thus, this research is guided by the research question: "*What are Green IT adoption practices towards sustainability?*" To achieve the goal of the study, a qualitative approach using multiple case studies was employed involving higher education institutions in the Philippines. Hence, this study argues that the understanding of GIT adoption in HEIs not only significant to the Philippines, and is similarly important to other rising economies.

The remaining sections of this paper are presented as follows: GIT in education and overview of the Philippine higher education institutions, discussion of the research methodology, the data analysis is presented, discussion of findings, explanation of implications to both research and practice, and conclusion and future work.

2. REVIEW OF LITERATURE

2.1. Green IT

The environmental challenges covering the rising carbon footprint emissions, depletion of natural resources and increasing waste ending in landfills is gaining more attention and discussion among public and private stakeholders (Hilty and Aebischer, 2015). These challenges resulted in the formation of accords in various regions to understand the implications of human safety, business, technology development, and environmental sustainability (Nisha et al., 2013). Conversely, it is a significant area of research in the information systems and environmental education. Thus, sustainability through Green IT was conceived as an important strategic focus for organizations today. GIT is an efficient resource consumption using IT infrastructure as well as applying managerial and human practices, and organizational policies towards sustainability (Molla et al., 2014). To date, many organizations have been proposing their GIT agenda (Ardito and Morisio, 2014), and anchoring it to the sustainability mission and vision (Hernandez and Ona, 2016), to realize the full benefits of GIT, both for economic and environmental performance. Previous studies suggest that adoption of GIT in organizations have been very limited (Khor et al., 2015), especially in developing countries (Hernandez and Ona, 2015). It requires technological and organizational readiness, and support from the external environment to progress from simple to broad – complex GIT adoption activities (Deng and Ji, 2015). Hence, there is a greater need to explore and initiate GIT adoption in organizations.

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2.2. Green IT Practices in Education

The role of education sector has been realized for both research and practice, more importantly, in introducing innovations. Sovacool et al. (2017) state that the education sector should not only introduce new concepts or researches, however, it should also respond to the need for sustainability. Thus, the education sector is seen to thrive in institutionalizing sustainability practices, and allow generation of ideas and spur involvement among students, faculty members, and employees to achieve the goals of GIT (Thongmak, 2012).

Previous studies suggest that the education sector has initiated GIT adoption. First, a growing practice on energy-consumption reduction and conservation were initiated by higher education institutions. Nazari and Karim (2011) found that a university in shifted to energy-efficient ICT operations to reduce energy consumption by 35 percent, whereby, personal computers used was set to optimum energy saving option through end-user pc power management software. Similarly, the University of Edinburgh measures IT power consumption as an approach to making students, faculty members, and employees aware of their role and contribution towards energy conservation (Dovi et al., 2009). It was also a good platform to remain relevant in addressing energy saving needs, through some energy-conservation strategies and use of systems (Van Bokhoven and Bloem, 2013). These practices were developed through the availability of procurement procedures which allows the provision to buy energy-efficient IT equipment. Conversely, Bala et al. (2008) noted that the provision for GIT in organizational procurement procedures and practices resulted in rising interest to minimize environmental impacts of IT. More specifically, it means that higher education institutions were evaluating purchased computers based on a variety of GIT criteria, ranging from energy-consumption, extended life options, and eventual disposal alternatives (Ho et al., 2010). Further, these practices address the need for lesser toxicity and hazardous materials level, which is easily recycled, and end with lesser e-waste. Hence, the HEIs initiated a growing number of GIT efforts to save energy and reduce its equivalent carbon footprint.

Second, consolidation of IT equipment and systems were on the rise in HEIs. Suryawanshi and Narkhede (2013) found that printer consolidation was significant in addressing the need to reduce paper use and IT infrastructure setup of HEIs. Essentially, it reduces the number of physical setups. Therefore, it produces lesser carbon footprint and could lessen power use. Similarly, some universities initiated server consolidation and virtualization, through cloud computing. Okai et al., (2014) noted that cloud computing is a priority to greening IT infrastructure. It was evident that disasters, power growth, and issues became a recovery challenge for organizations. Thus, this GIT practice does not only result in financial budget savings, however, addresses the cost of downtime, patching and power issues during a disaster situation (Khambayat et al., 2015). More recently, virtualization through cloud computing became a major platform to reduce physical storage requirements by 40 percent, and decommissioning of servers with cooling equipment was expected to reduce IT power consumption by 35 percent annually (Suryawanshi and Narkhede, 2012).

Third, the HEIs also began with unified communication systems to reduce employees' dependence on multiple communication software and devices. Ramachandiran (2012) found that improving the use of unified communication software resulted in an increasing participation of employees in ideation, resolving customer concerns, and efficient, responsive feedback needs. For instance, Bolton et al. (2017) note that unified communication software allows efficient access and sharing of files on a range of mobile and desktop devices, thereby saving paper use and printing solutions. Similarly, it allows employees to communicate and work remotely with others in the education institutions, thereby, enabled inclusive

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participation for mobile workers (Silic et al., 2016). On the other hand, these technologies could result in increased productivity among all employees in the education institution (Boyd et al., 2017). Also, workflow outcomes become more integrated, efficient, and requires fewer resources, therefore, decreases business operations costs.

Finally, HEIs were more concerned about electronic waste (e-waste) disposal, recycling, and reuse options. E-waste is a global concern, and a threat to occupational safety, public health, and environment. Moreover, the growing e-waste contributes to carbon footprint emissions and toxicity, and depletion of natural resource used to produce electronic equipment. However, HEIs started their efforts to green e-waste disposal. For instance, a university in the United Kingdom allows disposal of e-waste more responsibly by letting suppliers collect e-waste disposals (Chai-Arayalert & Nakata, 2011). The employees were advised to dispose their mobile handsets and batteries to suppliers. It is legal to accept e-waste from employees as a practice. The employees were aware of the environmental implications of ending their e-waste in a landfill, and not be disposed to prevent the emission of toxic substances (Elsaadani, 2015). Moreover, the university allows segregation of wastes using colored bags as part of e-waste management with special focus on IT waste.

Likewise, a university concentrated on conducting e-waste audit to measure avoidance from carbon footprint and toxic materials (Geng et al., 2013). E-wastes were accounted, monitored and controlled annually (Ansari et al., 2010). The collected e-waste was sent to accredited formal recycling stream or service provider and paid by the university to recycle and recover components which can be recovered. Gomez et al. (2017) noted that the HEI also encourages the donation of e-waste for refurbishing and recycling efforts. These practices allowed the employees to take part and become responsible for their respective unit's e-waste. Moreover, a GIT committee was formed to tackle the growing concerns on e-waste and other sustainability needs of the university (Shea et al., 2017). Hence, these GIT practices were initially started by HEIs to cope with the growing need for sustainable waste management, thereby, reducing the impacts of e-waste on occupational health, safety, and environment.

2.3. Overview of Higher Education Institutions in the Philippines

The Philippine higher education system consists of two segments, private and public universities. In the segment, 88 percent or equivalent to 1,700 accounts for private, and only 12 percent or equivalent to 224 public higher education institutions (Ricafort, 2009), catering around 3.8 million of students. In the past, the Philippine higher education system was in a challenging state as the quality of education continually declines due to some factors such as (a) availability of qualified-competent faculty members, (b) lack of up-to-date facilities for research, and lacking years of primary education (c) among others (Chapman and Sarvi, 2017). Thus, the Philippine government started working on education policies and programs to address these concerns, and continuously enhance the quality of education. For instance, Outcome(s)-Based-Education (OBE) was implemented in the last 2010 to align the desired outcomes of program offerings to the needs of the employers and industry, and allow Filipino students to access global education opportunities (Borsoto et al., 2014; Rogers et al., 2017) as well as the recent implementation of K12 program (Adarlo and Jackson, 2017), thus, ensuring graduates become globally competitive. Also, these government efforts transpired into global recognition of some colleges and universities program offerings in the field of Engineering, Computing, and Business.

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However, these higher education institutions were also challenged by the need for sustainability. Hence, these HEIs confronted this global challenge by allowing them to introduce sustainability efforts on a day to day operations, and financial resources, and environment. Thus, these consequent events lead to the introduction of green efforts to attain sustainability (Ogundele and Laguador, 2017). To date, some universities focused on infusing green practices to gradually shift from traditional to sustainable activities (Commission on Higher Education, 2014). Furthermore, HEIs have recently started offering programs and relevant courses on sustainability. Likewise, the Sustainable Development Goals (SDG) was considered part of the HEIs' efforts to attain sustainability (De La Salle University, 2014).

3. METHODOLOGY

3.1. Multiple Case Studies

The goal of this study is to identify the GIT adoption practices by Philippine higher education institutions. This study employs qualitative approach through multiple case studies to explore on GIT phenomenon by exploring the experiences of the participants within the universities. Multiple case studies are preferred compared with a single case study as it offers a compelling, robust and intuitive approach to investigate GIT adoption phenomenon (Yin, 2013; Stake, 2013). Thus, it provides a comprehensive understanding of the emergence of GIT adoption practices, processes, and experiences of the participants.

GIT is adoption relatively new concept in higher education institutions in both developed and developing countries, thus, exploring the experiences of the participants is relevant to elicit a better understanding of the phenomenon. An interview is a widely accepted data gathering procedure in qualitative research. It offers in-depth information about the phenomenon involved. Thus, it allows gaining comprehensive insights about GIT adoption experience within higher education institutions. This study utilizes open-ended to semi-structured interview questions to allow the participants to freely communicate their ideas, thoughts, and opinions about GIT adoption within the organizations.

3.2. Questionnaire Development

The interview questionnaire was developed based on Yin (2013). There were two versions of the questionnaire, a detailed version of a guide of the interviewer, and a short version for the participants. The interview questionnaire covers three sections: (1) demographic profile of the participant, (2) background on GIT adoption, (3) practices and processes on GIT. The first version of the interview questionnaire was piloted to a single case study to reduce the risk that the interview questionnaire will not produce results. It also aimed to reduce the problems and biases, hence, ensuring that the questions were understandable to the participants. The first revision was meant to verify the appropriateness of wordings and relevance of the GIT adoption practices questions. Lastly, the final version of the interview questionnaire was validated by experts and used after the pilot test.

3.3. Data Gathering, Validity and Reliability

The Chief IT Officers or similar roles ranging from Management Information Systems Manager, Head of Information Technology Services, and or Senior IT Manager were interviewed as they play an es-

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sential role in decision-making and implementation. Moreover, this study considered the participation of employees which had direct involvement and knowledgeable on the adoption of GIT practices within the higher education institutions. Thus, the participants with GIT adoption experience served as key informants during the data collection activities.

Table 1 presents the participating higher education institutions with program offerings specialization. This study involved three universities: (1) a university specializing in engineering education, (2) university with specialization information technology education, and (3) a university specializing in both engineering and information technology education. A short background of the universities selected is available in the Appendix. These universities were identified to have initiated sustainable practices through GIT adoption in the past three years.

Face to face interviews were conducted, and each interview session spanned 60-90 minutes. Each participant had at least three interview sessions, digitally recorded, and transcribed for analysis. Also, follow-up interviews were initiated to clarify the practices further, and cover all areas of GIT adoption. The interviews were conducted from June to November 2016. To address the reliability and validity of the data collected, the participants verified the transcribed data, the results, and conclusions drawn from all interviews conducted.

4. DATA ANALYSIS

4.1. Paperless Transactions and Digital Archiving Systems

The participants of University A revealed that 80% of their day to day business transactions ranging from academic systems, planning and monitoring of financial budget and spending, quality and knowledge management resulted in 65% paper reduction across all departments in the university. This paperless implementation was elaborated by the Chief IT Officer:

We have upgraded our software to allow integration of information and efficient collaboration. Now, we seldom print documents. Instead, we created PDF version, and use it for processing. It is more convenient, easy to maintain and mandatory for all us.

Table 1. Profile of participants

University	Participant	Year(s) in Position
A	Chief IT Officer	11 years
	Purchasing Officer	7 years
	Facility In-charge	4 years
B	MIS Manager	5 years
	Facility and Pollution Officer	9 years
C	Head of IT Services	6 years
	Purchasing Head	15 years
	Facility Officer	7 years

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In University B, utilization of electronic systems was widely accepted as major GIT practice. Most of the work procedures were performed in electronic form, digital approval systems, and payments processing with suppliers were implemented in conjunction with electronic channels to reduce costs in handling business transactions with customers. Also, the university has been implementing digital archiving systems in the past three years to convert paper-based data and provide real-time access to information needed by the stakeholders of the university. This situation was described by the MIS Manager:

We have 80% work processes in digital format. Our employees are more aware about environment than before. I think, it's because of the of the climate change caused by carbon footprint in business. It leads to our decision to do our business online and taken seriously. We respond to it positively.

In University C, a major process streamlining effort was conducted to identify business process inefficiencies resulting 35% savings in human resource requirement, IT equipment, and associated costs. Similarly, the University also introduced the use integrated communication tools and video conferencing systems allowing more employees, students, and faculty members to engage in university-wide initiatives including online discussions on research project proposals with foreign collaborators, attendance to web-based technology-driven training, and participation in forums. It was elaborated by the Head of IT Services:

We always conduct process improvement, we try to throw away of inefficient process and make them streamlined. We are challenged to identify a business process concern which leads to inefficiency, and then solve it. For instance, we now have integrated communication systems, before, every communication was scattered in different software application. It's not making our work productive and inconvenient.

These efforts resulted in a change of attitude and behavior of the employees towards GIT adoption. This success was attributed to the top management support and strategic direction in achieving sustainability.

4.2. Resource Efficient IT Equipment

The interviews conducted with University A participants revealed a strong utilization of energy-efficient IT equipment. The university procurement policies and guidelines on IT equipment were changed to cover a necessary provision on purchasing IT equipment that conforms to energy-efficiency, allowable greenhouse gas, and related footprint. It was elaborated by the Purchasing Officer of the university:

I will continue to apply GIT and support it, as long as it adds value, and not harm our environment. We certainly prefer energy-efficient IT devices, as it brings more savings and fewer footprints.

In University B, the purchasing personnel together with planning officer were trained in assessing and evaluating electronic and IT equipment compliant with environmental regulations and standards. This effort resulted in the conversion of all old electronic equipment into efficient resource equipment, more specifically, this approach was made through a leasing agreement with a multinational equipment vendor. It allows the university to continually upgrade their IT equipment and related resources based

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on newer environmental and energy standards, which resulted in 65 percent reduction in operating costs and better IT asset management in the university. This practice was explained by the Facility and Pollution Officer of the university:

Our employees are interested in GIT, as such, we are trying to do our purchasing using greener policies and standards. We are aware of the key benefits of green purchasing.

Similarly, University C confronted the need for resource-efficient IT equipment due to the rising electricity costs in the Philippines, as well as the growing energy-consumption of IT equipment through an analysis conducted. The university also significantly promotes the use of environment-friendly office equipment including multi-function printing devices, virtual fax, toner-saving solutions, and integrated IT asset management solutions. This action was transpired in one of the interviews with the Purchasing Head of the university:

…75% of our deployed IT equipment our Energy-Star certified. Some have energy-management software to take control of energy while achieving an optimum performance and lesser waste.

Also, the university widely accepted that transitioning to GIT to address sustainability can be achieved through the use of resource efficient equipment, and use of environmentally-friendly IT products. Most energy inefficient systems were retired, and data center cooling and airflow management were enhanced to apply newer standards in energy-efficiency. Thus, the university is more likely to prefer suppliers and vendors that have a green track record and offers end of life schemes, such as take back options.

4.3. IT Waste Disposal, Recycling and Reduction

In University A, the IT services team designed an IT waste disposal strategy to handle toxic and or hazardous components of electronic equipment sold or have reached its end of life. The university was providing an incentive program to employees for waste reduction. The employees were provided with e-waste bin in which they can donate and dispose of their IT waste regularly. This effort resulted in a growing recognition of the importance of responsible waste disposal among employees of the university. On the other hand, the organization performs a waste audit on a quarterly basis to monitor its potential environmental impacts and minimize wastes in the university. It was better explained by the Facility In-Charge of the university:

I know that there are environmental issues with regard to e-waste. I have been sent to trainings to gain knowledge about mobile devices, PC, and batteries, which have related environmental issues.

In University B, the employees were guided by the implementation of e-waste management policy aims to encourage active participation in waste reduction efforts in the university. The employees were a prime source of portable electronics, mobile phones, digital cameras, batteries, and laptops. The goal of this program is to achieve zero e-waste in all offices that are potentially harmful to the environment. This practice also offers convenience and accessibility to all employees to participate in the environmental awareness and education program of the university. It was highlighted by the Facility and Pollution Officer in one of the interview sessions:

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At first, I am not aware of the hazards of e-wastes. Proper disposal of e-waste is necessary. We can destroy our environment, but, I can at least help by not throwing garbage anywhere.

In University C, a major GIT practice towards e-waste includes recycling through re-use of assets and consumables. The employees were all encouraged and practiced recycling to achieve major cost reduction and introduce change in handling e-waste in the university. Also, the university encourages the electronic distribution of bulletin of information such as university program offerings, tuition fees, and customer evaluation among others. In the past three years, an average of 65 percent of paper use was reduced, likewise, its toner solutions. It was explained by the Facility Officer:

Our employees understand very clearly the effects of using too much paper, before they don't care about it. We know at this time how to save it, instead of letting them in shredders.

More recently, the university implemented a waste reduction scheme through recyclable outlets positioned in the different areas of the university in which employees, students, and faculty members can donate used, damaged or unwanted electronic items for recycling. This scheme resulted in the enhanced participation of the university stakeholders in training the younger generation of students and employees in environmental sustainability and education.

4.4. Awareness and Environmental Stewardship

The environmental awareness and steward remains imperative to University A. The employees were provided with environmental sustainability training emphasizing individual's role in assisting the university in making a difference on environmental issues, for instance, reducing energy-consumption and waste disposal. Also, the university employs a dedicated officer-in-charge for sustainable use of IT resources to cover awareness and education efforts. Significantly, these initiatives contribute to change the employees' perspective towards sustainable environment behavior gradually. For instance, more employees are actively engaged in turning off or shutting down PC display screens during lunch breaks or shutting off for unused IT equipment. The Chief IT Officer elaborated on this matter during one of the interview sessions:

We are aware because of the training programs about energy-savings as part of our green IT practices. We participate to it seriously.

In University B, a structured environmental education program was launched two years ago. The goal of this program is to encourage all employees to actively participate in environmental stewardship, develop the necessary skills and attitude, and respond to the growing appreciation of sustainability goals in the Philippines, as initiated by the government. More specifically, an environmental leadership circle was commenced to serve as a platform to develop environmental leaders to work with the academic group including faculty members and students and community-based organizations with environmental sustainability agenda. It is a voluntary undertaking and full commitment from the employee. An environmental leader receives a certificate after demonstrating the desired outcomes of the program. It was elaborated by MIS Manager in the university:

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We are more motivated by GIT as it definitely addresses environment concerns. We respond to it by attending seminars and workshops, and it was designed to capture our attention and apply it. I firmly believe, not all employees will agree with GIT, but, I see big change right now, they are more particular with GIT practices.

In University C, the environmental, safety and pollution group piloted the "Resources Rethinking," a web-based platform encouraging employees to facilitate the discussion of environmental sustainability approaches, issues, and challenges, and hold regular events relevant to environmental sustainability. For instance, this group initiated the development of a mobile application introducing e-waste collection system encouraging employees to dispose of e-waste more responsibly through an accredited e-waste collector, electronic equipment retailer or reseller visiting the university campus on a regular basis. The collected e-waste from the employees is converted to cash or redeemable points, an example of charge-back effort, as elaborated by Facility Officer:

Our awareness on e-waste was raised when saw e-waste bins in our campus. It was interesting that more employees disposit their e-waste, and prepare for e-waste collection. They also earn from it, and plus, they donate when possible.

This effort allows the employees to understand that they can contribute to a positive and significant change within their university and future communities. Moreover, a way to design action projects that offer real perspective for understanding environmental sustainability concerns within their community.

5. DISCUSSION OF FINDINGS

5.1. Paperless Transactions and Digital Archiving Systems

The three universities significantly adapt to paperless transaction processing as major GIT practice. Similarly, it reduces the number of papers for procurement leading to savings and enhances efficiencies on data processing requirements by stakeholders of the universities. Arney et al. (2012) found that paperless processing requires a major shift in digitally doing business. However, it brings positive impact not only reducing costs as well as to the environment. This study proved that the universities in the Philippines are striving to go for paperless transaction processing, therefore, setting the groundwork of other universities to adopt it, as the growing benefits become more observable and quantifiable within these universities. Hence, a major carbon footprint reduction is along with these efforts.

It is also found that user education on paperless processing and digitization efforts improved the efficiency of core business processes. Most organizations strategically highlight paperless processing to pursue new approaches of doing business, and harness the opportunities to communicate business ideas across multiple channels, and attract new customers, and increase revenue (Chen et al., 2012). Conversely, these efforts assisted the universities in workflow automation, document security, increase efficiency and immediate access to the most relevant data of the universities, decrease its environmental impact by eliminating unnecessary paper processing, therefore, reducing the carbon footprint.

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5.2. Resource Efficient IT Equipment

The results of the study indicate that the universities involved substantially deployed resource efficient IT equipment. These universities initiated the replacement of IT assets to increase the efficiency of management. All IT asset purchases were driven by the need for energy efficiency to help the universities monitor their energy consumption and green gas house emission, which is aligned with the GIT governance and management program. The results also revealed that there were rules related to purchase and use of environment-friendly IT equipment. Therefore, this IT equipment conforms to WEEE (Waste of Electrical and Electronic Equipment), Energy-Star, and or Restriction of Hazardous Substances (RoHS) which greatly consider the environmental impact while and after use.

Similarly, Jin et al., (2013) found in his study that server virtualization and use energy-efficient IT equipment is significant to realize reduced environmental impacts. The top management discussed GIT issues as a priority considering the concerns with environmental impacts of IT use, waste and green gas house emissions.

Also, the universities initiated efforts on energy-conservation through switching off unused IT resources, it is seen that the three universities have the culture of use of energy as per need and educates employees as prime responsible to conserve natural resources. Likewise, the universities also planned to sustain the energy-efficiency efforts by exploring options from suppliers through constant collaboration and communication of the universities IT equipment needs. Lastly, the universities encouraged extending the lifespan of IT equipment to maintain resource efficiency through scheduled performance maintenance audits and monitoring activities.

5.3. IT Waste Disposal, Recycling and Reduction

The results of the study indicate that IT waste in three universities was managed in a centralized and decentralized approach. First, each university IT services team conducts IT waste disposal through an accredited e-waste service provider to take account of all items disposed of. Second, employees were encouraged to participate in e-waste donation and collection campaign using the e-waste bins strategically positioned within the university premises. The universities also initiated resource reduction scheme through electronic data interchange systems to facilitate the major reduction of resources. Lastly, a more accountable approach to IT waste disposal, recycling, and reduction covers influencing all employees to actively involve themselves in awareness and education efforts to enhance personal responsibility towards GIT adoption. Hence, the universities were becoming more responsive to the need for conservation of natural resources needed to create an electronic equipment, and reduction of e-waste disposed to the natural eco-systems or landfills.

5.4. Awareness and Environmental Stewardship

The three universities managerial support and commitment towards enhancing awareness and environmental education considerably affects the attitude and behavior of the employees towards GIT adoption practices and processes. Most the participants revealed a formal system is in place to educate the employees on the effects of GIT adoption as sustainability effort to achieve economic, environmental and social benefits.

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The main emphasis of the awareness and education program is to enhance personal responsibility and commitment towards collective efforts on GIT adoption. Although Green IT is on infancy stage in the universities, individual support and commitment were significant in spurring efforts that further top management strategic actions in designing, implementing, assessing and evaluating relevant programs which were measurable through individual's contribution. Conversely, the awareness efforts remain acceptable across these universities. It could be attributed to the fact the positive attitude contributes to a rapid adoption of innovation. Bose and Luo (2012) state that attitude towards innovation signified similar positive actions and participation in innovation adoption. Therefore, by providing awareness and education programs considerably affects the perception of employees towards having a positive perspective towards GIT adoption.

6. IMPLICATIONS

6.1. Theoretical Implications

This study aims to explore the GIT practices of three universities in the Philippines. The findings suggest that GIT practices could further the achievement of sustainability goals of the universities. Thus, the results could be used to develop a conceptual model of GIT practices, and factors influencing its adoption. It could be used as an initial understanding and develop frameworks relevant to the Philippines, as an example of a developing country. Moreover, developing economies such as the Philippines have considerable economic and socio-cultural differences which may affect the rate of adoption in universities. Hence, it could give better insights as to how these factors, enablers or disablers influence the adoption of GIT in organizations. Also, this study was able to identify some links as to why the universities adopt GIT such as attitude, the formal structure of IT unit in the university, and managerial support. Thus, this could be further investigated from a theory perspective. Overall, this study contributes to theory building in many ways.

6.2. Practical Implications

Regarding practical implications, the findings of this study could be used to develop policies and guidelines toward the adoption of GIT across all higher education institutions in the Philippines. More specifically, it aims to accelerate GIT adoption level by allocating resources, designing more relevant approaches and strategies, applying standards, practices, and assessing its benefits and impacts in a more structured way. To date, the Philippine higher education sector is struggling to stay competitive; this study could lead other universities to initiate GIT as a university practice and tackle the participation of stakeholders in full implementation of widely accepted GIT practices.

Moreover, the Philippine higher education sector experiences a constant decline in global rankings of top universities as researches is not becoming a platform to improve the quality of education and likely limited. Hence, these universities could use GIT as a research area to explore its potential opportunities to enhance the quality of researches toward sustainability. Also, Institutional Sustainability Assessment (ISA) is becoming a standard for HEIs in the Philippines and a requirement by the Commission on Higher Education (CHED), thus, GIT adoption, an area of assessment could lead to exploiting the potentials and opportunities towards a more sustainable university through the development of relevant GIT agenda,

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strategy, and assessment. More recently, the ISA framework introduced IT infrastructure and support services whereby green practices were embedded to shift from traditional delivery of instructions to using digital platforms such as e-learning and other forms of learning management systems.

7. CONCLUSION AND FUTURE WORK

This study aims to explore the GIT adoption practices of three universities in the Philippines. First, GIT adoption practices spanned in the areas of paperless and digital archiving systems, use of resource efficient IT equipment, responsible IT waste disposal, recycling and reduction, and awareness and education. These areas of GIT adoption practices insinuate that HEIs have started their efforts to green their practices and procedures, and responsibilities are defined within each GIT initiative. Second, HEIs adopt GIT to achieve its benefits and stay sustainable. However, a clear green agenda could strategically enhance its adoption to provide a comprehensive understanding of its challenges, opportunities, and directions. Lastly, there are considerable GIT practices. However, individual contribution is not measured and do not offer any substantial reward or incentive program to encourage full participation from all employees. Hence, GIT emerged as a practice and appear to achieve an initial stage of adoption.

Despite the contributions of this study to literature, it is also not free from limitations. First, the study explores GIT adoption in three universities within the Philippine context. The universities in the Philippines have different characteristics, IT infrastructure setup, program offerings, and commitment to sustainability, therefore, a study involving other universities with different GIT adoption and sustainability perspective would reveal additional insights on the current state of GIT adoption practices in higher education in the Philippines. Second, this study did not explore the internal and external factors which affect the rate of adoption in universities. For instance, regulatory agencies may have roles developing policies and guidelines, monitoring, and evaluation of universities in GIT adoption. By exploring on these factors, new insights could emerge regarding GIT adoption. Third, this study did not include students and faculty members of the universities. Thus, future work may elicit experiences of these participants to offer new insights in this emerging field. Lastly, this research only covered a limited number of case studies. Therefore, it is not generalizable for the Philippine context, although, the findings are interpreted carefully based on a relevant perspective. For future research, investigating GIT adoption in a more statistical approach could result in a GIT model covering the counter-intuitive or interesting experience of the universities in the Philippines.

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APPENDIX

Profile of the HEIs

University A: One of the largest universities in the Philippines with an average of 25,000 students, both in the undergraduate and graduate levels. It specializes in engineering, science and technology, business, and education. The university has some programs recognized by international accreditation agencies. To date, it is one of only few universities in the Philippines that institutionalized sustainability framework and initiatives to respond to the need for reduction of energy-consumption, waste management, and natural resource conservation. The HEI initially developed a sustainability framework in which objectives, procedures and metrics are implemented across all organizational units and engage employees in GIT adoption.

University B: One of the only few HEIs in the Philippines with strong emphasis on sustainability. It is one of leading universities in the Philippines with a good research track and experts, employer reputation, and wide range of programs ranging from arts, social science, business, education, engineering and technology. The university started its sustainability efforts in 2013 by assigning a dedicated officer to handle GIT practices and initiatives within the university. A sustainability agenda was presented to the employees during its 1st year of implementation. University B also transitioned to the use of green building, to accommodate natural lighting, recycling of waste water, and use of solar energy as source of power. The employees were also involved with GIT practices such as digitization, e-waste donation drive, and consolidation of IT equipment and other related resources.

University C: has a good mix of local and international students, both in the undergraduate and undergraduate level. The HEI has an average of 38,000 students enrolled in various programs including science, arts, engineering and technology, education, business, agriculture, and marine sciences, among others. The university is one of the few pioneers of environmental management education, and have successful experience in implementing sustainability initiatives within the university and to its adopted communities, including coastal areas, low income communities with limited source of electricity, and partnered with government for waste management research and initiatives. To date, the university developed its sustainability framework aligned with the mission vision of institutionalizing green practices and initiatives. The university encourages research and constantly seeks external funding to work on green source of energy, waste management, and utilization of IT infrastructure and resources. It transformed from paper-based to digitized information management, accounting for 75% of its operations. To date, the university also proactively participates and supports the Sustainable Development Goals by the government and external parties, both private and public agencies.

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Chapter 64
Selecting Demolition Waste Materials Disposal Alternatives Using Fuzzy TOPSIS Technique

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ABSTRACT

This article describes how in developing countries, millions of tons of construction and demolition wastes (CDWs) are lost every year due to lack of knowledge of recycling significance and/or procedures. Despite the high value of CDWs, high percentage of this waste is either dumped illegally or disposed in the landfills. Disposal methods should consider saving natural resources and maintaining the environmental conditions through maximizing the value of CDWs. This article aims at choosing the most sustainable disposal alternative using Multi-Criteria Decision Making (MCDM) Process, considering several sustainability measure indicators. The research introduces a list containing the most relevant and significant sustainable indicators that affect the selection of alternative for disposal of CDWs. Then, fuzzy TOPSIS technique is applied considering the significant indicators on each alternative to rank and choose the best alternative for disposal of CDWs.

1. INTRODUCTION

In the developing countries, demolition wastes range from 20% to 30% of the total annual solid wastes (Al-Ansary, 2002), which can express how big the problem is. Construction and Demolition waste (CDWs) doesn't contain much hazardous waste compared to what found in municipal solid waste but CDWs still has its own problems. One of the major problems is the huge bulk of CDWs, without regard to the very long lifetime of CDWs which means occupied landfill for extremely long time before moldering of CDWs (Dantata et al., 2004). EPA (2002) has organized a composition for CDWs materials into a list of eight groups. This paper is concerned with only on the first group "concrete, bricks and tiles".

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Peng et al. (1997) presented a hierarchy of CDWs managing options; including reduce, reuse, recycle, compost, incinerate and landfill. Reduce refers to any activity to avoid waste creation, Design stage is considered as the most effective stage in Project Life Cycle to implement waste reduction. At this stage, designer can consider using of re-usable materials or design a building with a long lifespan. Reusing is the next stage of waste management options; it can be described as using the same material more than once without the need for reprocessing. Recycling is the third option, which means the reprocessing of a reclaimed material and converting it into a new material or use. Composting is the next option; the term 'compost' refers to the organic material that can be used as a soil amendment or as a medium to grow plants. Incineration is considered the fifth option of waste management; the CDWs are burned to recover electrical energy or heat. Wood and plastic wastes are considered as the most applicable CDWs in this phase. The last option for CDWs management is a landfill. A landfill is a place where material is dumped as an end-stage.

Choosing the wrong alternative for demolition waste disposal will cause not only high economic losses, but also hazardous environmental and social impacts as well. That's won't be an easy task for decision maker, since it's affected by several indicators, for that reason MCDM have been introduced to aid the decision maker to choose the right decision. MCDM is a tool that can be implemented in optimizing the decision-making problems considering a number of criteria (Kahraman 2008). MCDM techniques have been developed long time ago. Nowadays, there is such a wide list of these techniques; each of them has its own features and weakness. Of the many MCDM methods, Technique for Order Preference by Similarity to Ideal Solution (TOPSIS) has been applied in different application areas.

TOPSIS method is a technique to evaluate alternatives' performance, considering the similarity with the ideal solution (Behzadian et al., 2012, Krohling and Campanharo, 2011). TOPSIS is capable to combine between different indicators with various units simultaneously (Ekmekçioğlu et al., 2010); However, TOPSIS in its standard form is deterministic and doesn't consider uncertainty which is considered as one of its main weakness (Gavade 2014). This encourages several attempts to introduce the term "Fuzzy/Uncertainty" in TOPSIS technique (Jahanshahloo et al., 2006, Jahanshahloo et al., 2009, Krohling and Campanharo, 2011). Determining the exact value for the elements of decision matrix (weights or performance values) aren't reachable in many practical cases as they pass through human judgments which could be vague or including fuzzy or interval data.

Uusitalo et al. (2015) have been reported that the uncertainty of environmental model outcomes needs to be estimated when they are utilized for decision support. The Fuzzy Logic Technique is based on the Fuzzy Set theory that has been proposed by Zadeh (Zadeh 1965). The membership function is used to assign a grade of membership which ranges from zero to one. In order to provide a better understanding of the theoretical foundations of the Fuzzy Logic, a comparison between ordinary (Crisp) set and fuzzy set shall be represented. In the Crisp Logic, variables are provided with the value: "true" or "false", black or white; however in real life applications there is a place for a gray zone which includes all of imprecise, uncertain, and vague data provided by human judgments. This gray zone can be described as Fuzzy Set. This paper proposes a modified fuzzy TOPSIS methodology to make a multi-criteria selection among demolition waste disposal alternatives (reusing, recycling into three different products, and landfilling). An application in the demolition waste disposal options area of Cairo is presented in order to demonstrate the potential of this methodology.

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2. SUSTAINABLE INDICATORS

Flowchart of the proposed model is depicted in Figure 1. The indicators take into consideration for this study are summarized in Figure 2 and are described in more detail below. Figure 2 represents the three pillars of sustainable development, which include social, environmental, and economic aspects. These indicators/sub indicators are numbered from C1 to C15, and are classified into Objective Group and Subjective Group. Objective group deals with quantitative terms (can be expressed numerically), while subjective group represent the indicators that have been failed to be expressed as numerical numbers, and are expressed in terms of judgments instead.

2.1. Objective Group

2.1.1. Energy Consumption

This indicator referred to the Total Energy that was consumed during the process of recycling/disposal of CDWs. It includes energy consumption in electric forms (e.g. electric equipment & crushing plants). Energy consumption can be obtained through Equation (1):

$$\text{Energy Consumption(mega joule)} = \text{Horsepower(hp)}*\text{duration})/(2.684) \quad (1)$$

Figure 1. Flowchart of the proposed model

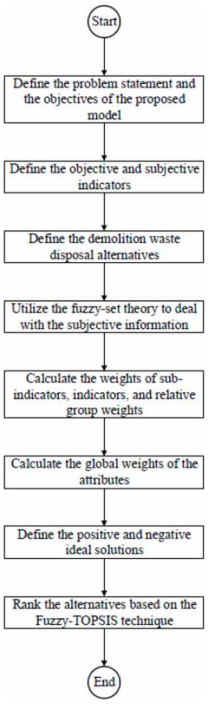

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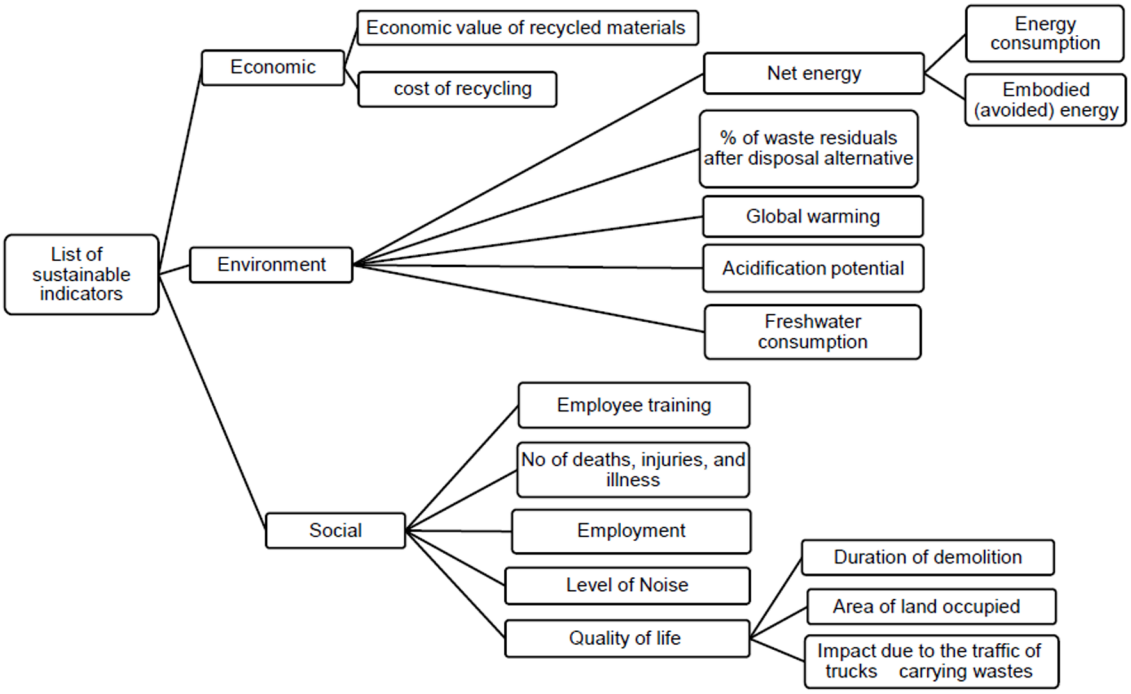
Figure 2. Indicators taking into consideration for sustainable disposal alternatives of CDWs



2.1.2. Avoided Energy Consumption

The Avoided Energy Consumption represents the avoided initial energy investment necessary for the construction products which includes: energy consumed in both forms of direct fuel and electricity consumption associated with raw material extraction and manufacturing, fuel consumption for transportation (Roussat et al., 2009). The Avoided Energy Consumption can be calculated using Equation (2):

Avoided Energy Consumption = Volume of Material*Embodied Energy (2)

2.1.3. Global Warming Potential

Greenhouse Gases warm the Earth by absorbing energy and slowing the rate at which the energy escapes to the space where they act like a blanket insulating the Earth (EPA, 2008). Global Warming Potential can be presented as kilograms of CO2 equivalents. It consists of the following three components of Equation (3) which can be found in (Petho et al., 2011, EPA, 2008):

CH4=0.5*Fuel Consumption (diesel)

N2O=0.22*Fuel Consumption (diesel) (3)

CO2=10.1*Fuel Consumption (diesel)

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After introducing components of global warming potential, the following Equation (4) that is found in Acquaye and Duffy (2010) is used to calculate global warming potential:

$$\text{Total Global Warming Potential} = CO2 + (21*CH4)/1000 + (310*N2O)/1000 \quad (4)$$

where the unit of the equation is in (kg of CO2 equivalents).

2.1.4. Acidification Potential

Some compounds released in the air, for example (SO_2, NO_x) may be oxidized and transformed into rains. Then, the acid compounds are present in streaming waters and in watercourses resulting in a decrease in the pH-value of rainwater. This leads to significant damages on the eco-systems. The Acidification Potential is given in Sulfur dioxide equivalents (SO_2-Eq.) (OCED, 2005). Acidification Potential which can be presented as pounds of SO_2 equivalents consists of the following two components of Equation (5) that are found in (USEPA, 1995):

$$SO2 = 0.00205*\text{Power}*\text{Duration}$$

$$NOx = 0.031*\text{Power}*\text{Duration} \quad (5)$$

Equation (6) shows how to combine the foregoing two components as found in Veleva and Ellenbecker (2001):

$$\text{Total Emissions} = SO2+0.7*NOx \quad (6)$$

2.1.5. Duration of Demolition

Duration of Demolition is considered as a sub-indicator of "Quality of Life" indicator. Duration of Demolition represents the total time for a demolition activity which is considered significant since it takes into consideration the nuisances for the local residents due to demolition. Equation (7) shows how to calculate the demolition duration:

$$\text{Demolition Duration} = \frac{\text{volume of demolished material}}{(\text{productivity}*\text{no of crews})} \quad (7)$$

Impact due to the traffic of the trucks carrying the CDWs is an indicator that belongs to the "Quality of Life" group, which represents the traffic jams that could occur due to the passing of CDWs' trucks in the urban and inter urban area. Equation (8) is used to represent this impact (Roussat et al., 2009):

$$\text{Impact} = \text{Number of Trucks}*(\text{interurban distance} + 5*\text{urban distance})*10^{-4} \quad (8)$$

where, the factor (5) represents the ratio of population density between the urban area and the interurban area in Cairo:

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$$\frac{\text{population density in Cairo City/km2}}{\text{population density in suburbs/km2}} = \frac{35000}{7000} = 5$$

2.1.6. Level of Noise

This indicator refers to the noise produced by various sources (labors/equipment) in different activities of disposal alternatives' processing (e.g. demolition process, size reduction process, crushing) which may lead to serious problems that affect both labor and resident health. The Level of Noise can be calculated through Equation (9) which found in Marzouk et al. (2008):

$$E\ Noise = 10\log\left(\frac{\sum_{i=1}^{n} 10^{\left(\frac{Li}{10}\right)}}{N}\right) \tag{9}$$

where 'E Noise' is equivalent to sound level; Li is noise level of source i at receptor point, and N is total number of sources. The List of noise level of different sources for Equation (9) can be found in (European Commission, 2006; Federal Highway Administration, 2006).

Economic Benefit Generated by Recycled is an indicator that aggregates all the benefits that could be generated from selling the recycled materials, economic benefit. The indicator can be calculated using Equation (10) given by Hsiao (2002):

Economic Benefits = Volume of Material * unit cost of recycled material (10)

In order to obtain the absolute benefit value, cost of land filling residuals after recycling shall be subtracted from the value of economic benefit for each alternative.

2.1.7. Financial Cost for Recycling Alternatives

This indicator aggregates all the possible costs which different alternatives could go through. It includes the following components (Zhao et al., 2009):

1. Annual Fixed Investment, which expressed the total investment of equipment including fixed equipment cost which can be obtained through price quotations. It worth to be mentioned that this cost shall be divided by the number of working years (6-7 years) in order to represent the annual fixed equipment cost, where:

Annual fixed equipment cost = 0.15 * Fixed equipment cost

Maintenance cost = 0.06 of Total equipment price

Insurance = 0.01 of equipment price

2. Electricity consumption

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3. Fuel cost
4. Labor wages
5. Miscellaneous, Structural, electrical, starters, chutes
6. 6. Lab & office cost:

Cost for Recycling = Annual Fixed Investment + Electricity Consumption + Fuel Cost + Labor Wages + Miscellaneous + Lab and Office Cost (11)

2.1.8. Job Opportunities

This indicator represents the number of jobs provided through different disposal alternatives.

Percentage of CDWs residuals after disposal alternative is an indicator that represents the percentage of CDWs which could not return back to recycle after the initial processing due to contamination or improper size, and which goes directly to the land fill area.

2.2. Subjective Group

Subjective Indicators tend to have linguistic/ qualitative definition. The rest of sustainable indicators are considered subjective.

2.2.1. Fresh Water Consumption

This indicator refers to the estimation of Fresh water quantities used in the process of different disposal alternatives.

2.2.2. Area of Land Occupied

This indicator takes into account the diminishing land space due to the incremental quantities of demolition wastes which leads to increasing the area of landfill. It also takes into consideration the area needed for sorting, size reduction, crushing, and storage of the recycled products.

2.2.3. Average Number of Hours Used for Employee Training

This indicator refers to the number of hours that actually being consumed in acquisition the basic skills for trainees.

2.2.4. Probability of Occurrences of Injuries, Death

This indicator refers to the possibility of injuries between employees for different activities in various disposal alternatives.

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3. DEMOLITION WASTE DISPOSAL ALTERNATIVES

In this study, five demolition waste disposal alternatives specifically for bricks are presented through research (Sadek, 2008). Each alternative has different environmental, economic, and social consequences, eventually they are evaluated through the fifteen foregoing indicators. The demolition waste disposal alternatives are determined as reusing, recycled tennis surface court, recycled aggregate, recycled fill material, landfilling. These alternatives will be described briefly in Table 1.

4. FUZZY TOPSIS METHODOLOGY

A triangular membership function is considered as one of the most popular functions in representing fuzzy set problems, due to its simplicity and fast computation. Therefore, it has been chosen to be implemented in this research, but there are some important basic definitions based on recent work of Ding (2011) which are introduced first.

Definition 1: In a universe of discourse X, a fuzzy subset A of X is defined by a membership function $f_A(x)$, which maps each element x in X to a real number in the interval [0, 1]. The function value $f_A(x)$, represents the grade of membership of x in A.

Table 1. List of alternatives of the proposed model

Alternative Name	Alternative Description
Reusing blocks (A1)	In this alternative, walls are dismantling using an electric saw in order to maintain the condition of the brick unit for reusing, then a cleaning process is taken place to remove mortar residuals from brick units, after that loads of the cleaned bricks are transported to distributors (estimated distance = 25 km) while residual mortar are transported to landfill (estimated distance = 50 km). At the end of process, produced bricks can be packaged.
Recycled tennis surface court (A2)	Dismantling of walls and cleaning process tend to be manually, since there is no need to maintain brick units as long as bricks particles won't be contaminated, then loads of the cleaned bricks are transported to recycle center (estimated distance = 50 km), while residual mortar are transported to landfill (estimated distance = 50 km), after that a manual reduction of particles size is taken place before going to the crusher system. The next step brick particles are landed through loader into hopper, which transfers loads to the crusher through a conveying belt. The rate of crushing of this belt shall not exceed rate of crushing of the jaw crusher to avoid the jamming of the crusher. After crushing, the crushed bricks are transferred through the conveyor belt to the vibrating screen to separate the crushed particles from other particles. While bigger particles will be transferred back to crusher through third conveying belt, proper sized particles are transferred to milling process. The grinder of the European hammer mill is used with maximum inlet size of 40 mm and producing smaller size particles of 3 mm, which could be appropriate for producing tennis court surface.
Recycled aggregate (A3)	In this alternative, walls are dismantled manually, then loads of the demolished bricks are transferring to the recycle center (estimated distance = 50 km), after that a manual reduction of particles size is taken place before going to the crusher system, finally it ends with crushing process where the proper sized particles are transferred to storage facility.
Recycled fill material (A4)	The only difference between alternative A3 and A4 is that in recycled fill material there is no need for crushing process, since it has less restrictive specification about size control, so manual reduction of particles size will be sufficient.
Land filling (A5)	This alternative is considered the worst scenario since it's' salvage value equals zero. This research takes this alternative into account just to spotlight the volume of losses that occurred when the decision maker selects the wrong decision. It simply involves two actions, dismantling of walls manually, then transferring loads into landfill (estimated distance = 50 km).

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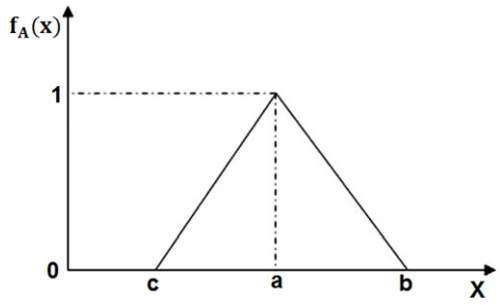
Figure 3. Triangular fuzzy number A = (c, a, b)



Definition 2: A fuzzy number A in real line $\Re$ is a triangular fuzzy number if its membership function $fA:\Re\to[0,1]$ is:

$$\mathrm{F(x)}=\begin{cases}\dfrac{x-c}{a-c} & c\le x\le a\\ \dfrac{x-b}{a-b} & a\le x\le b\\ 0 & \text{otherwise}\end{cases} \tag{12}$$

With $-\infty<c\le a\le b<\infty$. The triangular fuzzy number can be denoted by (c, a, b) as shown in Figure 3.

Definition 3: Let A1 = (c1, a1, b1) and A2 = (c2, a2, b2) be fuzzy numbers. According to the extension principle, the algebraic operations of any two fuzzy numbers A1 and A2 can be expressed as:

$$A1\oplus A2=\left(c_1+c_2,a_1+a_2,b_1+b_2\right) \tag{13}$$

$$k\otimes A2=\left(kc_2,ka_2,kb_2\right)\qquad k\in\Re,k\ge 0 \tag{14}$$

$$A1\otimes A2\cong\left(c_1c_2,a_1a_2,b_1b_2\right)\qquad c_1\ge 0,c_2\ge 0 \tag{15}$$

$$\left(A1\right)^{-1}=\left(c_1,a_1,b_1\right)^{-1}\cong\left(\frac{1}{b_1},\frac{1}{a_1},\frac{1}{c_1}\right)c_1>0 \tag{16}$$

$$A1\varnothing A2\cong\left(\frac{c_1}{b_2},\frac{a_1}{a_2},\frac{b_1}{c_2}\right)c_1\ge 0,c2>0 \tag{17}$$

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Definition 4: Let A1 = (c1, a1, b1) and A2 = (c2, a2, b2) be fuzzy numbers. Then, the Modified geometrical distance can be denoted by:

$$\delta_M\left(A_i + A_j\right) = \sqrt{\left[\frac{1}{4}\left(\left(c_i - c_j\right)^2 + 2\left(a_i - a_j\right)^2 + \left(b_i - b_j\right)^2\right)\right]} \tag{18}$$

The procedure for ranking alternatives using fuzzy TOPSIS methods follow:

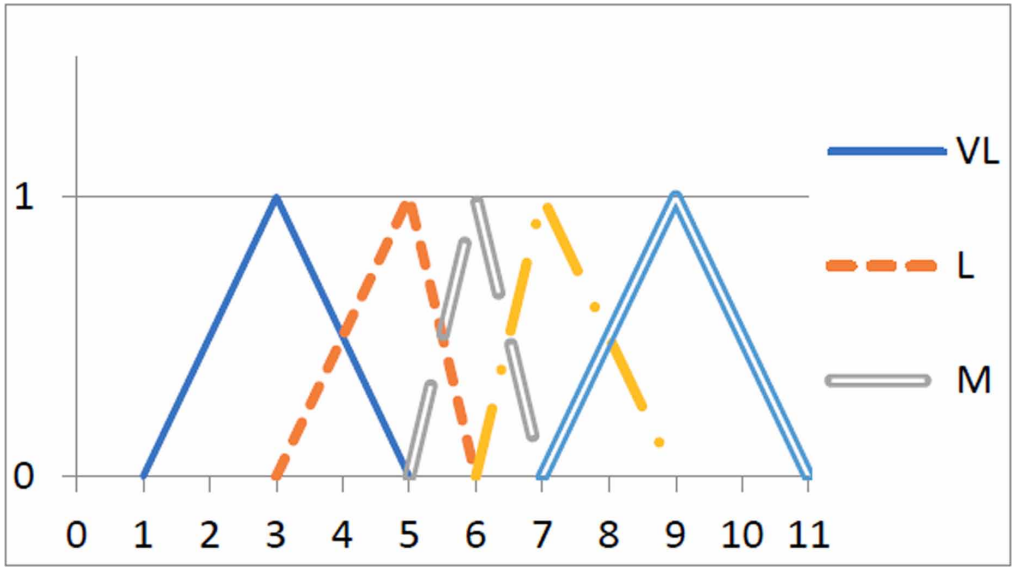
Step 1. Classifying the Sub-Indicators Above the Alternatives Layer Into Subjective and Objective Categories: Indicators are classified into Objective Group and Subjective Group, while objective group deals with quantitative terms (can be expressed numerically), the subjective group is for those indicators that have been failed to be expressed as numerical numbers, and will be expressed in terms of judgments instead.

Step 2. Computing the Global Weights of All Sub-Indicators Above the Alternatives Layer Through Applying the Analytical Hierarchy Process (AHP): The AHP is used to decompose the problem into a hierarchy of sub problems which can more easily be comprehended and subjectively evaluated. Global weights can be determined through multiply local weight by group's relative weight.

Step 3. Estimating the Superiority of Alternatives Versus All Sub Indicators: As mentioned earlier indicators that influenced alternatives selection are classified into subjective indicators and objective ones. The calculations of performance values for subjective indicators are differed from the objective indicators.

Case I. Subjective Indicators Calculations: The subjective indicators tend to be more of qualitative data, and there are no means for numerical measurements. Linguistic values (e.g. high, medium, and low) will be used instead. Triangular Fuzzy Numbers are used to express linguistic values as shown in Figure 4.

Figure 4. Superiority of alternatives versus subjective indicators



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As shown in Figure 4, Very Low (VL), Low (L), Medium (M), High (H), and Very High (VH) are the linguistic values, while the corresponding triangular fuzzy numbers for these linguistic values are Very Low (1,3,5), Low (3,5,6), Medium (5,6,7), High (6,7,9), Very High (7,9,11), respectively.

Case II. Objective Indicators Calculations: Estimating the superiority of alternatives versus objective indicators is implemented through numerical calculations and can be expressed by numbers, thoughfuzzy rates is essential to be applied for objective indicators, since it takes into consideration historical records or estimated values (Ding 2011). As an illustrative example of how fuzzy data can be implemented for the objective indicators, let x_1, x_2… x_n represent the quantities of demolition waste for different years, then the fuzzy rating of the quantities of the demolition waste could be used by the geometric mean method to express the fuzzy values (c, a, b) as shown below:

$$c=\min_i(x_i),\ a=\sqrt[k]{\Pi_{i=1}^{k} x_i}\ ,\ b=\max_i(x_i), \text{ where } i=1,2\ldots n, \text{ and } k=n \tag{19}$$

Step 4. Normalization of the Constructed Fuzzy Matrix: It is worth noting that fuzzy superiority (performance) values are converted to dimensionless indices in order to ensure compatibility between the fuzzy ratings of objective indicators and linguistic ratings of subjective indicators. The fuzzy ideal values with minimum values in negative (cost) indicators or maximum values in positive (benefit) indicators should have the maximum rating.

Based on the principle stated above, normalization can then be achieved through the following Equations:

In case of positive indicators, Equation 5-9 is utilized:

$$\text{Sij} = \left\{\frac{cij}{\alpha ij}, \frac{aij}{\alpha ij}, \frac{bij}{\alpha ij}\right\} \text{ where } \alpha ij = \max \text{ of } bij \text{ (for each criterion)} \tag{20}$$

For negative indicators, Equation 5-10 is utilized:

$$\text{Sij} = \left\{\frac{\beta ij}{bij}, \frac{\beta ij}{aij}, \frac{\beta ij}{cij}\right\} \text{ where } \beta ij = \min \text{ of } cij \text{ (for each criterion)} \tag{21}$$

Step 5. Calculating the Fuzzy Ideal Solution and Anti-Ideal Solution: In order to determine the fuzzy ideal and anti-ideal solution, there is a need first to defuzzify the fuzzy normalized decision matrix, since it would be simpler to compare between crisp values instead of fuzzy ratings. The Graded Mean Integration Representation (GMIR) Method is used to defuzzify the triangular fuzzy numbers. For calculating GMIR let S_i= (c_i.a_i,b_i), i.= 1, 2... m be a triangular fuzzy number. By the GMIR method, the (GMIR) R (S_i) of S_i is:

$$R\left(S_i\right) = \frac{cij + 4aij + bij}{6} \tag{22}$$

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The alternative with max value of $R(S_i)$ or each indicator will represent fuzzy ideal value S_i^+. while alternative with min value of $R(S_i)$ for each indicator will represent fuzzy anti-ideal value S_i^-. Finally, define the fuzzy ideal and anti-ideal solution through the following Equations:

$$I^+ = \left(S_1^+, S_2^+, \ldots, S_j^+, \ldots, S_n^+\right) \quad AI^- = \left(S_1^-, S_2^-, \ldots, S_j^-, \ldots, S_n^-\right) \tag{23}$$

Step 6. Computing the Distance of Different Alternatives Versus the Fuzzy Ideal Solution and Anti-Ideal Solution: In order to obtain the distance between different alternatives and the fuzzy ideal and anti-ideal solution, the Global Normalized Weights of Indicators shall be taken into consideration. Let w_j (j = 1, 2… n) be the global normalized weights of (j) indicators that have been calculated through AHP technique; then the distance between alternative S_{ij} and the fuzzy ideal solution can be obtained by considering the weights of indicators into Equation (24) as follows:

$$Dj^+ = \sqrt{\sum_{j=1}^{n} \left\{ w_j^{\,2} * (\delta m\left(Sj^+, Sij\right))^2 \right\}} \tag{24}$$

where, by the same consideration, the distance between alternative S_{ij} and the fuzzy anti-ideal solution can be obtained using Equation (25):

$$Dj^- = \sqrt{\sum_{j=1}^{n} \left\{ w_j^{\,2} * (\delta m\left(Sj^-, Sij\right))^2 \right\}} \tag{25}$$

where:

$$\delta m\left(Sj^-, Sij\right) = \sqrt{0.25 * \left(cj^- - cij\right)^2 + 2 * \left(aj^- - aij\right)^2 + \left(bj^- - bij\right)^2}$$

Step 7. Calculating the Relative Approximation Value of Each Alternative: The relative approximation value can be obtained by calculating RAVi using Equation (26). The best alternative is the alternative that has the highest value of RAV_i, since it is the closest to the positive fuzzy ideal solution and the farthest away from the fuzzy anti-ideal solution:

$$RAVi = \left(\frac{d_i^-}{d_i^- + d_i^+} \right) \tag{26}$$

5. STUDY AREA

In Egypt, the daily quantity of Construction and Demolition (C&D) Waste has been estimated to be 10,000 tones. This is equivalent to one third of the total daily municipal solid wastes generated in Egypt

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(Ansary, 2004); however most of this generated waste is not currently properly disposed. Egypt suffers from lack of data concerning quantities of CDWs and imprecise of the existing ones which may be either over exaggerated or less than expected. Furthermore, there is no available data for distribution of these quantities for different CDWs materials, which cause an obstacle for any attempts of using other disposal alternatives instead of landfilling.

A modified model was presented by El-Nouhy (2004) to estimate the general rubble is re-considered to give an approximate composition for different demolition waste materials in residential buildings. It's assumed that typical building consisted of 56 units with dimension (M*M), where the value of "M" ranges between "3, 3.25, 3.5 … 6" meter. As reported by CAPMAS (2011), there are about 220 buildings in average being demolished annually in Cairo. Using data from the estimation model and multiply it by (220) "number of demolished building" creates a wide breakdown of various materials quantities for different values of module size (M), however these values need to be more specific in order to be applicable in fuzzy TOPSIS technique. A Module Size of M equals 4.6 m, which is equivalent to average quantity of demolition waste is chosen to represent data from the estimation model along with the lower module size of M equals 3 m, and the upper size of M equals 6 m. these three values for module size (M = 3, 4.6, 6 m) are used as fuzzy rates for acquiring values of objective indicators against different alternatives.

Table 2 shows the annual quantities for demolition waste materials in residential buildings in Cairo for the forgoing module sizes (M = 3, 4.6, 6 m), however the main interest in this paper is brick quantities for different values of M.

6. RESULTS AND DISCUSSION

After determining the evaluation Indicators and the alternative set convenient for disposal of demolition waste, the steps of the modified fuzzy TOPSIS algorithm are executed. Indicators are classified into: Objective Group and Subjective Group. While subjective indicators include: fresh water consumption, area of land occupied, average number of hours used for employee training, and probability of occurrences of injuries, death and any other kind of accident, the rest are considered objective ones.

The second step is to compute the global weights of all sub-indicators above the alternatives layer through applying the analytical hierarchy process (AHP). Several research papers have been gathered to represent relative importance for the foregoing indicators. These relative weights are found in (Ekmekçioğlu et al., 2010; Bakhoum and Brown, 2012). Data gathered from those papers have been implemented through analytical hierarchy process to acquire both local weight and the integrated weight. First, sustainable indicators shall be divided into three groups: environmental, economic, and social. These groups are considered the first level of hierarchy, while indicators within each group represent the 2nd level; similarly sub indicators represent the 3rd level.

Table 2. Estimated annual demolished waste quantities (tons) in Cairo

Module (m)	Concrete	Steel	Brick	Tiles	Sand	Sanitary	PVC pipes	Wood	Sum
3	53774	4839	49116	8219	5322	172.5	65.1	4468	125,978
4.6	117984	10619	80550	18779	12513	172.5	65.9	8963	249,646
6	209893	18890	108055	31495	21289	172.5	66.3	14448	404,310

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6.1. Calculation of Global Weights

There are six pairwise comparison matrices that represent the comparison among the three levels. Table 3 shows the local normalized weights or indicators/sub-indicators with their corresponding global weights, where global weights are calculated as per Equation (27):

global weights = (group relative weight*local weights)*subindicators weights (27)

As per Table 3, the weights of the three main groups, i.e., environmental, social, and economic indicators are the same. Global warming has the highest global weight in the environmental group with 9.9%. Accident hours sub-indicator has the highest global weight in the social group with 15.7%. The two sub-indicators in the economic group are of equal weight.

After acquiring indicators weights (eigenvector), there is a need to check consistency for comparison matrix through calculation of consistency ratio C_R. Saaty (2008) argued that, if C_R (A) ≤ 0.1, the pairwise comparison matrix is considered to be consistent enough. Consistency ratio (C_R) for all six pairwise comparison matrices is calculated and found to be in range "0 to 0.04", which are less than 0.10. Thus, the comparison results can be considered consistent and convenient for an AHP procedure.

Table 3. Overall weight distribution

List of Groups	Weights of Relative Group	List of Indicators	Local Weight	List of Sub-Indicators	Sub-Indicators Local Weights	Global Weights
Environmental	0.333	Energy	0.328	Consumption	0.5	5.5%
				Avoided	0.5	5.5%
		Acidification potential	0.077	Acidification potential	1	2.6%
		Global warming	0.274	Global warming	1	9.1%
		Waste percentage	0.264	Waste percentage	1	8.8%
		Water consumption	0.057	Water consumption	1	1.9%
Social	0.333	Job opportunities	0.115	Job opportunities	1	3.8%
		Level of noise	0.052	Level of noise	1	1.7%
		Training hours	0.115	Training hours	1	3.8%
		Accident occurrence	0.470	Accident occurrence	1	15.7%
		Quality of life	0.249	Demolition duration	0.2	1.7%
				Impact traffic	0.4	3.3%
				Land occupied	0.4	3.3%
Economic	0.333	Cost of disposal	0.5	Cost of disposal	1	16.7%
		Benefit from disposal	0.5	Benefit from disposal	1	16.7%

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6.2. Estimation of the Superiority of Alternatives

Next step is to estimate the superiority of different alternatives against all indicators, a large fuzzy decision matrix (15x5) has been developed assembling all the fuzzy values of all indicators related to the five alternatives. This matrix is depicted in Table 4; indicators are classified into two groups: Benefit Group of indicators which includes (avoided Energy, Job opportunities, Economic value of recycled materials, and Training hours) and Cost Group that includes all other indicators.

To obtain the fuzzy ratings of objective indicators in fuzzy decision matrix, these calculations shall be implemented for the different values of estimated demolished brick quantities (49115, 80550, 108055 ton), which represents the minimum, average, and the maximum values of the module size (M) in the

Table 4. Fuzzy Decision Matrix (sustainable indicators versus possible alternatives)

Indicators	Reuse Blocks (A1)	Recycled Tennis Court Clay Surface (A2)	Recycled Aggregate (A3)	Fill Material (A4)	Landfill (A5)
Energy consumption (C1)	215957, 331222, 475125	601884, 923050, 1324073	392224, 588721, 808755	170197, 261043, 374465	170197, 261043, 374465
Energy avoided (C2)	101203325, 155220933, 222647314	91514679, 140360847, 201332191	3668946, 5627258, 8071680	3261285, 5002007, 7174827	0, 0, 0
Acidification potential (C3)	1916, 2938, 4214	5337, 8185, 11741	3478, 5220, 7171	1510, 2315, 3321	1510, 2316, 3321
Global warming (C4)	138650, 212620, 304983	236016, 355429, 505139	239307, 365406, 519443	204148, 313115, 449126	204148, 313115, 449126
Job opportunities (C5)	24, 35, 50	55, 76, 97	45, 61, 77	32, 47, 64	27, 40, 54
Demolition duration (C6)	4477, 4706, 4926	4254, 4398, 4680	4254, 4398, 4680	4254, 4398, 4680	4254, 4398, 4680
Level of noise(C7)	93.22, 93.22, 93.22	102.2, 102.46, 102.66	97.52, 97.55, 97.61	100, 100, 100	96.14, 96.14, 96.14
% waste disposal after recycle (C8)	0.2, 0.2, 0.2	0.28, 0.28, 0.28	0.1, 0.1, 0.1	0.2, 0.2, 0.2	1, 1, 1
Cost of recycling (C9)	394404, 580489, 833464	953788, 1282252, 1645619	830257, 1125139, 1441339	466363, 708712, 992159	441975, 671304, 938509
Benefit of waste (C10)	2741538, 4204844, 6031385	5281899, 8101130, 11620178	1425006, 2185608, 3135013	75577, 115918, 166270	-26817, -18696, -12189
Impact of waste trucks on traffic (C11)	102, 415, 530	132, 302, 579.3	132, 302, 579.3	132, 302, 579.3	132, 302, 579.3
Water consumption (C12)	3, 5, 6	6, 7, 9	6, 7, 9	5, 6, 7	5, 6, 7
Area of land occupied (C13)	1, 3, 5	5, 6, 7	5, 6, 7	5, 6, 7	6, 7, 9
Training hours (C14)	5, 6, 7	6, 7, 9	6, 7, 9	3, 5, 6	3, 5, 6
Accident occurrences (C15)	6, 7, 9	5, 6, 7	5, 6, 7	3, 5, 6	3, 5, 6

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estimation model. On the other hand, linguistic values are used to express superiority values of different alternatives versus subjective indicators. Table 5 represents the fuzzy normalized matrix, which is obtained by applying Equations 20 and 21 to the benefit and cost indicators' performance values that are listed in Table 4. After Normalization of the constructed fuzzy decision matrix, fuzzy TOPSIS technique is applied.

Fuzzy ideal and anti-ideal solution are determined through implementing Graded Mean Integration Representation (GMIR) method for defuzzication process, then alternative with max value of $R(S_i)$ for a certain indicator will represent the fuzzy ideal value S_i^+ for this indicator and vice versa.

By applying Equation (22) to the fuzzy values in Table 5, the different values of $R(S_i)$ are obtained, where fuzzy ideal solution will be the corresponding fuzzy values for R max of each indicator, and vice versa for the anti-ideal solution. Table 6 presents the calculated GMIR method and the fuzzy ideal/anti-ideal solution, respectively. Distances between different alternatives and fuzzy ideal/anti-ideal solution can be determined by applying Equations (24) and (25) which has taken into consideration the global normalized weights of indicators that have been calculated through AHP technique. Results for applying of this Equation are listed in Tables 6.

6.3. Ranking of The Alternatives

The final step in determination the rank of disposal alternatives for demolition waste is to obtain Relative Approximation Value (RAV). This could be implemented by applying Equation (26) on the values of Table 7. Relative Approximation Values (RAV) is used for ranking the suggested alternatives, where the higher value of *RAV* is, the better alternative will be, since it is closer to the fuzzy ideal solution and

Table 5. Fuzzy Normalized Decision Matrix

Indicator	Alternative				
	A1	A2	A3	A4	A5
C1	0.359, 0.514, 0.789	0.129, 0.185, 0.283	0.211, 0.29, 0.434	0.455, 0.652, 1	0.455, 0.652, 1
C2	0.455, 0.698, 1	0.412, 0.631, 0.905	0.017, 0.026, 0.037	0.015, 0.023, 0.033	0, 0, 0
C3	0.359, 0.514, 0.789	0.129, 0.185, 0.283	0.211, 0.29, 0.435	0.455, 0.653, 1	0.455, 0.652, 1
C4	0.455, 0.653, 1	0.275, 0.391, 0.588	0.267, 0.38, 0.58	0.309, 0.443, 0.68	0.309, 0.443, 0.68
C5	0.248, 0.361, 0.516	0.568, 0.784, 1	0.464, 0.629, 0.794	0.33, 0.485, 0.66	0.279, 0.413, 0.557
C6	0.864, 0.904, 0.951	0.909, 0.968, 1	0.909, 0.968, 1	0.909, 0.968, 1	0.909, 0.968, 1
C7	1, 1, 1	0.909, 0.91, 0.913	0.956, 0.956, 0.956	0.933, 0.933, 0.933	0.97, 0.97, 0.97
C8	0.5, 0.5, 0.5	0.358, 0.358, 0.358	1, 1, 1	0.5, 0.5, 0.5	0.1, 0.1, 0.1
C9	0.474, 0.68, 1	0.24, 0.308, 0.414	0.274, 0.351, 0.476	0.398, 0.557, 0.846	0.421, 0.588, 0.893
C10	0.236, 0.362, 0.52	0.455, 0.698, 1	0.123, 0.189, 0.27	0.007, 0.01, 0.015	-0.0024, -0.0017, -0.0011
C11	0.228, 0.471, 1	0.177, 0.339, 0.778	0.177, 0.339, 0.778	0.177, 0.339, 0.778	0.177, 0.339, 0.778
C12	0.5, 0.6, 1	0.334, 0.429, 0.5	0.334, 0.429, 0.5	0.429, 0.5, 0.6	0.429, 0.5, 0.6
C13	0.2, 0.334, 1	0.143, 0.167, 0.2	0.143, 0.167, 0.2	0.143, 0.167, 0.2	0.112, 0.143, 0.167
C14	0.556, 0.667, 0.778	0.667, 0.778, 1	0.667, 0.778, 1	0.334, 0.556, 0.667	0.334, 0.556, 0.667
C15	0.334, 0.429, 0.5	0.429, 0.5, 0.6	0.429, 0.5, 0.6	0.5, 0.6, 1	0.5, 0.6, 1

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Table 6. Defuzzication of Fuzzy Normalized Matrix and fuzzy ideal/anti-ideal solution

Indicators	$R(A_1)$	$R(A_2)$	$R(A_3)$	$R(A_4)$	$R(A_5)$	Fuzzy Ideal Sol.			Fuzzy Anti-Ideal Sol.		
						C	a	B	C	a	B
C1	0.534	0.191	0.300	0.677	0.677	0.455	0.652	1.000	0.129	0.184	0.283
C2	0.707	0.639	0.025	0.023	0.000	0.455	0.697	1.000	0	0	0
C3	0.534	0.191	0.300	0.677	0.677	0.455	0.652	1.000	0.129	0.184	0.283
C4	0.677	0.404	0.394	0.460	0.460	0.455	0.652	1.000	0.267	0.379	0.579
C5	0.368	0.784	0.629	0.488	0.414	0.567	0.784	1.000	0.247	0.361	0.515
C6	0.905	0.963	0.963	0.963	0.963	0.909	0.967	1.000	0.864	0.904	0.950
C7	1.000	0.910	0.956	0.932	0.970	1.000	1	1.000	0.908	0.91	0.912
C8	0.500	0.357	1.000	0.500	0.100	1	1	1	0.1	0.1	0.1
C9	0.698	0.314	0.359	0.579	0.611	0.473	0.679	1.000	0.24	0.308	0.414
C10	0.367	0.707	0.191	0.010	-0.002	0.455	0.697	1.000	-0.0023	-0.0016	-0.001
C11	0.517	0.177	0.177	0.177	0.177	0.23	0.469	1.000	0.177	0.339	0.777
C12	0.650	0.425	0.425	0.505	0.505	0.500	0.6	1.000	0.333	0.429	0.500
C13	0.422	0.169	0.169	0.169	0.142	0.200	0.333	1.000	0.111	0.143	0.167
C14	0.667	0.797	0.797	0.537	0.538	0.667	0.778	1.000	0.333	0.556	0.667
C15	0.425	0.505	0.505	0.650	0.650	0.5	0.6	1.000	0.333	0.429	0.500

Table 7. Distance of suggested alternatives vs. Fuzzy ideal solution and anti-ideal solution

Indicators	Positive Distance					Negative Distance				
	A1	A2	A3	A4	A5	A1	A2	A3	A4	A5
C1	6.90E-09	3.92E-08	3.92E-08	3.92E-08	3.92E-08	3.92E-08	0.00E+00	3.84E-09	7.90E-08	7.90E-08
C2	0.00E+00	1.63E-07	1.63E-07	1.63E-07	1.63E-07	1.63E-07	1.33E-07	2.09E-10	1.65E-10	0.00E+00
C3	1.50E-09	8.55E-09	8.55E-09	8.55E-09	8.55E-09	8.55E-09	0.00E+00	8.40E-10	1.72E-08	1.72E-08
C4	0.00E+00	7.54E-08	7.54E-08	7.54E-08	7.54E-08	7.54E-08	7.40E-11	0.00E+00	4.16E-09	4.16E-09
C5	2.54E-08	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.54E-08	9.82E-09	2.15E-09	2.90E-10
C6	8.58E-11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.58E-11	8.58E-11	8.58E-11	8.58E-11
C7	0.00E+00	2.40E-10	2.40E-10	2.40E-10	2.40E-10	2.40E-10	0.00E+00	6.21E-11	1.44E-11	1.07E-10
C8	1.93E-07	1.24E-07	1.24E-07	1.24E-07	1.24E-07	1.24E-07	5.10E-08	6.26E-07	1.24E-07	0.00E+00
C9	0.00E+00	4.67E-07	4.67E-07	4.67E-07	4.67E-07	4.67E-07	0.00E+00	5.95E-09	2.33E-07	2.90E-07
C10	3.50E-07	4.11E-07	4.11E-07	4.11E-07	4.11E-07	4.11E-07	1.52E-06	1.12E-07	4.03E-10	0.00E+00
C11	0.00E+00	2.37E-09	2.37E-09	2.37E-09	2.37E-09	2.37E-09	0.00E+00	0.00E+00	0.00E+00	0.00E+00
C12	0.00E+00	3.14E-09	3.14E-09	3.14E-09	3.14E-09	3.14E-09	0.00E+00	0.00E+00	2.74E-10	2.74E-10
C13	0.00E+00	2.13E-08	2.13E-08	2.13E-08	2.13E-08	2.13E-08	8.99E-11	8.99E-11	8.99E-11	0.00E+00
C14	3.15E-09	3.17E-09	3.17E-09	3.17E-09	3.17E-09	3.17E-09	1.17E-08	1.17E-08	0.00E+00	3.66E-14
C15	2.06E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.80E-08	1.80E-08	2.06E-07	2.06E-07
Di+/ Di-	8.87E-04	1.15E-03	1.15E-03	1.15E-03	1.15E-03	1.15E-03	1.33E-03	8.88E-04	8.16E-04	7.73E-04

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Table 8. Ranking of demolition waste disposal alternatives

Alternatives		RAV	Rank
A1	Reuse Blocks	0.564	1
A2	Recycled Tennis Court Clay Surface	0.559	2
A3	Recycled Aggregate	0.412	3
A4	Fill Material	0.369	4
A5	Landfill	0.332	5

farther away from the fuzzy anti-ideal solution. Results of relative approximation value (RAV) for each alternative, as well ranking of these alternatives are represented in Table 8. The results indicate that the most sustainable (preferred) alternative out of the five suggested alternatives is the first alternative A1 (i.e. Re-using Blocks). These results contribute in strengthening the hierarchy presented by Peng et al (1997) of disposal options for C&D waste, which sets the reusing option in a higher rank, followed by recycling and land filling respectively.

7. CONCLUSION

This research is focused on waste materials resulted from the demolition stage of residential buildings. The first objective of this study is to present the indicators that measure sustainability between various demolition waste disposal alternatives. These indicators are taken into consideration the three clusters of sustainability development; Economic, Social, and Environmental aspects. The second objective of this study is to compare between different disposal alternatives in terms of sustainable indicators using fuzzy TOPSIS technique. TOPSIS method is particularly adapted for sustainable development problems, as it defines the ideal solution and anti-ideal one which represent the best and worst results against all indicators respectively, then it be used as a measure tool to express closeness of each alternative to ideal and negative ideal solution, however this study is used fuzzy TOPSIS to manage combination between all of imprecise, uncertain, and vague data provided by human judgments and objective results from equations. The results from fuzzy TOPSIS technique showed that the most sustainable (preferred) alternative out of the five suggested alternatives is Re-using. Also, it proves the superiority of reusing over recycling and for recycling over land filling. The current research can be extended to include more indicators and sub-indicators. Moreover, more demolition waste disposal alternatives can be investigated. Finally, other MCDM can be utilized and compared with the fuzzy TOPSIS such as grey relational analysis (GRA), Elimination and Choice Translating Reality (ELECTRE I), Preference Ranking Organization Method for Enrichment Evolution (PROMETHEE II), etc.

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Chapter 65
Toward Achieving Environmental Sustainability in the Computer Industry

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ABSTRACT

The computer industry has come under increasing scrutiny in terms of energy consumption, the carbon emissions and e-waste. Shipment of e-waste to developing countries where it is often disposed of in unsafe ways is another major issue. Organizations and individuals have a tendency to throw away or store their aging computer technology assets which is not environmentally sustainable and or cost effective. Implementation of an end-to-end computer and related products' sustainability management strategy by incorporating the reuse of existing technology can make a major impact on the environment. Computer industry sustainability management includes design and development of energy efficient computer products, refurbishing of computer assets, purchasing of green or refurbished components and providing sustainability metrics procedures. By implementing sustainability programs, organizations can contribute in reducing the amount of energy spent to develop new computer technology products, help in reducing carbon emission, keep e-waste out of landfills and recycle them. This paper discusses different aspects of sustainable computer industry program and proposes that computer makers take ownership of disposing of e-waste by following safety standards. The paper also proposes adopting reverse supply chain process for possible reuse, recycle or disposal of computers.

1. INTRODUCTION

The information technology (IT) industry accounts for approximately 2 percent of global carbon dioxide (CO_2) emissions (Gartner, Inc. 2007). About 75% of the ecological footprint comes from IT products usage and 25% constitute embodied carbon in IT products (The Climate Group, 2008). IT products include data centers, servers, personal computers (PCs), telecoms networks and devices, and printers. This paper limits the scope of this research to Personal Computers (PCs).

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Research firm, Gartner, Inc. (2015) reported that worldwide combined shipments of devices (PCs, tablets, ultra-mobiles and mobile phones) for 2015 are estimated to reach 2.5 billion units, an increase of 3.9 percent over 2014. This projected number of computer device sold indicates how much energy would be consumed worldwide. This also references materials used to build these computer products. Energy consumption, carbon emissions, natural resources consumption and landfill of computers (after end of life) are the key concerns. Given the intensity of natural resources and energy consumption by computer products indicates the need for the computer industry to be environmentally sustainable.

The term sustainability has been defined in many different ways by different people, institutions and organizations. One widely accepted definition is from the Brundlandt Report, "sustainable development is the development that meets the needs of present without compromising the ability of future generations to meet their own needs" (World Commission on the Environment and Development, 1987). Sustainability is "a characteristic of a process or state that can be maintained at a certain level indefinitely" (Jabareen, 2008). The major driving force for sustainability is the public concern about the environmental impact of the present fossil fuel based energy system (Rahman and Akhter, 2010). We need to satisfy our needs by judiciously using renewable resources, recycling wastes, and reversing environmental degradation (Duan et al. 2009).

Sustainability starts from a sustainable design. Sustainability can and should be a central focus of interaction design (Blevis, 2007). A sustainable approach to design and engineering involves evaluating where a product or system has the greatest environmental impact and then prioritizing strategies which reduce that impact (Gaughran et al. 2007). Intelligent manufacturers must take into account all the indicators of energy demands and supply in planning their chain supply, and processing strategies. All these apply to computer products. Reduction of waste including energy waste shows not just corporate responsibility, but is also seen to make sound economic sense (Gaughran et al. 2007).

Nidumolu et al. (2009) assert that sustainability should be taken as one of the main drivers of innovation. Instituting sustainability starting from design (sustainable products and services) helps a company to be compliant with regulations enforced by countries in different regions. In fact forward looking companies take compliance as an opportunity to make their products follow regulations set by countries globally. They add sustainability to value chains – supply, operations, and returns (reuse returned products).

Our research was based upon a few questions. Can the computer industry improve environmental sustainability to help contribute to a greener planet? Where do computers go after end of use? Are they recycled or hoarded or go to landfill? To answer to these questions, we did an extensive review of existing literature. We went through research and industry papers written by researchers, practitioners, and environmental sustainability advocacy group. Based on insights drawn from academy and industry papers we propose measures that needs to be adopted to achieve sustainability in terms of environmental, energy and material consumption.

2. LITERATURE REVIEW

The computer industry is an important area from an environmental sustainability standpoint. Sustainability has been a research topic for more than three decades. The research is mostly related to ecological, economic and social aspects of sustainability. Tukker (2003) suggests there is the potential of CO_2 reduction from household consumption by fulfilling final consumer needs by Product-Service Systems (PSS).

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Edward Deming (Neave, 1990) advocates the understanding of change through the System of Profound Knowledge (SOPK). He professes that the prevailing style of management must change and is necessary but not sufficient. We must understand what changes to make. To understand what and how to change one first needs to understand the subject matter in terms of theory. Deming maintains that without comprehending the theory there is no comprehensive knowledge to effect change to the environmental problems related to the computer industry. In this paper we may think of computer industry's product life cycle analysis in terms of systems thinking, which is a unique approach to problem solving, in that it views certain 'problems' as part of the overall system so focusing on these outcomes will only further develop the undesired element or problem. A comprehensive systems approach is proposed by Fiksel (2006), to better understand the dynamic, adaptive behavior of complex systems and their resilience in the face of disruptions.

Krajnc et al. (2008) discuss the cultural influences and barriers to the rational use of energy. The suggestions for reducing energy consumption come mainly from a technical innovations standpoint, but there is also a need to pursue all other possible approaches to tackle this problem. Sustainable consumption is a link between economic prosperity and resource conservation. In rich countries, the population needs to build a habit of adequate consumption as opposed to excessive consumption. It does not make sense to have a computer connected to power outlets on a twenty four by seven basis. Education has been given a crucial role when shifting from unsustainable to sustainable consumption patterns (Krajnc et al. 2008).

Advances toward sustainability will require system specific metrics to assess both current performance and the impact of operational, technological or regulatory changes on that performance (Rahman and Akhter, 2010; Atlee and Kirchain, 2006). Currently, there are few operational metrics by which to practically assess progress toward sustainability. We think that there are opportunities to use reliable performance indicators towards achieving sustainability in development, manufacture, and use of computer products (Rahman and Akhter, 2010).

In order to reduce environmental footprints caused by computer industry business organizations need to embrace strategic transformation which includes business model development, redesign of business processes (Sherringham, 2011; Ghose et al., 2009), and development of effective communication of environmental improvement activities within industry (Parker et al., 2010). Banerjee et al. (2013) propose a theoretical framework that includes management, technological, marketing, financial and regulatory elements as part of motivations to have non-green organizations in adopting green information and communications technology (ICT). For smaller organizations Capra et al. (2013) propose achieving green objectives with a more incremental approach to deal with infrastructure and significant upfront investment requirements. Kongar (2010) proposes Data Envelopment Analysis (DEA) model to calculate and rank the technical efficiencies of conventional and alternative green initiative-based energy sources by taking into consideration such factors as economies of energy sources and other environmental criteria including CO_2, emissions and damage cost.

Mouchet et al. (2014) propose using carbon footprint auditing tool for individual ICT organizations which can motivate them and support decision making to adopt sustainability activities. Their research also called out the need for consistent management of hardware in ICT organizations. Philipson (2011) reports that most organizations are unable to identify which areas to address to achieve environmental sustainability. To help ICT organizations achieve green ICT sustainability the author proposed a comprehensive green ICT framework consisting of four pillars including lifecycle, end-user-IT, enterprise and data center IT and IT as a low-carbon enabler. Then he proposes five dimensions including attitude, policies, practices, technologies and metrics under each of those four pillars. Adopting this framework would encourage organizations to measure and compare metrics among one another.

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Rahman and Akhter (2010) propose a comprehensive sustainability metrics against which ICT organizations could measure carbon footprint reductions activities and capture benchmarks. Fostering such comprehensive metrics will allow organizations to measure and compare metrics amongst one another. Pradhan (2011) propose leveraging ISO standard in carbon footprint assessment. The ISO 14001 helps an ICT organization to maintain an environmental management system (EMS) to plan, execute and review environmental performance.

Verguts et al. (2016) propose utilizing industrial symbiosis as sustainable development strategy. "Industrial symbiosis (IS) is the coordination of energy and material flows among geographically proximate firms to increase economic performance while reducing environmental impact" (Verguts et al., 2016). Muduli et al. (2016) propose that green supply chain management minimize wastes and emissions and enhance performance. Metaxas and Tsavdaridou (2014) report that CRS was adopted amongst some European companies to tackle issues of recycling, environmental pollution, energy conservation, and environmental education.

Lindahl et al. (2016) propose an analytical framework for exploring pathways to sustainability. They propose five steps towards exploring pathways: identify actors, explore actors' frames, explore actors' activities, analyze institutions and governance, and explore alternative pathways to sustainability. Galia et al. (2015)'s study indicate that investment in environmental innovation is influenced by internal factors of the farm. These factors include size, performance, training, cooperation and openness that contribute to significant impact on green innovation. Bradford and Saad (2014) suggest that absorptive capacity is a key that speaks for a firm's ability to recognize the value of, acquire, internalize, and exploit external new knowledge and apply.

3. SUSTAINABILITY OF THE COMPUTER INDUSTRY

In order to achieve sustainability PC makers have been adopting different active programs including recycling, sustainable manufacturing, and compliance regulations of foreign countries. For example, Dell has programs to reduce hazardous substances in its computers while a global consortium of computer companies, including AMD, Dell, IBM, and VMware made an alliance with the goal of improving energy efficiency in computers and data centers (Kurp, 2008). Nonetheless, societies and governments are concerned about increasing environmental impact of energy usage, carbon footprints and toxic waste caused by computer industry given computer usage has significantly been in increasing all over the world (Cater-Steel and Tan, 2010; Araujo, 2012). Computer industry needs to come up with comprehensive measures to address environmental concerns (Rahman and Akhter, 2010; Murugesan, 2008). Measures need to be taken to decrease the use of toxic-heavy metals and technology innovation is needed to reduce energy consumption (Son et al., 2016).

In computer industry sustainability programs include actions to reduce the use of physical resources, the adoption of reuse, refurbish and recycle programs, the use of renewable rather than deplete-able resources, the redesign of production processes and products to eliminate the production of toxic materials, the protection and restoration of natural habitats and environments valued for their livability or beauty. Figure 1 shows energy consumption and e-waste/emission points of a product's life cycle. Measures need to be taken in each of these phases to ensure environmental sustainability.

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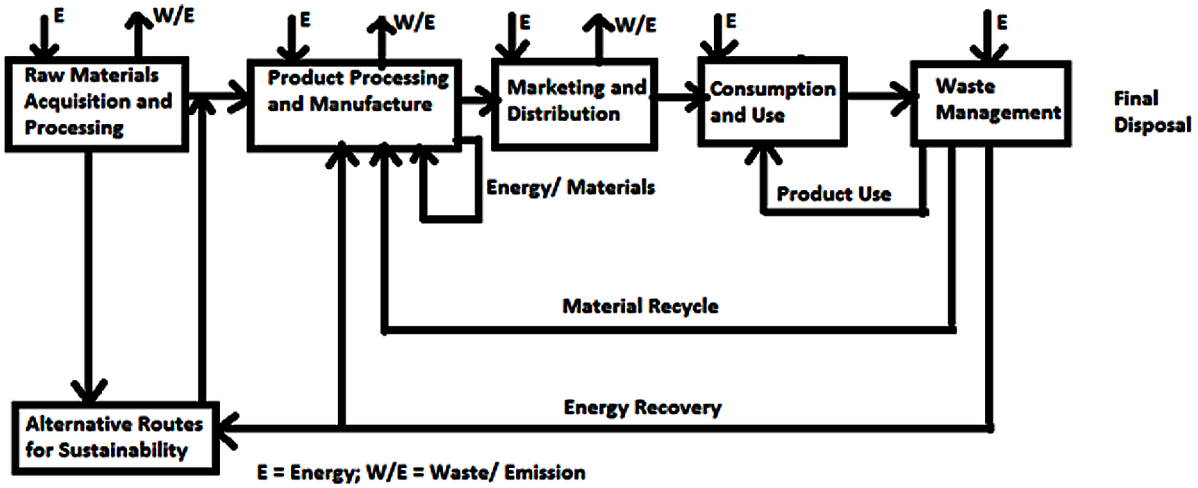
Figure 1. Examples of process loops identifying sustainability pathways (Culaba and Purvis, 1999)



A desktop uses about 600 kWh and emits 175 kg of CO_2 per year (energyguide.be, 2016) when it runs for eight hours a day. On the other hand a laptop that is on for eight hours a day uses between 150 and 300 kWh and emits between 44 and 88 kg of CO_2 per year (energyguide.be, 2016).

The U.S. Environmental Protection Agency (EPA) (2016) has Energy Star programs that strengthen requirements for computers earning the Energy Star certifications. In order to certify computers and workstations as energy efficient these products must meet maximum power consumption requirements. To be compliant with energy use guidelines the computers must have "off" and "idle" operations. EPA gradually sets stringent requirements for computers to be ENERGY START certified. Computer manufactures have motivation in getting this certification for their products as it helps in product marketing and promotion. The EPA estimated that if all computers that are sold in the United States were Energy Star certified that would incur a savings of more than one billion dollars energy costs per year. That would also prevent about 15 billion pounds of annual greenhouse gas emissions.

The U.S. Environmental Protection Agency (EPA) should have computer life time standards for PCs to ensure PCs could be used for at least five years. The EPA also needs to enforce other important requirements such as amount of toxic content a PC might emit and percentage of materials that could be extracted for re-use or recycling.

3.1. The Material Aspects of Sustainability of the Computer Industry

Life-cycle analysis (LCA) studies show that manufacturing and use of computer devices are of the highest environmental importance. Manufacturing devices such as the integrated circuits (ICs) and the Liquid Crystal Display (LCD) are contributing most to the environmental impact (Duan et al, 2009). To achieve ecological sustainability the design aspects of PCs need to be continuously evaluated. Currently, computers have life span as low as 2-3 years (Rahman and Akhter, 2010; Kahhat and Williams, 2009). The expanding user base of computers and continual buying of new computers every two or three years prevents society from reaching ecological goals.

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What percentage of energy savings is achieved through energy efficiency measures? How much increase of efficiency is achieved in PCs? How much savings achieved through process redesign and exergy analysis in the LCA? All these initiatives by PC makers could speak for proactive efforts to improve energy efficiency through technological improvements of processes (Rahman and Akhter, 2010).

AT&T, Advanced Micro Devices (AMD) and Cisco are transitioning from excessive consumption to impressive designs to take advantage of potential improved business opportunities. As a result these companies are bringing productivity leaps to the non-digital economy. AMD expects a 2,500% gain in energy productivity for its computer processors by 2020 (Shireman, 2015). In each phase of manufacturing process energy efficient design and reusability must be adopted. Most of the computer parts must be made so that they are reusable and recyclable. Computer life-time needs to be increased from 2-3 years to at least five years. To achieve that goal computer parts must be made of good quality. Computer manufactures might want to consider standardizing the product parts.

Not everyone will be willing to give up the materialism that drives unsustainable behaviors. Therefore, design must influence more sustainable consumption and the computer industry must find tools that can allow designers to do so. They must embrace principles of designing according to the perspective of sustainability. Blevis (2007) proposed a set of design principles that include linking invention and disposal, promoting renewal & reuse, promoting quality and equality, de-coupling ownership and identity, and using natural models and reflection. To minimize the environmental impact of e-waste all efforts must be made to increase useful materials recovered from the waste before it goes to landfills. Design for environmental (DFE) tools need to be used for creating products which makes it easy to recover, reuse, or recycle PCs. This type of tools help in examining environmental effects during design phase (Hart, 1997). PC makers need to have a sustainability vision that will promote product stewardship, pollution prevention, and efficient technology to move them toward sustainability.

3.2. E-Waste of Computer Products

Industrial nations are shipping millions of obsolete computers to developing countries which has been causing ever-growing set of global environmental change (Rahman and Subramanian, 2012; Williams et al., 2008; Nnorom and Osibanjo, 2008b). Some companies (both exporting and importing) might consider it a significant business opportunity, given the volumes of e-waste being generated and the content of both toxic and valuable materials in them. The fraction including iron, copper, aluminum, gold and other metals in e-waste is over 60%, while pollutants comprise 2.70% (Widmer et al. 2005). Developing countries are becoming environmentally polluted very fast. Iles (2004) proposes an environmental justice approach that will help illuminate the impacts of technology and material flows. The author advocates a framework that takes into consideration global production systems, development models, and regulatory actions (Iles, 2004).

Given the developed countries use poor countries as a dumping place for the obsolete computers the author proposes that exports from the developed to the developing world be completely banned. This notion is supported by other researchers as well (Kahhat and Williams, 2009). One compelling reason for this ban is that in developing countries e-waste is not disposed of properly. A good number of researchers reported that in those countries they do ‘informal’ recycling’ or ‘backyard’ recycling which causes potential emissions of toxics from disposal in poorly managed landfills and impacts workers and communities involved. (Williams et al., 2008).

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Despite excessive consumption of energy and materials, in developed countries the levels of pollution are relatively low (Hart, 1997). This is because of stringent environmental regulations, the greening of industry, and the relocation of the most polluting activities (such as commodity processing and heavy manufacturing) to the developing nations. Hart (1997) called out that this greening of the developed world is at the expense of environmental degradation in developing countries. On the other hand, Meadows et al. (2004) reported that "environmental degradation often affected the poorest groups in society, as they were unable to protect themselves from the environmentally destructive activities of richer and more powerful people."

According to Electronics Takeback Coalition (2014), in 2010 423 thousand tons (51 million units) of computers were disposed of out of which 255 thousand tons (31 million units) were trashed and 168 thousand tons (20 million units) were recycled. That means only 40% of those computers were actually recycled and the rest ended up in landfills. On the other hand, 595 thousand tons (35 million units) of monitors are disposed of, 401 thousand tons (24 million units) trashed and only 194 thousand tons (11 million units) of monitors recycled (recycling rate, 33%). A report by the EPA (Skye, 2016) shows that by 2010 computers and other e-waste consisted of 70% of heavy metals found in U.S. landfills. EPA report stated that computer and other electronics are fastest growing types of waste in the U.S.

Keeping electronics out of landfills is recommended by the EPA since they contain materials such as lead, nickel, cadmium and mercury which can be a risk to individuals' health as well as the environment (Moss and Scheer, 2015). As for laptops, recycling one million of them could save energy equal to the electricity used by 3,657 homes a year. Recycling one million cell phones would save us 35,274 pounds of copper, 772 pounds of silver, 75 pounds of gold, and 33 pounds of palladium (Moss and Scheer, 2015).

E-waste can be minimized by increasing recovery from the waste stream through reverse supply chains (Kahhat and Williams, 2009; Williams et al., 2008). "Reverse supply chain is a process by which a manufacturer systematically accepts previously shipped products or parts from the point of consumption for possible reuse, remanufacturing, recycling, or disposal" (Rahman and Subramanian, 2012). The domestic reverse supply chain of PCs takes into consideration extensive collection, reuse, and recycling (Kahhat and Williams, 2009). Ravi et al. (2005) propose determining the "key reverse logistics variables, which the top management should focus on to improve the productivity and performance of computer hardware supply chains."

Research suggest that availability of resources, coordination and integration of recycling tasks and the volume and quality of recyclable materials, are critical for computer recycling operations (Rahman and Subramanian, 2012). Studies emphasize on on-site waste minimization and associated sustainability characteristics in relation to environmental impact assessment and process improvement (Culaba and Purvis, 1999). One way of minimizing the environmental impact of e-waste is to increase the amount of product materials recovered from the waste stream through recycling operations (Rahman and Subramanian, 2012).

Formal recycling of e-waste using efficient technologies and state-of-the-art recycling facilities are rare in most of the countries of the world. Most of the countries of the world including developed countries adopt some inappropriate methods after their life span. These include holding them in closets of the house (health hazard), backyard of the house, and disposing in open dumps or surface waters (Nnorom and Osibanjo, 2008a). Similarly, there is no integrated framework regarding the monitoring and management of toxic and hazardous materials and wastes in underdeveloped countries (Nnorom and Osibanjo, 2008a).

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There needs to be an easy system of computer disposal to encourage users to sell or trade-in their computer products in a timely manner so they can be refurbished and used for another few years before they are transformed into raw materials (Nealson, 2015). Recycling of these items could be the last option. Back in 2010 Americans disposed about 384 million consumer electronics according to EPA (Nealon, 2015). Some of these materials contain hazardous materials such as cadmium, lead, and mercury. This is an issue because these toxics can leak from the electronic devices and enter drinking water supplies.

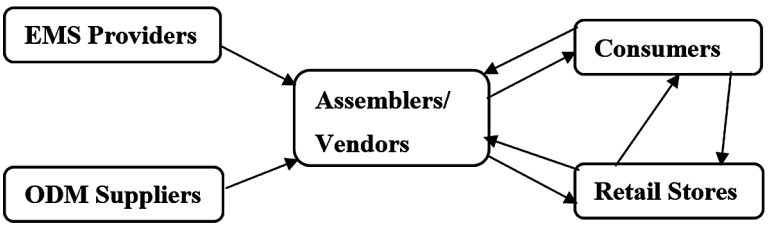
Governments of each country must promulgate required laws and enforce them strictly. The first and foremost law could be to make it compulsory that computer manufactures have to take responsibility for collecting their end-of-life items from the users. Rules and regulations need to be adopted to compel computer stores (retail, wholesale, etc.) to receive end-of-life from users. That way users are expected to deposit their end-of-life items to stores which will eventually be collected by computer manufactures to perform proper disposal such as reuse, refurbish and recycle. Manufactures have obligations to retake and dispose of. Kahhat et al. (2008) propose a solution for e-waste that will be electronically registered and tracked via a radio-frequency identification device (RFID) placed on the product." Figure 2 shows paths to return end-of-life computer products to assemblers/ vendors as part of reverse supply chain program.

Computer makers get their laptops built by contract manufacturers (CM), original design manufactures (ODM), or Electronic manufacturing services (EMS) (Akhter and Rahman, 2014). The top ten ODM companies include Pegatron, Quanta Computer, Compal Electronics, Wistron, Inventec, Lite-On Technology, Cal-Comp Electronics & Communications, Qisda Corporation, MiTAC Holdings, and Wistron NeWeb. Leading EMS companies include Foxconn, Flex, Jabil, FIH Mobile, Sanmina, Celestica, Advanced Semiconductor Engineering, Plexus, Benchmark Electronics, and SIIX. Most of these ODM and EMS companies are located in China and the rest are in other Asian countries including Taiwan.

State governments might employ auditors to audit the disposal processes of computer manufactures. This is expected to help significantly in reducing environmental emission, pollution and health hazards. It is reported that Best Buy, an electronics retailer, offers a complete appliance and electronics recycling program in America (Moss and Scheer, 2015). Best Buy offers free recycling and accepts all appliances, regardless of where they were purchased. This indeed speaks for corporate social responsibility.

To achieve sustainability individual companies, government agencies, and industry groups need to collaborate and provide recommendations on best practices, metrics, and technologies that will improve PC and data centers' energy efficiency" (Kurp, 2008). Sikder (2007) proposes considering sustainability in terms of global, regional, institutional or business, and technological sustainability systems. Global sustainability should take care of issues that involve multi-national efforts. Regional systems are meant to resolve sustainability at local level using regulatory means. The institutional or business

Figure 2. High-level flow of end-of-life PC's return to assemblers/vendors



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system should tackle multinational and local issues via legal and ethical framework of the institution or business organization. Technological sustainability systems should address sustainability concerns by product stewardship and process improvements (Sikder, 2007). Morelli (2011) suggests that achieving regulatory compliance should be the critical role of the environmental manager in industry. Research suggests that government legislation compels computer makers to take environmental sustainability efforts. Due to regulations in Australia computer makers such as Dell and Toshiba, two original equipment manufacturers entered into strategic alliance in order to reducing e-waste by implementing reverse logistics processes to end-of-life (EOL) computers (Rahman and Subramanian, 2012).

4. SUSTAINABILITY AND CONSUMER HABITS

To achieve complete sustainability in the computer industry, efforts should be made to not only make improvements in extraction, manufacturing, and distribution, reuse and recycle but also in consumption patterns. A complete ''sustainable consumption'' policy should not only include ecological but also social aspects. Purchase limit of computer products per family needs to be considered. Computer products need to be turned off when not used. It would not be enough to minimize energy consumption at production level, while allowing it unrestrained at the consumption level. Keeping computers turned on twenty-four-by-seven cause huge energy consumption. These habit needs to be changed. A social movement is needed to encourage private and public offices and individual citizens not misuse energy.

"Does technological innovation to improve the efficiency of energy-using products and systems lead to lower energy consumption and hence reduced environmental impacts? The answer given by economists since the mid-19th century is 'no'" (Herring and Roy, 2007). This means that energy consumption reduction efforts by PC makers is not enough. Similar effort needs to be made from consumer side as well to make sure computers are not turned on unnecessarily and thus avoid excessive energy consumption. PC makers' promoting technical innovation to reduce energy consumption and emissions will be defeated unless consumers show certain degree of responsibility and sustainability measures. Experts in this field suggest that other policies such as taxation or regulation are required (Herring and Roy, 2007; Zaccai, 2008).

In 1994, at a Norwegian government hosted symposium on 'sustainable consumption' Gro Harlem Brundtland reported in her keynote address that: "An average person in North America consumes almost 20 times as much as a person in India or China, and 60 to 70 times more than a person in Bangladesh. It is simply impossible for the world as a whole to sustain a Western level of consumption for all." (Meadows et al., 2004).

"Capitalism, notoriously, depends on the creation of new desires and new markets for its dynamic." (Meadows et al., 2004). Kopnina (2016) observed that, "environmental unsustainability is due to both structural features and historically specific characteristics of industrial capitalism resulting in specific patterns of production and consumption." The author also reported that sustainability literature is critical of the established corporate and political power hegemonies that are interested in maintaining economic growth, but on the other hand individual citizen-consumers are compromising with that by virtue of not taking counteract measures or being ethical enough to address unsustainability (Kopnina, 2016). Suki (2015)'s research findings based on a survey in Malaysia found consumers are supportive of environmentally sustainable products or green products.

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Panchal and Moschandreas (2015) emphasize that public literacy is an important factor of sustainable development. They identify three domains of responsibility for sustainability: global responsibility (national governments) local responsibility (state, city or municipality governments), and individual responsibilities (individual citizens, non-experts). In regards to individual responsibility the authors assert that, sustainability is not all about technology and regulations. Regulators and scientists alone cannot achieve global sustainability. Non-expert individuals, the majority of citizens, must be drawn in to understand their responsibilities and act accordingly (Panchal and Moschandreas (2015).

El Idrissi and Corbet (2016) propose the idea of modernity perspective of green IS research in which one of the patterns includes the importance of individuals' participation in solving environmental sustainability issues. The authors suggest that, "individuals' comprehension of the impact of their behavior is as important factor in moving toward a more sustainable future." Foth et al. (2009) compare environmental responsibility into issues of personal moral choice which should start at the point of consumption (for example, in the supermarket). An organizational level consumption should be measured and be compliant with sustainability. For example, "Intel IT is engaged in developing a broad, ongoing sustainability strategy to help Intel consume fewer resources and emit less waste" (Wellsandt and Snyder, 2009). Intel also developed a sustainability framework and defined a set of metrics to measure and help ensure success with addressing consumption and waste, setting challenging goals, redesigning business processes, and encouraging participation (Wellsandt and Snyder, 2009).

5. CONCLUDING REMARKS

Computer industry has an important role to play in achieving environmental sustainability given that desktop and laptop computers use huge material and energy resources. The computer industry needs to take a holistic approach in reducing environmental footprints. In this paper, we elaborated the energy and material consumption and e-waste aspects of computer products. We have pointed out that computer design and manufacturing need to be done with technological innovation and efficiency. The manufacturing of computer devices significantly contributes to environmental pollution. Each of the manufacturing phases needs to adopt energy efficient design and reusability measures. Computer products need better design to ensure less raw material usage and judicious use of natural resources. Computer designs need to address issues of energy consumption and carbon emission. To achieve ecological sustainability the design aspects of computers need to be continuously evaluated.

The computer industry must embrace different measures to reduce the global carbon dioxide emissions. Consumers must recycle and/or dispose of computer products appropriately. Regulation of recycling and proper disposal system must be adopted by the governments to prevent e-waste. All kinds of e-waste exports from developed countries to developing countries must be banned. Laws could be enacted to make it compulsory for computer manufactures to take responsibility for taking back end-of-life items from the users.

The computer makers need to work towards a sustainability portfolio (Hart, 1997) that takes clean technology into consideration, achieve major improvements through new technology, prevent significant waste and emission streams from existing operations and reduce costs and risks by eliminating wastes in source and manufacturing processes. The computer industry needs to have a vision to solve sustainability issues in terms of lowering hazardous waste, preventing natural resource depletion and decreasing toxicity

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potentials from heavy metals (Son et al., 2016). They need to maintain a stewardship in product design and all phases of product's life cycle. The responsibility to ensure sustainability falls on the shoulder of the computer industry. At the same time consumption patterns also needs to move toward sustainability.

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Chapter 66
Remanufacturing, an Added Value Product Recovery Strategy

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ABSTRACT

Organizations offer a variety of products to the market with affordable prices. The popularity of a product rapidly disappears with the introduction of a new one and consequently end-of-life products and waste disposal rates increase. In the past, there were not strict regulations and sufficient public awareness about the disposal of products. Companies had limited concern for the consequences of their products sold. Nowadays there are economical and environmental motivations for organizations to look for alternative ways to value their end-of-life products. For that reason, alternative means of disposals of these products such as recycling, direct reuse, repair, refurbishing, and remanufacturing have growing attention. Among these only in remanufacturing used products are brought at least to the original equipment manufacturer performance specification. Worn-out parts are removed and replaced. It conserves the product identity and seeks to bring the product back into like-new condition. In this chapter the features of remanufacturing is presented.

INTRODUCTION

Green production and resource efficient systems are major issues today. Scarce resources make organizations look for alternative ways to value end-of-life products and turn waste into a resource. Alternative product recovery options have growing attention. In the past there were no regulations and public concern about the end-of-life products, firms did not feel any obligation for the consequences of the products after sold to customers. Today, both customers and authorities make firms to be concerned about their used products. Cost reduction is always a reason for change and to look for new methods but today product recovery has been receiving growing attention not only because of cost reduction and value recovery from the used products but also regulations, consumer awareness, social responsibilities and environmentally consciousness. These days better environmental image is important for organizations due to consumer awareness. Intending to reduce the needs for raw materials and energy in production,

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recovered products are good for business, for customers, and for the environment. In addition, because it integrates waste back into the manufacturing cycle, it is also a method for avoiding waste limitation penalties (Subramoniam et al, 2013).

Defined product or component recovery options in the literature are: Recycling, direct reuse, repair, refurbishing, and remanufacturing (Thieery et al., 1995; Oh & Hwang, 2006; King et al., 2006a). Each of the recovery options involves collection of used products and components, reprocessing, and redistribution (Thiery et al., 1995).

- **Recycling:** Series of activities by which discarded materials are collected, sorted, processed and used in the production of new products (King et al., 2006a). In recycling, the identity and functionality of products and components is lost. The purpose of recycling is to reuse materials from used products and components (Thieery et al., 1995).
- **Direct Reuse:** No components or materials are replaced. Products are reused directly or after minor maintenance and cleaning.
- **Repair:** Damaged parts are replaced or upgraded to working order (Tang & Naim, 2004). It is the correction of specified faults in a product. The quality of the repaired product is inferior compared to remanufactured and refurbished products (King et al., 2006a). It usually requires only limited product disassembly and reassembly (Thierry et al., 1995).
- **Refurbishing:** Used products are disassembled into modules then all critical modules are inspected and fixed or replaced. Approved modules are reassembled into refurbished products. The purpose of refurbishing is to renovate and bring used products up to specified quality where quality standards are less precise than those for new products (Thierry et al., 1995).
- **Remanufacturing:** In remanufacturing used products are completely disassembled and all modules and parts are extensively inspected (Thierry et al., 1995). Worn-out parts are removed and replaced to bring the quality standard of final product to like-new condition. It conserves the product identity and seeks to bring the product back into like-new condition by carrying out the necessary disassembly, overhaul, and replacement operations (Oh & Hwang, 2006). It preserves most of the added value by giving a second life to the product and reduces the use of energy by eliminating production steps (Bernard, 2011). It is the only product recovery method where used products are brought at least to the original equipment manufacturer performance specification (King et al., 2006a). See Table 1 for different characteristics, and main differences between the product recovery options.

Table 1. Comparison between product recovery options (Thieery et al., 1995)

	Level of Disassembly	Quality Requirements	Resulting Product
Repair	To product level	Restore product to working order	Some parts fixed or replaced by spares
Refurbishing	To module level	Inspect all critical modules and upgrade to specified quality level	Some modules repaired/replaced; potential upgrade
Remanufacturing	To part level	Inspect all modules and parts and upgrade to as new	Used and new modules/parts combined into new product; potential upgrade
Recycling	To material level	High for production of original parts; less for other parts	Materials reused to produce new parts

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Repair, refurbishing, and remanufacturing upgrade used products in quality and/or technology. These options differ with respect to the degree of upgrading. Repair involves the least upgrade while remanufacturing involves the most (Thierry et al., 1995). Repair returns a used item to working order. Refurbishing brings an item up to a specified quality while remanufacturing brings an item up to a like-new quality (Teunter, 2001a). Remanufacturing is distinctly different from repair and refurbishing operations, since products are disassembled completely and all parts are returned to like-new condition. Remanufacturing focuses on added value recovery, rather than just materials recovery (recycling) (Guide, 2000). There is a major distinction between material recovery (recycling) and added value recovery (remanufacturing) (Kenné et al., 2012). Selecting the most advantageous product recovery option depends on (Thierry et al, 1995): (1) Technical feasibility; (2) Supply of suitable used products and components; (3) Demand for reprocessed products, components, or materials; (4) Economic and environmental costs and benefits.

The concept of product recovery is not new, and remanufacturing has been more and more common industrial activity since the Second World War. However, after the late 1970s interest in remanufacturing as an academic research topic began to emerge with Prof. Robert Lund's original studies of the remanufacturing industry (Hatcher et al., 2011). Gungor and Gupta (1999) later Ilgın and Gupta (2010) present a comprehensive summary of the environmentally conscious manufacturing and product recovery literature. They organized the literature into four main areas: (1) Product design; (2) Reverse and closed-loop supply chains; (3) Remanufacturing; (4) Disassembly. Also Fleischmann et al. (1997) review the extant literature and their paper is one of the most cited review paper in the field of product recovery. They subdivided the field into three main areas: (1) Distribution planning; (2) Inventory control; (3) Production planning.

OECD and Eurostat defines eco-industries as: *Activities which produce goods and services to measure, prevent, limit, minimize or correct environmental damage to water, air and soil, as well as problems related to waste, noise and eco-systems. This includes technologies, products and services that reduce environmental risk and minimize pollution and resources*. The estimated total turnover of eco-industries in the EU is €227 billion. The largest national markets for eco-industries are France and Germany which make 49% of total turnover in 2004. The three following countries are UK, Italy and the Netherlands that make 24% (EU, 2006). Based on this definition remanufacturing is part of the eco-industry.

OECD began to work on a program called Extended Producer Responsibility (EPR) in 1994 which is an environmental policy approach under which the responsibility of producers for their products is extended to the stage where products get to its end-of-life. EPR is applied both to industrial wastes and to packaging and post-consumer waste (OECD, 2001; Smith, 2005; OECD, 2014). The goal of EPR program is (OECD, 2014): (1) Increased collection and recycling rates; (2) Reduction of public spending on waste management; (3) Reduction in overall waste management costs; (4) Design for environment innovations. It is increasingly recognized worldwide as an efficient waste management policy to help improve recycling and reduce land filling of products and materials. Producers assume responsibility for managing the waste generated by their products put on the market. Since its first developments in the early 1990s, it has contributed to significant increases in recycling rates and reductions on waste management cost in many countries (OECD, 2014).

Two features of EPR is (OECD, 2001): (1) Producers of products should take responsibility (physical and/or financial) from government or municipal units; (2) To provide incentives to producers to consider environment from design to disposal stages of their products. The ultimate objective is to reduce the amount of landfill and hazard caused by the end-of-life products. In order to realize these objectives, policy makers have a range of policy instruments. There are four broad categories of EPR policy instru-

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ments (OECD, 2014): (1) Product take-back requirements: Take-back policies require the producer or retailer to collect the product at the post-consumer stage; (2) Economic and market-based instruments: These include measures such as deposit-refund schemes, advanced disposal fees, material taxes, and upstream combination tax/subsidy that incentivize the producer to comply with EPR; (3) Regulations and performance standards: Such as minimum recycled content. (4) Accompanying information-based instruments: These policies aim to indirectly support EPR programs by raising public awareness.

Under conventional waste management practices for household wastes, the collection and disposal of end-of-life products is typically under the responsibility of local or municipal governments, and the cost is somehow charged to households. In comparison with this conventional system of waste management, EPR involves a number of distinctive differences (Smith, 2005): (1) EPR shifts direct financial responsibility (fully or partially) for the costs of waste management upstream to the producer, and away from the municipality and taxpayer; (2) EPR often involves the producer in some physical aspects of waste management (such as waste collection, or the management of collective waste management organizations), in addition to its financing; (3) EPR is designed to make the producer deal with the costs of end-of-life disposal of their products, and thereby to make the producer to take account of these future costs while designing and marketing their products.

When products can be freely discarded by consumers without any responsibility and waste management costs are carried by municipalities, producers can design and market products which will have high end-of-life future waste management costs. Requiring producers to carry financial responsibility for the end-of-life products can make them produce and market products that will have low end-of-life waste management costs. Producers who can reduce these costs may benefit in higher profits or in higher market share if they can reduce their selling prices relative to their competitors (Smith, 2005). Many EPR programs in operation have three common elements (Smith, 2005): (1) Physical or financial obligations on the producer concerning the collection (take-back) of product packaging or end-of-life products; (2) Responsibility for the costs of proper waste management of the collected products and materials; (3) Rules or targets conducting the policy, actions, affairs, and methods of waste management of recovered products, for example specifying minimum required rates of reuse or recycling.

OECD began to work on EPR program in 1994 and in 2001 published a guidance manual for conducting the policy, actions, and affairs on EPR that provides the key issues, general considerations, and the potential benefits and costs associated with EPR. Most OECD countries have now implemented EPR policies in key sectors such as packaging, electronics, batteries, and vehicles. Certain emerging economies in Asia, Africa, and South America have also started to develop EPR programs in recent years. EPR is an effective policy instrument to engage producers in going for green growth and a resource efficient economy (OECD, 2014).

EPR requirements first appeared in policy and law in the early 1990s in several European countries, including Germany, Sweden, and France. Today, EPR programs have spread and developed rapidly around the world. Policy makers in OECD and emerging economies are now implementing EPR policies as an efficient target oriented environmental tool along with traditional instruments and regulations such as landfill taxes or emission standards for waste treatment facilities (OECD, 2014).

The current status of EPR applications in the world is as follows (OECD, 2014): At the *EU* level, all member countries have implemented EPR schemes on the four waste streams: Packaging, Batteries, End-of-Life Vehicles, and Electrical and Electronic Equipment. In addition, a number of member countries have put in place additional schemes for products like tyres, graphic paper, oil, and medical waste that are not directly addressed in EU-wide legislation. In the US and Canada, EPR programs cover a wide

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group of products and the rules and regulations are set and implemented by states and provinces. In the US, there is no federal law governing EPR so that individual states have developed and implemented their own policies depending on local conditions and each state's specific political dynamics. Between 1991 and 2011, US states have performed more than 70 EPR laws, which generally require manufacturers to implement EPR programs. In parallel, producers have themselves implemented voluntary programs to organize the collection and recycling of their products. In Latin America and the Caribbean, several countries including OECD members Chile and Mexico, as well as Brazil, Argentina, and Colombia have implemented their first EPR schemes in recent years, in particular covering the large markets for potentially hazardous electronic waste market. The current situation of EPR in Asia varies significantly across countries and between OECD and non-OECD members. Industrialized OECD economies like Japan and the Republic of Korea have already well established EPR schemes and regulations on the key waste streams, supported by a solid monitoring and enforcement framework. Some rapidly emerging economies, such as the People's Republic of China, India, and Indonesia have started to develop EPR programs even though these are generally not yet fully implemented and functioning.

Apart from OECD's EPR program, in the US many of the electronics companies have voluntary take-back programs. Having a voluntary program means offering take-back and recycling options even when there is no law requiring it. Some of the examples from the industry are (electronicstakeback.com)**:** Acer let customers drop off old Acer products at collection points operated by third party collector, and they reimburse the collector for the costs of collection, transportation, and recycling. This is an example of retailer/manufacturer partnership. Apple has a trade in program for working iPhones, iPads, and Mac or PC desktop and notebook computers. If item has any reuse value, customers can send it to Apple and have an Apple gift card in return. This program is run by a third party organization. Besides, Apple takes any brand of computer and monitor for free recycling. The program works with third party recycling company. Customers get no gift or discount in return for non-Apple products but make their end-of-life products recycled for free shipping. Apple also accepts iPods for recycling in their stores and customers get a 10% discount towards a new one. Customers can also mail back iPods and cell phones (any brand) for free without any discount coupon or trade in value. Asus has a mail-back recycling program for free shipping contracting with third party recycling company. Dell takes back Dell product for free shipping. HP is working with third party organization for collecting used products. Customers can take back many products to any location of the company in the US. HP also has a mail-back program for free recycling and shipping for HP products. Customers can also ship non-HP products, but it's not for free. They also offer free recycling and free shipping of used toner or inkjet cartridges. Canon has a mail-back take-back program for all of their consumer products and some of small office/home office product lines. But it is not for free. Kodak offers a mail-in trade-in/recycling program for its used printers, cameras, and lenses. The program works with a third party recycler. Lenovo has a free mail-back recycling program for Lenovo equipment, including free shipping. LG's program includes take-back of some TV types. To recycle an LG TV for free, customers can drop off products at LG's designated collection sites. The program works with a third party recycler. Microsoft partners with Dell's reconnect program to offer collection sites for recycling Microsoft products. Microsoft also has a mail-back take-back program for its Xbox games, consoles, computer accessories, and Zune players for free shipping. Xerox has a mail-back recycling program, but shipping is not for free. Toshiba takes back laptops and other smaller electronics using a third party company which allows customers to trade in their products for cash. Customers pay to ship them to company, and if products have value, company sends customers a check in return. To recycle Toshiba TVs and other larger Toshiba electronics for free, customers

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have to take them to one of the collection sites operated by third party recycling program. To recycle Samsung Televisions, Digital Cameras, Camcorders, Home Theater, Blu-ray and DVD players, printers, monitors, notebooks for free, customers must take them to one of Samsung's recycling locations. The program works with a third party recycler. Panasonic has laptop recycling and reuse program with shipping cost. Also old laptop may have a trade in value while buying a new one. To recycle Panasonic TVs or other Panasonic consumer electronics for free, customers must take them to one of the collection sites operated by the third party recycling program. Mitsubishi participates in third party operated recycling system. To recycle a Mistubishi TV for free, customer must drop it off at a designated collection site.

The rest of the chapter is organized as follows. In Section 2, reverse logistics is defined. In Section 3 remanufacturing industry is described. In Section 4 the production system with remanufacturing included which is called hybrid manufacturing/remanufacturing system is described and different policies used are defined within the system. In Section 5 the paper is concluded with final remarks.

REVERSE LOGISTICS

Collecting and recovering products leads to numerous complicated logistical activities. In the literature these backward activities is called Reverse Logistics (RL) which is a broader term and encompasses collection, transportation, inspection and sorting, inventory management, and production planning and scheduling of returned products. Logistics is defined by The Council of Logistics Management as (Rogers & Tibben-Lembke, 1998): *The process of planning, implementing, and controlling the efficient, cost effective flow of raw materials, in-process inventory, finished goods and related information from the point of origin to the point of consumption for the purpose of conforming to customer requirements*. RL includes all of the activities that are mentioned in this definition above. The difference is that reverse logistics encompasses all of these activities as they operate in reverse. Therefore, RL is (Rogers & Tibben-Lembke, 1998): *The process of planning, implementing, and controlling the efficient, cost effective flow of raw materials, in-process inventory, finished goods and related information from the point of consumption to the point of origin for the purpose of recapturing value or proper disposal*. More precisely, RL is the process of moving goods from their typical final destination for the purpose of capturing value, or proper disposal. Product recovery is a part of RL. It is clear that the overall amount of RL activities in the economy is large and still growing. See Table 2 for common RL activities.

In the literature there are two categories of reverse logistic systems (Kenne et al, 2012): Open and closed-loop, depending on whether the return operations are integrated or not with the initial operation. Also there are four basic types of returns (Östlin et al., 2008): (1) End-of-Life Returns: These are returns that are taken back from the market to avoid environmental or commercial damage. These used products are often returned as a result of take-back laws; (2) End-of-Use Returns: These are used products or components that have been returned after customer use. These used products are normally traded on an aftermarket or being remanufactured; (3) Commercial Returns: These returns are linked to the sales process. Other reasons for the returns include problems with products under warranty, damage during transport or product recalls; (4) Re-Usable Components: These returns are related to consumption, use or distribution of the main product. The common characteristic is that they are not part of the product itself, but contain and/or carry the actual product.

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Table 2. Common RL activities (Rogers & Tibben-Lembke, 1998)

Material	RL Activities
Products	Return to Supplier
	Resell
	Sell via Outlet
	Salvage
	Recondition
	Refurbish
	Remanufacture
	Reclaim Materials
	Recycle
	Landfill
Packaging	Reuse
	Refurbish
	Reclaim Materials
	Recycle
	Salvage

Savaskan et al. (2004) consider three options for collecting returned products: (1) One can collect them himself directly from customers, for instance Xerox corporation provides prepaid mailboxes so that customers can easily return their used copy or print cartridges to Xerox without incurring any costs. The company also remanufactures copiers. The used copiers are collected directly by Xerox as new ones are installed; (2) One can provide suitable incentives to an existing retailer (who already has a distribution channel) to make the collection. For instance Kodak Company receives single use cameras from large retailers that also develop film for customers. Each time a camera is returned to Kodak the retailer is paid a fixed fee per camera and the transportation costs; (3) One can subcontract the collection activity to a third party. In the auto industry, independent third parties are handling used product collection activities for the original equipment manufacturers.

RL has received considerable attention due to potentials of value recovery from the used products. Besides, legislations and directives, consumer awareness and social responsibilities towards environment are also the drivers for RL. Research on RL has been growing since the Sixties. The RL activity that has attracted most attention of the researchers is inventory management. Starting from repairable item inventory management in the 1960s, a lot of research effort has been put in so far for managing inventory of recoverable products and components (Mitra, 2007). Research on strategies and models on RL can be seen in the publications in and after the Eighties. The focus on RL is on waste management, material recovery through recycling, parts or product recovery through refurbishing or remanufacturing (Pokharel & Mutha, 2009).

Not all reverse supply chains are identical. However, most return supply chains are organized to carry out five key processes (Blackburn et al., 2004): (1) Product acquisition: Obtaining the used product from the user; (2) RL: Transporting the products to a facility for inspecting, sorting, and disposition; (3)

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Inspection and disposition: Assessing the condition of the return and making the most profitable decision for reuse; (4) Remanufacturing: Returning the product to original specifications; (5) Marketing: Creating secondary markets for the recovered products.

REMANUFACTURING INDUSTRY

Ebersole (1997) states that the symbol of 20th century industry was the assembly line, the symbol of 21th century industry may be the disassembly line. Many organizations like Xerox Co. and Eastman Kodak Co. design products not only for assembly but also for disassembly. Xerox remanufactures many parts and machines each year. Kodak collects millions of single use cameras, microfilm machines, photographic film base, etc., each year from different countries for remanufacturing. During the Second World War the remanufacturing industry increased, especially in the US since many manufacturers were focusing on military production (Östlin et al., 2008). Most developed countries have environmental regulations for manufacturers, generators, and users of chemicals regarding properly dispose of chemical wastes. In the mid-1980s this was commonly known as *cradle-to-grave* resource management. Today, modern environmental management makes sustainable manufacturing practices focusing on recovery of resources, recycling, and reuse which can be described as *cradle-to-cradle* resource management (Kumar & Putnam, 2008). Remanufacturing studies have increased after the 1980s, and researches have been studying on this subject since then (Sasikumar et al., 2010).

Environmental legislation is becoming increasingly strict, particularly in Europe. There are recent developments such as the Waste Electronics and Electrical Equipment (WEEE) and End-of-life Vehicle (ELV) directives and standards such as Germany's VDI 2243 and the UK's BSI 8887, Japanese Specified Home Appliances Recycling Law (SHARL), Japanese PC Recycling System, and state specific e-waste take-back programs in twenty four states in the US (Esenduran et al., 2012; Hatcher et al, 2011). Companies can meet these legislations with remanufacturing effectively in a profitable manner.

A material recovery system which may be named as a recoverable product environment, includes strategies to increase product life by means of: Repair, refurbishing, remanufacturing, and recycling of products. A major part of the recoverable product environment is the recoverable manufacturing system that focuses on the repair, refurbish, and remanufacture of products (Guide et al., 1997a). These systems are economic, environmentally friendly, and designed for sustainable development. Recoverable manufacturing is an economical way to achieve many of the goals of sustainable development. Recoverable manufacturing systems minimize the environmental impact of industry by reusing materials, reducing energy use, and reducing the need to landfill industrial products (Guide et al., 2000). A recoverable system is essentially a closed-loop industrial system with discarded items used in place of virgin materials as much as possible. While these systems are more complex to manage than traditional systems, the rewards for organizations are correspondingly higher (Guide et al., 1997b).

Remanufacturing is environmentally conscious and efficient as it aims to use less energy and materials compared to traditional manufacture with new raw materials. Since end-of-life materials are taken back the amount of landfill is decreased. Remanufacturers are a well doing and valuable set of companies. They create economic value in micro and macro level. Top remanufacturers are characteristically flexible and adaptable. Many need a wide skill set which can be hard to find. Workers in these businesses

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more often find their work motivating and interesting. They need to be capable of: Sourcing end-of-life products (cores), inspection and classification on arrival, disassembly, component testing, remediation, repair or replacement, re-assembly, assembly, testing, and dispatch (remanufacturing.org.uk).

Remanufactured products are cheaper than the traditionally manufactured products. Remanufacturing is practiced in many industries including photocopiers, computers, telecommunication equipment, automotive parts, office furniture, and tires. The actual process of remanufacturing is generally less expensive than producing a new product as many parts and components can be reused (Ferguson, 2009). The cost of remanufacturing is typically 40% to 60% of the cost of manufacturing a new product with only 20% of the effort. This is nice when the remanufactured product is in like-new condition and can be sold with warranty (Mitra, 2007). A remanufactured product can be sold for 45% to 60% of the price of a new one (Lund, 1996). In their recent studies Lund and Hauser (2010) state that they know of 113 product areas in which remanufacturing occur in the US. The major product areas are motor vehicle parts, electrical motors and generators, pumps, transformers, laser toner cartridges, industrial machinery, tires, industrial valves, and office furniture. The price of a remanufactured product is normally between 45% and 65% of the price of a comparable new product.

According to Kerr and Ryan (2001) sustainable production and consumption is only possible with closed loop systems in which resources are recovered from the used products. However, a system that closes the loop through recycling is less environmentally and economically efficient since in each stage of a closed recycling system energy is expended. Returning and reusing manufactured components or subcomponents rather than recycled raw materials is much more efficient. Remanufacturing is also preferable in comparison with other product recovery options, since the geometrical form of the product is retained and its associated economic and environmental values are preserved (Östlin et al., 2008).

There are various motives for product remanufacturing (Seitz & Peattie, 2004): Increased profitability, ethical responsibility, legislation, secured spare part supply, increased market share, and brand protection. Ferguson (2009) states that if a firm does not choose to remanufacture it may lose its environmentally conscious customers. Firm can find itself facing costly regulatory restrictions and government disposal fees in the future. This is already occurring in the electronics and automotive industries. One regulation requires a certain percentage of each automobile be recyclable (EU End-of-Life Vehicle Directive). Other regulation forces the electronic equipment producers to fund the take-back and proper disposal of their products (WEEE Directive).

Xerox Corporation, a global company offering products and services in printing business, is the pioneer company in remanufacturing. According to Kerr and Ryan (2001) Xerox has one of the most widely reported remanufacturing systems. It has recovered used equipment since the 1960s, but developed a more formal remanufacturing system in the late 1980s and early 1990s to maximize the profitability of remanufacturing operations. Today, by remanufacturing used photocopiers, Xerox has saved millions of dollars in raw material and waste disposal costs. It remanufactures used photocopiers and print and toner cartridges all around the world. It has remanufacturing facilities in the US, UK, Netherlands, Australia, Mexico, Brazil, and Japan, which helped Xerox to enhance its image as an environmentally conscious company. The integration of remanufacturing into the company's overall business strategy has also been critical to Xerox's success. Ferguson (2009) states that in 1991 Xerox obtained savings of around $200 million by remanufacturing copiers returned. Equipment remanufacture and the reuse and recycling of parts prevent millions of pounds of waste from entering landfills each year, 48,000 metric tons in 2008 alone (xerox.com). Xerox routinely offers new, newly manufactured, remanufactured, and certificated repaired versions of their products (Atasu et al., 2010). According to Murray (1995) Chairman and

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Chief Executive Officer of Xerox Corporation states that *environmental protection is considered by people from around the world to be one of the most critical issues of the 1990s. Xerox shares the public's concern about the environment and has integrated that concern into their business activities, making environmental values a key part of the Xerox corporate culture*.

On the other hand, there are other global companies that remanufacture. Ferguson (2009) presents three examples: Kodak is one of the classic examples of an original equipment manufacturer that has created a fully integrated manufacturing and remanufacturing strategy around its reusable camera line. Caterpillar is changing its strategy from only manufacturing and selling construction equipment to a leasing and remanufacturing strategy. This allows Caterpillar to create a new market among contractors who cannot afford to buy a Caterpillar product but prefer leasing. Caterpillar established a remanufacturing division that sells both equipment and parts. In 2007, this division had over $2 billion in sales and was the fastest growing division out of all Caterpillar's divisions. In 2007, the Global Asset Recovery Solutions division of IBM collected over one million units of used information technology equipment that was converted to billions of dollars in revenues on the second hand equipment, parts, and materials markets. According to Atasu et al. (2010) the imaging and printer group at Hewlett Packard (HP) has various contracts with third party remanufacturers and logistics providers to recover some of the costs associated with the substantial volumes of commercial returns from its inkjet printer lines. HP practices product recovery primarily to be good corporate citizen and as a way to avoid the environmental burden from land filling the returns. Reduced production cost also attracts independent remanufacturers (IRs). In 2005, IRs represented 54% of the aftermarket for automotive parts in Europe and 66% worldwide (Bernard, 2011).

Auto parts are the most remanufactured materials in the world. Up to two-thirds of remanufacturing businesses globally is estimated to involve auto parts. The remanufactured auto parts primarily include engines, turbo chargers, alternators, starters, compressors, transmissions, and steering units (Matsumoto & Umeda, 2011). Bernard (2011) states that alternators and starters represent 80% of remanufactured auto parts. Valeo and Bosch are two important alternator producers in Europe. They started remanufacturing activities in the early 1990's. Remanufacturing process requires a lot of handling (dismantling, sorting, cleaning, etc.), the removal of the hazardous content is a technological constraint that has made alternator remanufacturing commercially viable. In its lifetime, the same car goes through two or three alternators. Remanufactured alternators and starters cover more than 90% of the replacement market. They are produced with less cost compared to the original one: On average they require 14% of the energy and 12% of the material necessary for the production of new ones. In the alternator industry, more than 90% of the aftermarket is filled with remanufactured products.

Bourgeosi (2004), research associate in Renault Trucks, states that remanufactured parts (labeled Renault 100%) accounted for 16% of Renault Trucks' parts revenues in 2001. Remanufactured parts provide vehicle owners with a low cost, like-new replacement component, and added benefit of environmental consciousness. The most advantage of a remanufactured part over an original one is its price. For most components of Renaults Trucks, remanufactured versions are 30% to 50% cheaper. Remanufactured components, especially engines, often benefit from recent technology upgrades, which sometimes make them more efficient than the original component. Remanufacturing is quicker than rebuilding and provides cost savings over purchasing a new part. In 2000 Renault remanufactured parts turnover had reached $64 million (170000 units) with a product margin of $19 million. To compare, Renault trucks' turnover from its total parts business in 2000 was $488 million, with a product margin of $192 million.

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Lund and Hauser (2010) state that the remanufacturer not only competes with other remanufacturers, but is increasingly in competition with lower-priced new products, often imports. Robert Bosch Tool, North America offers remanufactured versions of its Bosch and Skil products. In addition to variety of reasons including cost saving, remanufacturing is also a way to reach customers who would not buy expensive new products but buy lower priced remanufactured version. With the price advantages coming with remanufacturing, company can compete with inexpensive imports. Bosch managers consider remanufacturing to be a core part of the business (Atasu et al., 2010). Kerr and Ryan (2001) attempt to quantify the life cycle environmental benefits achieved by incorporating remanufacturing into a product system, based on a study of Xerox photocopiers in Australia. The study finds that remanufacturing can reduce resource consumption and waste generation over the life cycle of a photocopier by up to a factor of three. They claim that reductions will be greater if a product is designed for disassembly and remanufacturing.

In the UK the range of products that are being remanufactured includes (remanufacturing.org.uk): Machine tools, electrical motors and compressors, starter motors, automatic transmissions, car and truck engines, office photocopiers, excavation equipment, power bearings, defense equipment, computer and telecoms equipment, air-conditioning units, pumps, industrial food processing equipment, aerospace, carpet tiles, and rolling stock. Lund and Hauser (2010) state that remanufacturing enterprises exist in a number of different forms. They have defined three categories to encompass all forms: (1) Conventional firms: They purchase cores, remanufacture them and sell them to new owners; (2) Contract firms: They agree with the owner of a product to remanufacture it and return it to the owner; (3) Original Equipment Manufacturers: They are manufacturers of a product who also remanufacture their product for resale. Original Equipment Manufacturers typically sell their remanufactured products through their dealer networks. Conventional remanufacturers may sell directly to individual customers, through distributors, or through retailers. Contract remanufacturers may provide products to individual owners. They may sell to customers with fleets, such as trucking companies (tires), airlines (engines), or banks (printers).

Matsumoto and Umeda (2011) investigate Japanese remanufacturing industry which is an important player in this sector and provide valuable information: Japanese remanufacturing practices are advanced in some product areas like photocopiers and single-use cameras, and lagging in fields like auto parts. Three major OEMs of photocopy machines in Japan are Fuji Xerox, Ricoh, and Canon. They account for about 90% of Japan's photocopier market and they are remanufacturing their used products. Fuji Xerox started remanufacturing in 1990s, and Ricoh and Canon began selling remanufactured machines in the 2000s. In Ricoh, 93% by weight of a typical remanufactured photocopy machine is composed of reused parts, its price is 30% to 50% of a new product, and profits from remanufactured machines are larger than those from newly produced machines. In Fuji Xerox's remanufacturing process, reused components are incorporated in new products. Thus, all products may include reused components and there is no distinction between new and remanufactured products. However Xerox in the US and Europe remanufactured products are distinguished from new products like in Ricoh and Canon.

Remanufacturing of single-use cameras is very common. Single use cameras began to appear in 1986 and in 1987, OEMs began to collect used products and recycle them. Fuji Film, Kodak, and Konica are the major Japanese camera OEMs. Fuji Film developed an automated production line for single-use cameras in 1992 and work on product designs that enabled recycling and remanufacturing. In 1998, it developed a remanufacturing line that fully automated all processes of product disassembly, parts cleaning, parts inspection, parts replenishment, reassembly, and final testing. The company reports that they reuse or recycle more than 82% by weight of all camera components.

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In Japan, 200 million ink cartridges are sold annually, primarily for use in personal printers. Remanufactured cartridges account for 15 million in sales. Ecorica, an independent remanufacturer (IR) founded in 2003, is Japan's largest ink cartridge remanufacturer, shipping approximately 10 million remanufactured products annually. Ecorica collects used cartridges from end-users, and remanufactures and sells them. 30 million toner cartridges are sold annually in Japan, mainly for office printers, 5 to 6 million of them are remanufactured. There are a number of independent toner cartridge remanufactures; 33 IRs formed the Association of Japan Cartridge Remanufacturers, and member companies account for 90% of remanufactured toner cartridges sold in Japan. Some OEMs do remanufacturing of printer cartridges. But most of remanufacturing in the product areas is done by IRs, and OEMs generally respond negatively to such activities by IRs as they earn most of their profit from selling ink and toner cartridges. Recently, OEMs began to recover used ink cartridges. Six OEMs, Epson, Canon, Hewlett-Packard, Brother, Dell, and Lexmark, collaborated to collect used ink cartridges. However, since remanufacturing ink cartridges costs more than manufacturing new cartridges, OMEs are not active remanufacturers but recycle the collected cartridges.

Ferguson (2009) states that despite all of these benefits from remanufacturing, most firms continue to ignore any remanufacturing or reuse of their used products. Many original equipment manufacturers spend the majority of their time and resources focusing on their new product sales, and thus simply not consider remanufacturing as a viable business model. Even some original equipment manufacturers that seriously consider remanufacturing may also do not remanufacture because they do not feel that they have the infrastructure and expertise to collect the used units and remanufacture them in a profitable manner. There are often significant costs associated with the logistics of remanufacturing.

Not all products are suitable for remanufacture. For example, if technology changes very quickly, or fashion causes a high turnover of designs and styles, or if the product is durable but basic, then remanufacturing will be hard to justify. Under these circumstances consider the role of secondary markets (remanufacturing.org.uk). Remanufactured products usually have shorter lead times. However, the high variability of remanufacturing operations makes the use of traditional operations management techniques difficult (Ilgın & Gupta, 2010). Individual repair requirements for every product returned, and coordination of several interdependent activities makes production planning complicated. Comparing to traditional manufacturing systems, no well-determined sequence of production policies exist in remanufacturing (Kenné et al., 2012). Labor is the major factor in remanufacturing, ranging from 34% to 45% of product cost. The cost of cores is an important cost factor, but for most companies it is lower than the cost of replacement parts and other materials needed to bring products to like-new condition (Lund & Hauser, 2010).

Guide (2000) reports on managerial remanufacturing practices via a survey of production planning and control activities at remanufacturing firms in US and identify seven complicated characteristics of remanufacturing: (1) Uncertainty in the timing and the quantity of returns; (2) Balancing returns with demands; (3) Disassembly; (4) Uncertainty in materials recovered; (5) Reverse logistics; (6) Materials matching requirements, (7) Routing uncertainty and processing time uncertainty. These uncertainties make resource planning, scheduling, shop floor control, and material management more difficult than in traditional manufacturing environments. Production planning in a remanufacturing system environment is very complex especially with uncertainties (Kenné et al., 2012). King et al. (2006b) explain and illustrate the process Xerox uses at its United Kingdom factory to return old photocopiers to a like-new product. They state that although Xerox has made a profitable business from remanufacturing, there are many barriers to its wider development. An original equipment manufacturer has a number of decisions

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to make in remanufacturing environment that are not present in a traditional manufacturing environment. See Table 3 to compare the recoverable manufacturing environment with traditional manufacturing environment by area of responsibility for the managers in different functions of business.

A verity of factors must be taken into account when making the remanufacturing decision (Atasu et al., 2010): Remanufactured product introduction timing, competition, supply constraints, last time buy decisions, and legacy systems. The original equipment manufacturer has more advantages over the independent manufacturer in terms of establishing the relationship with used product suppliers, remanufacturing operations, and marketing of the remanufactured products (Saavedra et al., 2013). If the marginal cost to remanufacture a used unit is lower than the price the remanufactured product can be sold at, and the profit generated from this effort over a certain time period exceeds any fixed cost investment required to set up a remanufacturing operation and sales channel, then the firm should choose to do remanufacturing (Ferguson, 2009). Subramoniam et al. (2013) develop a remanufacturing decision making framework (RDMF) to assist original equipment suppliers on their strategic decision-making processes.

Study of the link between product cannibalization and remanufacturing opportunities is also important in the remanufacturing sector (Vasudevan et al., 2012). According to Atasu et al. (2010) cannibalization occurs when the purchase of a remanufactured version of a product displaces the sale of a new product. It becomes concern when the remanufactured and new products are differentiable to customers. This is the case when a firm offers a remanufactured version of a product with a different price than the new version of that same product. The sales of remanufactured products may then reduce the sales of new product.

Table 3. Comparison of recoverable and traditional manufacturing environment (Guide et al., 2000)

Factors	Recoverable Manufacturing Environment	Traditional Manufacturing Environment
Environmental focus	Seeks to prevent post production waste	Environmentally conscious design and manufacturing, focus on pre production Pollution prevention and remediation
Logistics	Forward and reverse flows	Open forward flow
	Uncertainty in timing and quantity of returns	No returns
	Supply driven flows	Demand driven flows
Production planning and control	Need to balance demand with returns	No such need
	Material recovery uncertainty	Certainty in planned materials
	Stochastic routings and processing times	Fixed routings and more stable processing times
	Manufacturing system has three major components: disassembly, remanufacturing and reassembly	Manufacturing system has two major components: fabrication and assembly
Forecasting	Forecast both core availability and end product demand	Forecast only end products
	Must forecast part requirements because material recovery rates are uncertain	No parts forecasting needed
Purchasing	Highly uncertain material requirements due to variable recovery rates	Material requirements deterministic
	Cores and parts, components, replacement parts	Raw materials, new parts, and components
Inventory control and management	Types: cores, remanufactured parts, new parts, new and remanufactured substitute parts, original equipment manufacturer parts	Types: raw materials, work-in-process, finished goods
	Must track and provide accounting for all part types	Must track and provide accounting for work-in-process and finished goods

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On the other hand Atasu et al. (2010) states that cannibalization is not a major concern when remanufactured versions are perfect substitutes for new products. A perfect substitute means the remanufactured product cannot be distinguished by a customer. This allows the original equipment manufacturers to use remanufactured components and parts, reducing material costs, and does not require the firm to offer lower selling price. A firm in this situation can benefit from lower manufacturing costs and higher profit margins.

Ferguson (2009) claims that, most firms seem to have the fear that product cannibalization will reduce the demand for the firm's new product. For example, Bosch Power Tools restricted remanufacturing to products where the firm had less than a 50% market share. Their thinking behind this rule of thumb is that for products with more than a 50% market share, the remanufactured product will cannibalize sales of the firm's new product but if the market share is less than 50% then it will cannibalize the sales of their competitors.

Atasu et al. (2010) state that, although there are some cannibalization concerns, Bosch managers attempt to focus the introduction of remanufactured products to markets where Bosch does not hold a majority share, and use secondary channels. HP managers strongly believe remanufactured products cannibalize new product sales. Additionally, one manager at a global computer manufacturer informed Atasu et al. (2010) that for every four remanufactured products sold, one new product sale was cannibalized. According to Ferguson (2009) products do cannibalize the sales of new products but probably not to the degree that many firms fear.

All of these characteristics mentioned up to this point, make harder to manage the operations of such a production system with remanufacturing comparing to traditional regular production system. It causes researchers to develop models which solve the problems regarding production planning and control of these systems.

HYBRID MANUFACTURING/REMANUFACTURING SYSTEM

Many researches refer to the definition of remanufacturing made by Lund (1983): *Remanufacturing is an industrial process in which worn-out products are restored to like-new condition. Through a series of industrial processes in a factory environment, a discarded product is completely disassembled. Useable parts are cleaned, refurbished, and put into inventory. Then the new product is reassembled from the old and, where necessary, new parts to produce a fully equivalent and sometimes superior in performance and expected lifetime to the original new product*. During this process, the core passes through a number of remanufacturing operations like; inspection, disassembly, component reprocessing, reassembly, and testing to ensure meeting the desired product standards (Östlin et al., 2008).

Each of the processes in a remanufacturing systems is strongly dependent on each of the other processes. The remanufacturing system is composed of three highly dependent subsystems (Guide et al, 1999): A disassembly area, a processing area, and a reassembly area. A production planning and control of these systems have additional complexity of coordinating.

RL and remanufacturing are a customer relationship management challenge. Remanufacturing is typically discussed as a production and logistical challenge added on to a conventional system of consumption (Seitz & Peattie, 2004). There are three important and critical limitations that a remanufacturing

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firm needs to overcome: (1) Limited access of cores leaving the use phase; (2) Limited feasibility of product remanufacturing; (3) Limited market demand for the secondary output from remanufacturing (Geyer & Jackson, 2004).

The question of acquiring cores is an important issue for the remanufacturer in order to be able to satisfy the demand for remanufactured products to increase the performance of the remanufacturing system. Management of different types of relationships with the customer and suppliers is an important factor for the performance of the remanufacturing system. Regarding core acquisition, one of the most important issues is to focus on identifying different sources of cores and rating them according to their characteristics. Forecasting core availability is critical in order to balance supply and demand (Östlin et al., 2008).

There are a number of possible shop structures available for a remanufacturing facility. The most common type of remanufacturing facility is a general purpose remanufacturing shop with characteristics of both open and closed job shops with reassembly operations (Guide et al, 1999). Remanufacturing requires a lot of manual work. It is difficult to automate operations as they are not common for all remanufactured products.

In the literature a recoverable manufacturing system where it is possible to do direct manufacturing or remanufacturing depending on the system requirement, is called as a hybrid manufacturing/remanufacturing system. Integration of manufacturing and remanufacturing operations require realignment of the manufacturing process, information systems, and handling of returns for remanufacturing (Pokharel & Mutha, 2009).

The hybrid manufacturing/remanufacturing system is illustrated in Figure 1. The system works as follows (Tang & Naim, 2004; Zanoni et al., 2006; Corum et al., 2014): Cores collected from customers come to recoverable inventory from the collection points. They are remanufactured depending on the policy used. The remanufactured products are sent to serviceable stock and treated as like-new regular manufactured products. New customer demands are filled from serviceable stock. It is also possible to do regular manufacturing to fill the serviceable stock when needed. Demand and return are not correlated as the product has not yet reached the end of its life-cycle, there are typically more demands than returns. Hence some demands have to be satisfied by manufactured products (Teuter, 2001a). The main production strategy options for the hybrid manufacturing/remanufacturing systems are Push and Pull controlled hybrid systems. Other systems defined in the literature are extension of them.

The (R_m, Q_m, Q_r) Hybrid Push Strategy

Under the hybrid push strategy defined by Van Der Laan et al. (1999), remanufacturing starts when the recoverable inventory level reaches to Q_r which is the remanufacturing batch size. These Q_r products are batched and pushed to remanufacturing process which has a lead time of L_r per batch. The inventory level drops to zero in recoverable stock and increases by Q_r in the serviceable stock. When the inventory drops to R_m, manufacturing takes place in batches of Q_m with lead time of L_m per batch where s_m represents the safety stock. The timing of remanufacturing operations is completely return driven. As soon as sufficient returned products are in recoverable stock, these products are batched and pushed into the remanufacturing process. In this strategy remanufacturing operations are scheduled as early as possible. The timing of manufacturing operations is based on the serviceable stock position. See Figure 2 (a) for illustration.

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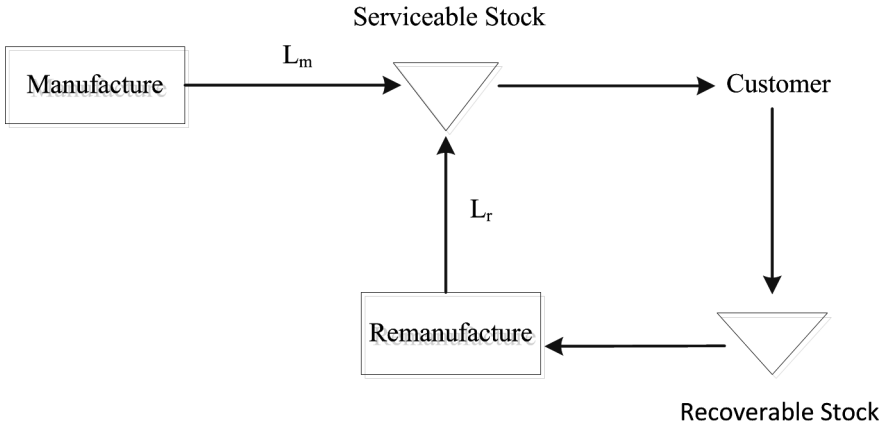
Figure 1. Material flow in a simple manufacturing/remanufacturing system
(Corum et al., 2014).



The (R_m, Q_m, R_r, Q_r) Hybrid Pull Strategy

Under the hybrid pull strategy defined by Van Der Laan et al. (1999), remanufacturing starts with two conditions one leading the other: First the inventory level of serviceable stock drops to R_r and second there is sufficient inventory level of Q_r to send to remanufacturing process. When these two conditions are satisfied the Q_r products are batched and sent to remanufacturing process having a lead time of L_r per batch. The inventory level drops by Q_r in recoverable stock while increases by Q_r in the serviceable stock. When the inventory drops to R_m ($< R_r$), manufacturing takes place in batches of Q_m with lead time of L_m per batch where s_m and s_r represent the safety stocks. The timing of remanufacturing operations depends on a composite of returns, future expected demands, and inventory positions. In this strategy remanufacturing operations are scheduled as late as suitable. The timing of manufacturing operations is based on the serviceable stock position. See Figure 2 (b) for illustration.

It is essential to accurately value the assemblies that influence holding cost rates while comparing inventory strategies in average cost models. Correct valuation method is critical to find the correct order batch size in hybrid manufacturing and remanufacturing systems. Teunter (2001b) proposes a method for valuing new, recoverable, and recovered assemblies (products, components, parts, etc.) in production systems with RL so called *RL Valuation Method:* The value of a new or an as good as new remanufactured assembly is the cost price of a new assembly. The value of a recoverable assembly is its net profit.

Total inventory cost is calculated as described in Teunter et al. (2000): Holding cost for recoverable item is $h_r = C_{core}*i$. Holding cost for serviceable items are based on holding cost rates of manufactured (weight 1-r) and remanufactured items (weight r), $h_s = i*[C_{reman}*r+C_{man}*(1-r)]$. Where;

i= Interest rate
C_{core}= Cost of returned products (cores)
C_{reman}= Unit remanufacturing cost
C_{man}= Unit manufacturing cost

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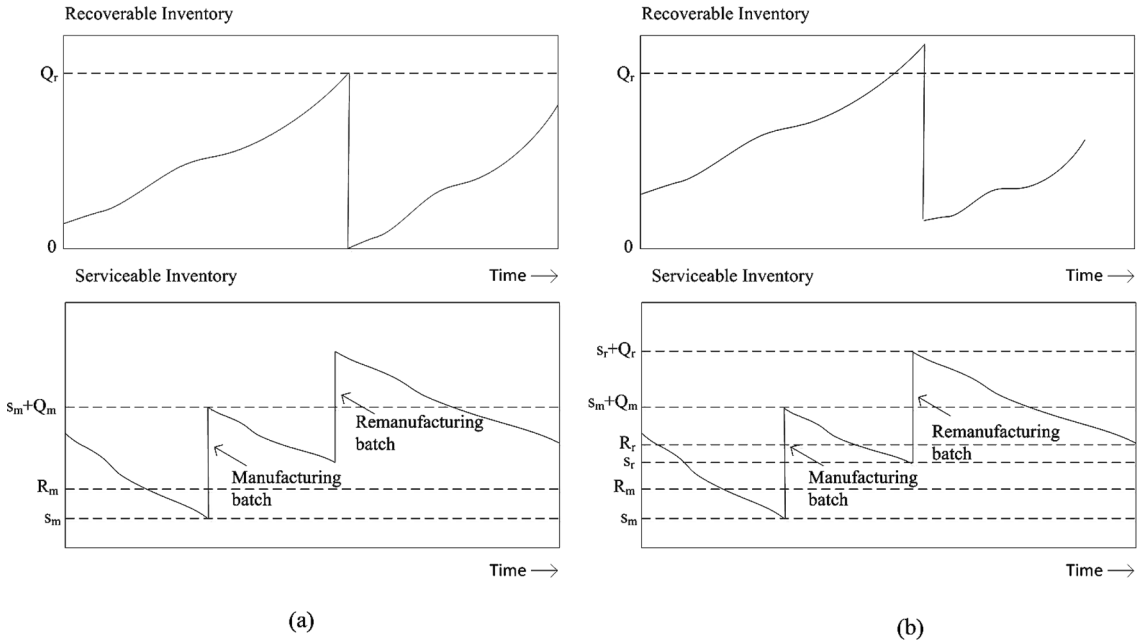
Figure 2. Push and pull controlled hybrid systems: (a) push control strategy (b) pull control strategy (Corum et al, 2014).



Pull system outperforms the Push system with respect to the total inventory costs when recoverable stock is valued *lower* than serviceable stock (Van Der Laan et al., 1999). Although Pull system is less costly than Push system, but management can still prefer Push system because it is relatively simple and easy to run it. Push system has independently controlled recoverable and serviceable inventory; the remanufacturing decision is based on only recoverable inventory level and the decided batch size. Pull system has dependently controlled recoverable and serviceable inventory; the remanufacturing decision is based on both recoverable and serviceable inventory levels and the decided batch size.

CONCLUSION

Recently, product recovery is one of the most important issues for the organizations. There are many motivations behind: Value recovery from the used products, the new regulations, and globally growing customer awareness, and environmental consciousness. Organizations consider different material recovery systems. One of them is remanufacturing where worn-out parts are removed and replaced. It is the only process where the quality standard becomes as good as a new product. A recoverable manufacturing system where it is possible to do direct manufacturing or remanufacturing depending on the system requirement, is called as a hybrid manufacturing/remanufacturing system. It is always complex to plan and control these systems because of the uncertainty existing in different stages of manufacturing. Management should take the remanufacturing decision after a detailed study. It is important to set up an effective and efficient collection system and plan the entire remanufacturing process. There can be hidden operating costs.

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KEY TERMS AND DEFINITIONS

Disposal: The action or process of throwing away or getting rid of something.

Hybrid Pull System: Production system where demand is satisfied both with manufacturing and remanufacturing. Collected used items are pulled for remanufacturing when end item stock level decreases to a certain level.

Hybrid Push System: Production system where demand is satisfied both with manufacturing and remanufacturing. Collected used items are pushed to remanufacturing.

Manufacturing: Produce something on a large scale using machinery.

Product Recovery: The action or process of regaining the possession of the lost value of a product.

Product Return: Return of used product to add a value.

Recycling: Series of activities by which discarded materials are collected, sorted, processed and used in the production of new products.

Refurbishing: To renovate and recondition a used product to a certain level.

Remanufacturing: Completely to disassemble a used product and inspect all modules and parts. Worn out parts are removed and replaced to bring the quality standard of final product to like-new condition.

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Chapter 67
Applicability of ANN in Adsorptive Removal of Cd(II) from Aqueous Solution

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ABSTRACT

Cadmium is frequently used and is extremely toxic in relatively low dosages and is one of the principal heavy metals that is responsible for causing kidney damage, high blood pressure, renal disorder, destruction of red blood Cells and bone fracture. Permissible limit to discharge in the inland surface water is 2.0 mg/l, discharge in public sewers is 1.0 mg/l and drinking water is 0.01 mg/l. Adsorption is the only user-friendly technique for the removal of heavy metal. We have developed an ANN model for prediction of percentage removal of Cd(II). A multilayer perceptron with a single hidden layer has been learnt separately by three different algorithms: Backpropagation, Levenberg-Marquardt and Scaled Conjugate Gradient algorithms for analysis purpose. Optimization for each one of the four standard transfer functions (in a single hidden layer) has been carried out in all three cases. The ANN model with Backpropagation algorithm, with the second transfer function and 25 processing elements gives the best predictability of the outlet concentration.

INTRODUCTION

The presence of heavy metals in the environment is a major concern as they are toxic in nature. Heavy metal pollutants are non-biodegradable hence environmentally persistent. Heavy metal exists in environment as natural components, and also their concentration has increased in the last century due to industrial revolution after World War II (Nriagu, 1979). As the heavy metals are non-biodegradable in nature, they are accumulated in the food chain via water–plants–animals–humans (Sciban & Klasnja, 2003). Hence

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the presence of heavy metal ions in water bodies, groundwater and soils from industrial waste water can pose a significant threat to ecological systems and also human health (Sen et al. 2002). For the protection of public health the heave metals removal from wastewater and water bodies are necessary. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries etc. Hence a cost-effective treatment for metals-contaminated wastewater is required, as environmental laws become stringent (Singha & Das, 2012, 2013).

Cd(II) is non-biodegradable and have great environmental impact for its presence in wastewater (Brower et al., 1997; Cay et al., 2004). Cadmium is introduced into the water bodies from different industrial activities like metal mining, plating, cadmium–nickel batteries, smelting, phosphate fertilizers, alloy industries pigments, stabilizers and sewage sludge etc. It is observed that the average Cd(II) concentration from metal plating industries are nearly 15–20 mg/l, and as high as 1000 mg/l concentration in lead mine acid drainage. The harmful effects of Cd(II) include acute and chronic metabolic diseases like testicular atrophy, disorders, renal damage, hypertension, emphysema and itai–itai disease, (Zhou et al. 1993; Chakravarti et al. 1995, Naiya et al. 2009a). Due to toxicity, the recommended maximum tolerance intake of Cd(II) by IS 10,500 for discharge in inland surface water and public sewers are 2.0 and 1.0 mg/l, respectively (IS 10500 1992, CPCB, 1995). The tolerance limits for heavy metal concentration in potable water and discharge into inland surface waters is shown in Table 1 (IS 10500 1992, EPA, WHO).

Cd(II) Removal Techniques

In general, various techniques are used for heavy metal removal effectively from the aqueous solution and they are the reduction and precipitation, coagulation, flotation, adsorption, ion-exchange and reverse-osmosis or electro dialysis, etc. (Zouboulis et al., 1997; Ravindran et al. 1999; Esalah et al. 2000; Canet et al. 2002; Pacheco et al., 2006; Sharma et al. 2009; Zhang & Fang, 2010; Gajda & Bogacki, 2012, Singha & Das, 2013). However it is observed in some instances, that these methods don't work properly with good efficiency. Many of these remediation technologies are expensive and time consuming and also have limitations particularly at low concentration of metal ions (Bhattacharya et al., 2006; Pacheco et al., 2006; Naiya et al., 2009a,b; Naiya et al., 2009). The precipitation method involves higher cost for heavy meal removal as voluminous sludge is produced which must be treated and disposed off properly (Hao et al., 2010). Ion-exchange and reverse-osmosis are effective and efficient, but expensive because of its high operational and maintenance cost. Adsorption, on the other hand, is a simple and cost-effective technology that has been widely used for remediation of numerous contaminants in waters, wastewaters, and soil (Stietiya & Wang, 2014). Adsorption onto activated carbon is considered as an effective technique and was extensively used in the last few years (Yiaocumi & Tien, 1995; Kandah, 2004). But considering the cost economics, recent research has focused on the development of low-cost readily

Table 1. Tolerance limits for heavy metal concentration in drinking water and discharge into inland surface water

IS 10500 1992			EPA	WHO
Drinking Water (mg/L)	**Discharge in Inland Surface Water (mg/L)**	**Discharge in Public Sewers (mg/L)**	**Drinking Water (mg/L)**	**Drinking Water (mg/L)**
0.01	2.00	1.00	0.005	0.003

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available alternatives using various agricultural, industrial, natural/biological waste materials including synthetic, modified model adsorbents. Several contributions have made in this area utilizing number of materials are reported in literature (Ferro-García et al., 1988; Low et al., 2000; Yalcinkaya et al., 2002; Bhattacharya et al., 2006; Memon et al., 2007; Bhattacharya et al. 2008; Naiya et al. 2009a,b; Naiya et al. 2009; Singha & Das, 2011, 2012, 2013).

Large electroplating facilities generally employ precipitation technique and it is in the form of either sulfide, carbonate, hydroxide precipitation or some combinations of these treatments for wastewater treatment (Peters et al., 1985). Peter and Ku (1984) reported the batch precipitation of cadmium as hydroxide and sulfide for various operating condition like pH, reaction time etc. They observed that cadmium hydroxide is colloidal in nature, and extremely low residual Cd(II) concentration had been obtained. But it generates large amount of sludge of relatively low density and create disposal problem. The carbonate precipitation occurs at lower pH than hydroxide precipitation but they are denser and hence easy to filter. For sulfide precipitation Na_2S used as precipitating agent for heavy metal by Bhattacharyya et al. (1979) and reported that the Cd(II) ion removal was more than 99% for copper smelting wastewater. Sulfide precipitation can be achieved by wide pH range (Bhattacharyya et al., 1979). The disposal of sulfide sludge is problematic as they are prone to oxidize and Cd(II) ions re-entered into the wastewater. In alkaline condition emission of hazardous H_2S gas is observed, hence pH must be properly monitored during the entire precipitation process. However the removal efficiency is more that 99.99% (Peters et al., 1984). Brantner and Cichon (1981) concluded that the precipitation techniques for Cd(II) removal is very effective method.

Nilsson (1971) reported the coagulation/flocculation method using aluminium sulfate and calcium hydroxide for the cadmium removal from wastewater. Mahvi and Bazrafhan (2007) studied electro coagulation process for cadmium removal using aluminum electrode. They observed that the applied current density is a major parameter to dictate the cadmium removal efficiency. Cadmium-cynide and nickel-cyanide containing wastewater from electroplating industry was successfully treated by using electrocoagulation method using iron plate electrodes in a electrochemical reactor by Kobya (2010). The main drawback of these processes is the huge sludge formation and high chemical consumption.

In wastewater treatment flotation plays an important role for the removal of heavy metals. Foam flotation, dissolved air flotation, ion flotation, precipitation flotation and adsorbing colloid flotation are mainly used (Fu and Wang, 2011). In foam flotation a surfactant is used which promote the non-surface active material to surface active and foaming the product to be removed by air bubbling. Huang et al. (1988) and Jurkiewicz (2006) demonstrated the useful application of flotation for Cd(II) separation. In ion flotation the metal ions are made to be hydrophobic by the use of proper surfactants and then removed by air bubbling. Yuan et al. (2008) studied this technique to remove Cd(II), Pb(II) and Cu(II) from the aqueous solution using tea saponin, a bio-surfactant. Salmani et al. (2013) studied the removal capability of cadmium(II) using sodium dodecyl sulphate as surfactant and ethanol as frother in ion flotation technique. Sabti et al. (2002) used adsorbing colloid flotation for the effective removal of heavy metals, Zn(II), Cu(II), Cd(II) and Pb(II) from dilute solutions. Sodium dodecyl sulphate and sodium oleate were used in single or mixed form as surfactant and $Fe(OH)_3$ as flocculant for colloid formation. The advantages of this methods are the removal capability of trace metal ions from natural and industrial wastewater streams, choice of proper surfactant and flocculant make the process highly metal selective and high removal efficient, rapid processing, simple design, small volume of final solution,

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concentrated sludge production, flexible operation (Sabti et al., 2002). But the major disadvantages are the high initial cost, high operation and maintenance costs, difficult to regulate as the process depend on several operating parameters.

Cementation is a powerful technique for removing heavy metals from wastewater. It consists of displacing the toxic metal ions from the wastewater by a more non-toxic metal. General reaction for cadmium cementation with other metal ions is represented as,

$$Cd^{2+} + M = M^{2+} + Cd \quad (1)$$

where M is a bivalent metal.

Gould et al. (1986) and Ku et al. (2002) reported that cadmium could be removed by cementation with magnesium and zinc powder respectively. Nosier (2003) reported the removal of Cd(II) ions by cementation on zinc in a batch stirred tank reactor lined with zinc sheet. The cementation process is a diffusion control chemical reaction and hence the removal efficiency depends on the operating parameters like stirrer speed, initial Cd(II) concentration, temperature and cementation time. The reactor is simple in design and operation, can operate in batch and/or continuous mode. The cadmium is deposited on zinc surface as a fine powder and can be collected by scraping the zinc surface. Thus saleable cadmium product improves the economy of the process. Younesi et al. (2006) reported the cementation of cadmium ions at pH 5.2–5.4 by zinc powder in a batch reactor and observed first-order reaction kinetics.

Ion exchange is basically an adsorption process where charged molecules, i.e., ions, in a solution are exchanged for another ions at the surface of adsorbant or resin either synthetic or natural solid. The common cation exchanger resin contain either strong acid like sulfonic acid group (-SO_3H) or weakly acid like carboxylic acid group (-COOH). Cadmium ions are exchanged for the hydrogen ions during the ion-exchange process as (Fu & Wang, 2011),

$$2R - SO_3H + Cd^{2+} \rightarrow \left(R - SO_3^-\right)_2 Cd^{2+} + 2H^+ \quad (2)$$

$$2R - COOH + Cd^{2+} \rightarrow (R - COO^-)_2 Cd^{2+} + 2H^+ \quad (3)$$

The exchange of metal ions on the ion exchange resin depends on different operating parameters, like pH, temperature, initial metal ion concentration and contact time (Gode and Pehlivan, 2006). This process has high selectivity, high treatment capacity, high removal efficiency, fast kinetics, wide applicability range of pH values and high regeneration potential (Kang et al., 2004). Researchers used different types of ion exchange resins (Koivula et al, 2000; Martinez et al., 2006; Pehlivan & Altun, 2006; Zhu et al., 2007a,b; Wong et al., 2014; Alyüz & Veli, 2009). Many researchers studied cadmium removal using different resins such as Amberlite IRC 718 (Malla et al., 2002), Dowex 50 W (Pehlivan & Altun, 2006), Amberlite IR 120 (Kocaoba, 2007), dolamite (Kocaoba, 2007) etc. Ion exchange process requires a high capital investment for equipments and also high operational cost due to the use of chemicals for resin regeneration.

Fu and Wang (2011) reported that the membrane filtration process has a great promise for cadmium removal due to their high removal efficiency, easy to operate and space saving unit. Researchers reported membrane filtration, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) for cadmium removal using different pressure and pore sized membrane to

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physically retain cadmium. Ritchie et al. (2001) used polycysteine and polygloutamic acid functionalized MF membrane for high concentration of cadmium solution. Zeng et al. (2009) reported the cadmium separation by the hybrid complexation-ultrafiltration process using ployacrylic acidsodium salt as complexing agent with polysulfone membrane. Han et al. (2012) used composite membrane prepared from hyperbranched polyamidoamine and polysulfone for removal of Cd(II). Salehi et al. (2012) immobilized 8-hydroquinone as a multi-dentate chelating agent on the PVDF MF membrane and observed Cd(II) adsorption was more favorable than other metal ions. Qdais and Moussa (2004) reported the removal of Cd(II) by RO and NF. They observed that for RO much higher pressure was required compare to NF. Saljoughi and Mousavi (2012a,b) developed an asymmetric polysulfone membrane for Cd(II) removal and obtained more than 98% separation. Bennani and M'hiri (2015) studied heavy metal separation using two commercial nanofiltration membranes (DL and DK) from industrial wastewater. They showed that the maximum rejection of heavy metal was obtained at 4 bar transmembrane pressure and cadmium rejection was 86%. The advantages of NF are ease of operation, comparatively low energy consumption, reliable in operation and high removal efficiency. The effectiveness of the membrane techniques is limited by their low permeate flux and high costs (Ballet et al., 2004). Sribudda et al. (2015) studied the separation of Cd(II) from industrial wastewater via hollow fiber supported liquid membrane (HFSLM). They examined the effect of pH of feed and stripping solutions, type and concentration of extractants and observed 97.08% extraction.

The use of electrodialysis technique for Cd(II) removal from synthetic water was demonstrated by Marder et al. (2003). In this process the metal ions were removed as solid metallic form, can be reuse. Ali et al. (2014) studied the removal of cadmium from brackish water by electrodialysis. They observed that the efficiency of this process depends on the demineralization rate, the removal rate and the transport flux of cadmium, the current efficiency and the specific power consumption. The advantages of this process are that there is no need to use other chemicals and hence there is no sludge formation. But this process is inefficient at low cadmium concentration (Rao et al., 2010).

Liquid-liquid extraction from aqueous solution using selective solvent is another technique for the cadmium removal (Nrogueia & Delmas, 1999; Gupta et al., 2001; Jia et al., 2004; Reddy et al., 1996). Reddy et al. (1996) used bis-2-ethylhexyl sunphoxide in benzene as solvent for Cd(II) and Zn(II) removal from thiocyanate solution. Reddy et al. (2006) used phosphorus based extractants such as TOPS 99, Cyanex 923, Cyanex 272, Cyanex 302 and Cyanex 301 diluted in kerosene for the solvent extraction to recover Cd(II), Co(II) and Ni(II) from the sulphate leached liquor of spent Ni-Cd batteries wastewater. The disadvantages are the use of large amount of solvent, costly stripping step to regenerate the solvent and very high recovery cost of cadmium if the concentration is very low.

All the techniques reported earlier have their own limitations such as at less effective at low concentration, sensitive operating condition, sludge production and problems of disposal, costly initial and operating cost etc. Another powerful technique is adsorption for the removal of toxic and heavy metals from wastewater stream. The advantages of the adsorption process are the use of low cost and easily available adsorbent, utilization of industrial and agricultural waste, low operating cost, ease of operation, regeneration and disposal of used adsorbents. Hence, adsorption is environmental friendly, cost effective and feasible method. Last few decades large amount of research have been reported in literature for the removal of toxic metals, cations, anions, organics and dyes etc. The adsorbents used are activated carbon; synthetic metal oxide like, activated alumina, silica, titanium oxide; polymers; nano materials; natural minerals and industrial waste, agricultural and plant materials; microbial materials etc.

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Activated carbon has been a widely used adsorbent and the adsorption capacity depends on the nature of the adsorbent, concentration and pH of the adsorbate solution. Activated carbon is used for various applications like heavy metal ions, other cations and anions, dyes and organic removal from wastewater (Purkayastha et al., 2014).

The activated carbon prepared from different raw materials having high carbonaceous materials, like bone char (Cheung et al., 2001), peanut husks (Ricordel et al., 2001), bagesse (Mohan & Singh, 2002), activated carbon prepared from almond husk (Hasar & Cuci, 2000), coconut shell carbon (Aziz et al., 2005), Wood (Rao et al., 2006), granulated activated carbon (Minceva et al. 2007), activated carbon (Wasewar et al., 2010), *Sesamum Indicum* Carbon (Venkatesan et al., 2014), neem oilcake carbon (Hema & Srinivasan, 2010), charcoal, rock melon activated carbon (Nurdin et al.,2015) etc. used for Cd(II) removal.

Synthetic metal oxide like mixed oxides of iron and aluminum (Srivastava et al., 1998), aluminum oxide (Sen & Sarzali, 2008; Naiya et al., 2009), manganese dioxide (Mishra & Tiwary, 1998; Tonkin et al., 2004; Zaman et al., 2009), etc. are used for Cd(II) removal. Other oxides like low grade ores containing metal oxide, sludges, fly ashes etc. are used for Cd(II) removal from aqueous solutions. These materials include calcite (Mcbridge, 1980), chabazite and clinoptilolite (Kesraoui-Ouki et al., 1993), natural and activated bentonite (Prsdasp et al., 1994), kaolinite (Angove et al., 1997), the montmorilonite (Barbier et al., 2000), goeteite (Christphi & Axe, 2000), activated kaoline (Yayuz & Aslan, 2002), clinoptilolite (Sprynskyy et al., 2006), Zeolite 4A (Rao et al., 2006)), Naural zeolite (Minceva et al., 2007**),** kaolinite, montmorillonite and their acid-activated forms (Gupta and Bhattacharyya, 2009), clarified sludge (Niaya et al., 2008), basic oxygen furnace slag (Xue et al., 2009), red mud (Apak et al., 1998; Han et al., 2002; Gupta and Sharma, 2002; Zhu et al., 2007a), coal fly ash (Apak et al., 1998; Mohan & Gandhimathi, 2009; Koukouzas et al., 2010), bottom fly ash (Khan et al., 2009), activated clay (Wasewar et al., 2010) etc.

Agricultural waste materials usually contain lignin, cellulose, hemicelluloses, lipids, many other compounds containing functional groups like, surface –OH, carboxyl groups, alcohols and esters, saturated and unsaturated groups, phenolic, amido, amino, -SO_3 groups, sulfonic acid, phosphoric ester group etc. (Singha & Das, 2011). These groups are responsible for the metal binding. These agro materials are saw dust, bark, peel, husk, leaves of different origin.

Saw dust of pinus sylvestris (Taty-Costodes et al., 2003), papaya wood (Saeed et al., 2005), poplar wood (Sciban et al., 2007), teak wood (Naiya et al., 2009), sunflower stalks (Sun and Shi,1998), maize cob (Abia et al. 2005), cassava waste (Abia et al., 2003), banana pith (Low et al., 1995) medicago sativa (Alfalfa) (Gardea-Torresdey et al., 1998), natural and $KMnO_4$ modified myrtus communis leaves (Dhabab et al., 2014), peels of banana (Anwar et al., 2010), rice husk (Ajmal et al., 2003; Kumar et al., 2010; Nhapi et al., 2011), base treatment of juniper fiber (Min et al. 2004), raw and EDTA modified maize husk (Igwe and Abia, 2007) Corn straw and corn cobs (Jamil et al., 2009), *Calotropis procera* root (Ramalingam et al., 2013), coconut shell (Khorasgani, 2013), magnetically modified peanut husk (Rozumova et al., 2013), eucalyptus bark (Ghodbane et al., 2008), neem bark (Naiya et al., 2009), orange peel (Li et al., 2007), mango peel (Iqbal et al., 2009), pine bark (Al-Asheh & Duvnjak, 1997), rice husk (Ajmal et al., 2003; Kumar & Bandyopadhyay, 2006), neem leaf (Sharma & Bhattacharya, 2005), olive tree leaf (Hamdaoui, 2009), *Hevea brasiliensis* leaf (Pandey et al., 2008), *Psidium guvajava* leaf (Rao et al., 2007) etc. used for Cd(II) removal from wastewater.

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ANN Techniques

Artificial Neural Networks (ANNs) are extensively studied in different fields of engineering, finance etc. with a basic objective of achieving prediction, classification, function approximation etc. It is a very powerful tool to identify underlying highly complex relationships from input-output data and represent both linear and non-linear relationship. It can learn this relationship directly from the data this is the reason it is a important tool for data mining. But Individual relations between the input variables and the output variables are not developed by scientific or engineering judgment. So far from the literature survey it is clear that the use of multilayer perceptron with backpropagation, Levenberg-Marquardt and Scaled Conjugate Gradient algorithms for various predictions had been very popular in the recent past (Bar et al., 2010a, 2010b, 2011; Bar and Das, 2011, 2013; Mitra et al., 2014; Singha et al., 2014; Das et al., 2015; Singha et al., 2015). The prediction of percentage removal for Cd(II) ion using ANN is very rare and not much of research had been done in this field as evident from literature review. This chapter discuss the adsorptive removal of Cd(II) ions from aqueous solution in batch and applicability of ANN for the predictability of the removal.

MATERIALS AND METHODS

ANN Methodology

In this chapter we have developed an ANN model for percentage removal of Cd(II). The adsorbent used are Saw dust of teakwood origin, Neem bark, Rice husk, Clarified sludge, Fly ash, Activated alumina and Fuller's earth. The effect of different operating parameters on the selectivity and sensitivity were reported. A multilayer perceptron with backpropagation (BP), Levenberg-Marquardt (LM) and Scaled Conjugate Gradient (SCG) algorithms have been used for the analysis. Four different standard transfer functions in a hidden layer and a linear output function are used. The analyses with each transfer function has been separately carried out in all cases and the network was optimized before final prediction.

RESULTS AND DISCUSSION

Characterization of Adsorbents

The adsorbents were subjected to characterization by a variety of methods such as X-ray diffraction (XRD), chemical analysis, thermo gravimetric analysis (TGA), particle size, BET surface area, and scanning electron microscope (SEM). Figure 1 shows the SEM micrographs (Model S415A, Hitachi, Japan) of all the adsorbents. It indicated that the surface was porous in nature for all adsorbents.

The constituents of activated alumina, rice husk ash, fly ash, clarified sludge were studied by using X-ray diffractograms (XRDs) obtained from an X-ray diffractometer (Model No. XRD 3000P, Seifert, Germany). The X-ray diffraction was analyzed by using Cu Kα as a source and Ni as a filter media, K radiation maintained at 1.52 Å. The diffraction pattern is shown Figures 2-6. The Brunauer–Emmett–Teller nitrogen adsorption technique (BET) was used to determine the surface area (Model 1750

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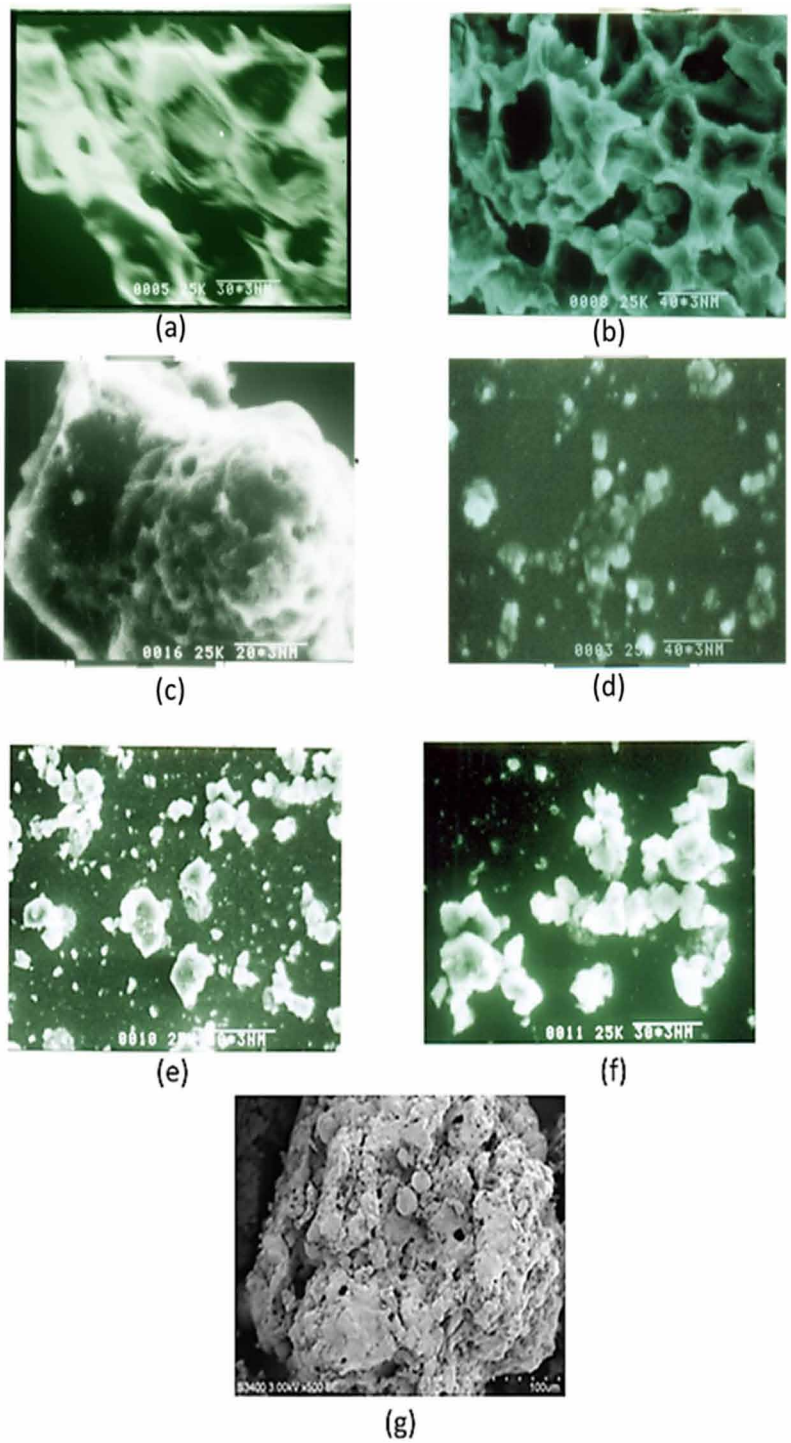
Figure 1. Scanning Electron Micrographs (SEM): (a) saw dust (b) neem bark (c) rice husk ash (d) clarified sludge (e) fly ash (f) activated alumina (g) Fuller's earth



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SORPTY, Carlo Erba, Italy). The particle size of 250–350 μm is analyzed in particle size distribution analyzer (Model 117.08, MALVERN Instruments, USA). The point of zero charge of the adsorbents was determined by the solid addition method (Srivastava et al., 2006; Singha and Das, 2012).

The properties of adsorbents are shown in Tables 2 and 3. FT-IR (FTIR RX-1, PerkinElmer, USA) spectrometer was used to determine the type of functional groups in saw dust and neem bark responsible for metallic adsorption.

Table 4 represents the shift in the wave number of dominant peak associated with the fresh and Cd(II) loaded saw dust and neem bark. These shift in the wave number indicated that there was metal binding at the surface of the adsorbent (Pravasnt et al., 2006; Naiya et al., 2009a). The shift of wave number of 1033.66 cm^{-1} (fresh saw dust) to 1031.73 cm^{-1} (Cd(II) loaded) and 1026.91 cm^{-1} (fresh neem bark) to 1027.87 cm^{-1} (Cd(II) loaded) indicated surface -OH is one of the functional group responsible for adsorption. Other major functional groups responsible for the adsorption are carboxylic acid N-H stretching and C-O stretching for saw dust and carboxylic acid N-H stretching for neem bark; amide C-O stretching and sulphonate S-O stretching for both adsorbents.

Effects of Initial pH on the Adsorption

The effect of pH on adsorption behaviour of cadmium by different adsorbents was shown in Figure 7. The pH of the solution varies from 2 to 8. The Cd(II) ions in the aqueous solution may undergo solvation and hydrolysis as follows,

$$Cd^{2+} + nH_2O = Cd\left(H_2O\right)_n^{2+} \tag{4}$$

Figure 2. X-Ray diffractograms of rice husk ash (XRD)

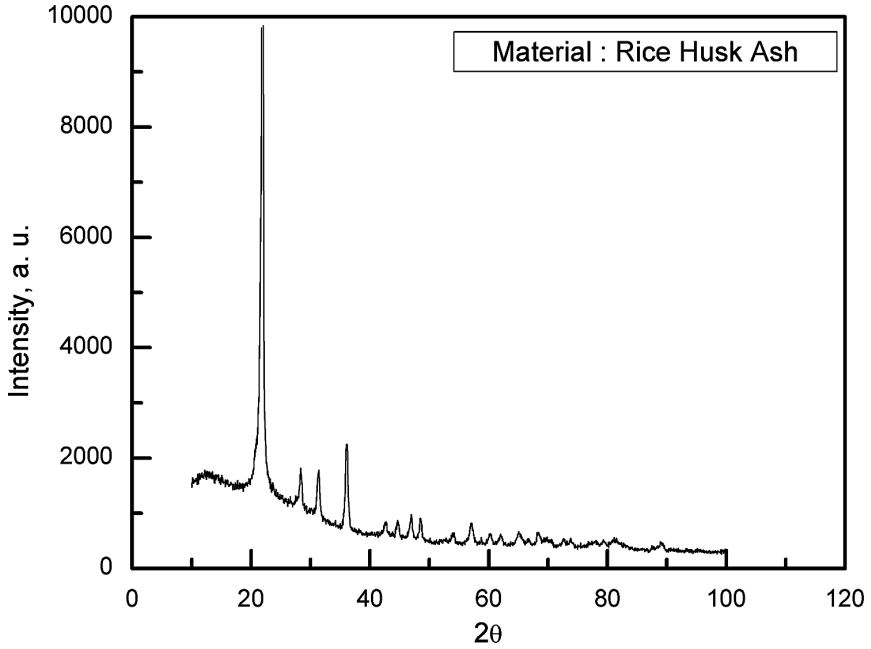

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Figure 3. X-ray diffractograms of clarified sludge (XRD)

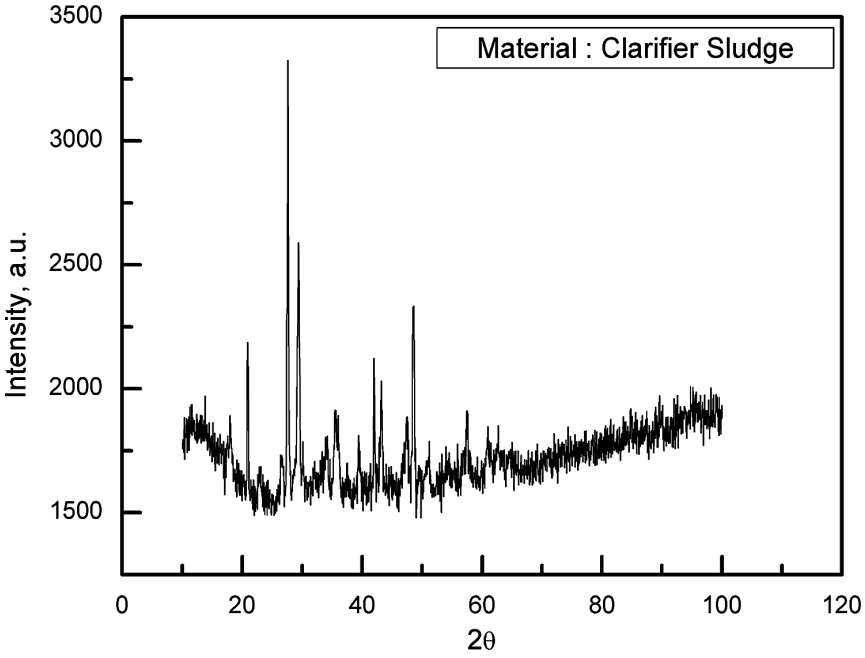

Figure 4. X-ray diffractograms of fly ash (XRD)

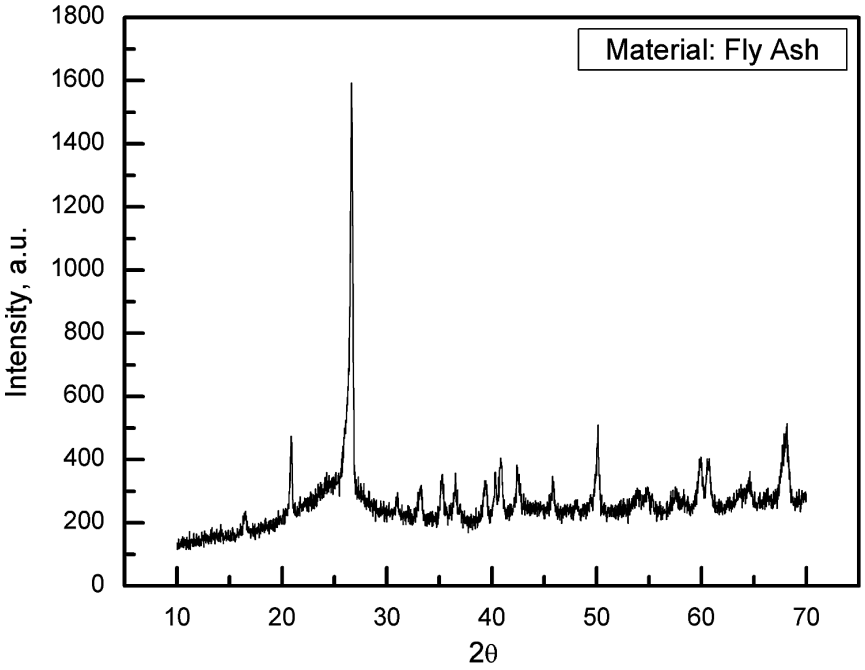

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Figure 5. X-ray diffractograms of activated alumina (XRD)

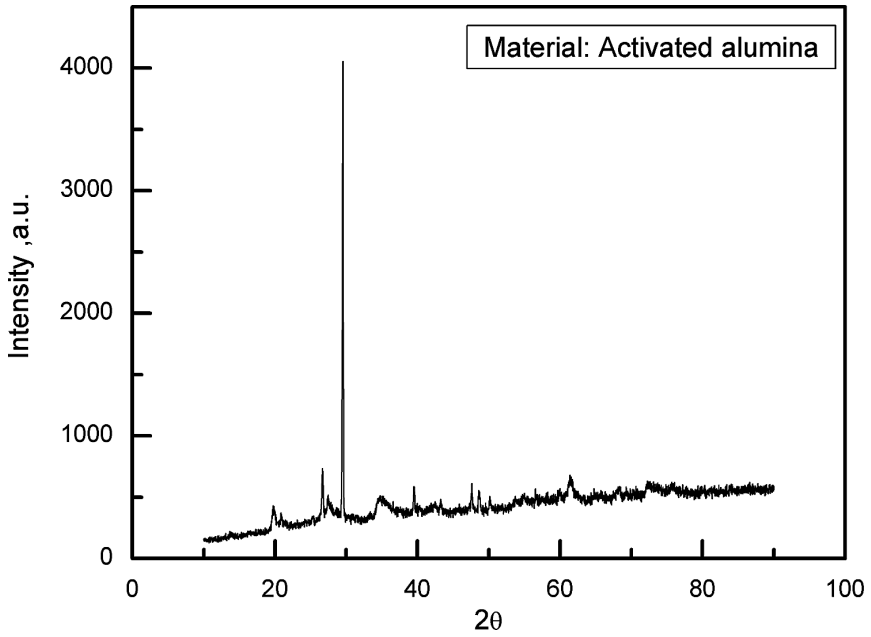

Figure 6. X-ray diffractograms of fuller's earth (XRD)

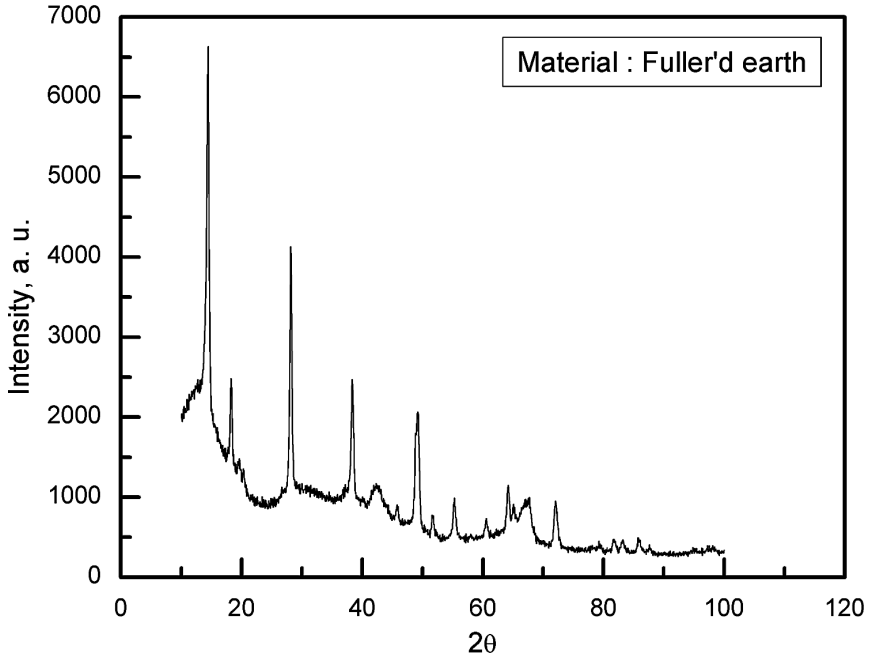

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Table 2. Properties of adsorbent

Adsorbent	Bulk Density (kg/m^3)	Surface Area (m^2/gm)	Point of Zero Charge, pH_{pzc} (pH)
Saw dust	530	3.85	3.9
Neem bark	560	3.47	4.5
Rice husk ash	960	57.5	8.52
Clarified sludge	1980	78.54	9.8
Fly ash	1760	63.7	7.21
Activated alumina	830	126.0	6.5
Fuller's earth	780	38.5	7.4

Table 3. Chemical composition of the adsorbent

Constituents	Percentage by Weight, %				
	Rice Husk Ash	Clarified Sludge	Fly Ash	Activated Alumina	Fuller's Earth
Loss on Ignition	12.2	12.0	12.00	6.70	7.05
Fe_2O_3	0.6	48.0	8.33	0.03	2.41
Al_2O_3	0.3	-	22.01	93.10	10.05
CaO	1.4	23.4	2.57	0.03	4.31
MgO	0.5	2.5	0.91	-	1.05
SiO_2	84.3	12.6	57.82	-	59.37
Na_2O	0.4	0.7	-	0.10	-
K_2O	0.2	0.5	0.45	-	0.84
MnO	-	0.2	-	-	-
Ti_2O	-	-	0.62	-	-
Moisture	-	-	1.20	-	13.19
Others	-	-	1.09	0.04	1.73

Table 4. Wave number (cm^{-1}) for dominant peak from FTIR

Group		Raw Saw Dust	Cd(II) Loaded Saw Dust	Raw Neem Bark	Cd(II) Loaded Neem Bark
Primary -OH		1033.66	1031.73	1026.91	1028.84
Carboxylic acid	O-H stretching C-O stretching	2917.7 1235.8	2914.88 1220.36	X 1026.91	X 1028.84
Amine	N-H stretching C-N stretching	3335.1 1321.9	3324.5 1324.86	3297.75 X	3259.11 X
Amide	C-O stretching	1594.04	1593.88	1606.31	1610.27
Sulphonate	S-O stretching	693.28	667.25	756.92	679.79

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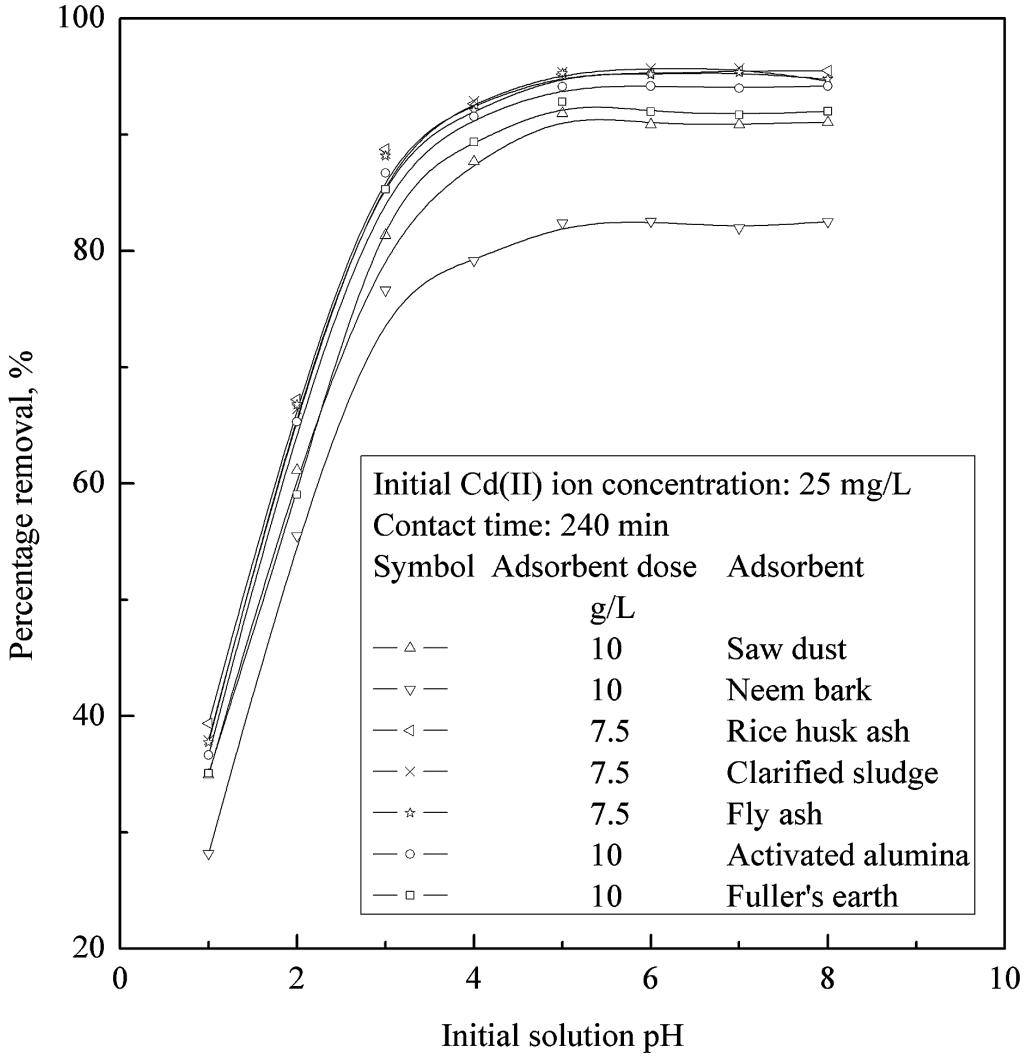
Figure 7. Variation of the initial solution pH on the removal of Cd(II)



$$Cd^{2+} + nH_2O \rightleftarrows \left[Cd\left(H_2O\right)_{n-1}\left(OH\right)\right]^{+} + H^{+} \tag{5}$$

The pK_a value is 10.1 for Equation (5). The oxides of silica, calcium, alumina and iron present in rice husk ash, clarified sludge, fly ash, activated alumina and fuller's earth which develop charge in contact with water. Zero point charge (pH_{ZPC}) of SiO_2, CaO and Fe_2O_3 are 2.2, 11.0 and 6.7 respectively (Srivastava et al., 2006). Hence, a positive charge develops on the surface of oxides of ashes in an acidic medium as,

$$-MO + HOH \xrightarrow{H^+} M - OH^{2+} + OH^- \tag{6}$$

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The sorption at low pH ranges take place with low removal efficiency. This occurs because there was a high concentration of proton in solution and the proton competed with metal ions in forming a bond with the active sites on the adsorbents (Srivastava et al., 2006). As the initial pH of the system increases, the number of positively charge sites decreases and negatively charge sites increases, hence electrostatic attraction increases on the surface of ash. The mechanism can be expressed as

$$-MOH + OH^- \xrightarrow{H^+} -MO^- + H_2O \tag{7}$$

$$2 - MO^- + Cd^{2+} \xrightarrow{H^+} M - O - Cd - O - M \tag{8}$$

Similar theories are also proposed by other researchers Viraraghaban and Rao (1991) and Mathialagan and Viraraghaban (2002). The similar trend has also been reported by other researchers using different adsorbents (Horsfall and Abia, 2003; Hawari and Mulligan, 2006; Hasan et al., 2006; Memon et al., 2007). Increase in adsorption with increase in pH can also be explained on the basis that hydrolysed species have a lower degree of hydration that is less energy is necessary for the molecules upon binding sites. At a further increase of pH (6-9) the solubility of Cd(II) decreases enough for precipitation to occur.

The adsorption of Cd(II) ions onto the surface of saw dust and neem bark can probably be explained by an ion-exchange mechanism based on the surface complex formation model, which is facilitated by the dissociation of different functional groups present and resulting in the formation of metal complex (Khalid et al. 2005; Naiya et al., 2009a)

$$m\left[RO_7\left(OH\right)_{11}\right] \rightleftarrows m\left[RO_7\left(OH\right)_9\left(O^-\right)_2\right] + mH^+ \tag{9}$$

$$Cd^{n+} + m\left[RO_7\left(OH\right)_9\left(O^-\right)_2\right] \rightleftarrows Cd\left[RO_7\left(OH\right)_9\left(O^-\right)_2\right]_m^{n-m} \tag{10}$$

The overall reaction can be represented by:

$$Cd^{n+} + m\left[RO_7\left(OH\right)_{11}\right] \rightleftarrows Cd\left[RO_7\left(OH\right)_9\left(O^-\right)_2\right]_m^{n-m} + mH^+ \tag{11}$$

where, Cd^{n+} and $-RO_7(OH)_{11}$ are the cadmium ion with n+charge and the acidic part of the adsorbent respectively and R represents the matrix part of the adsorbents. The reaction is reversible. The enhanced adsorption of Cd(II) ions with an increase in pH may possibly due to the condensation reaction between the hydrolysis products of sorbate ions and the sorbent carrying the –OH groups (Benes and Majer, 1980; Khalid et al. 2005; Naiya et al., 2009a). Hence the Cd(II) adsorption onto the saw dust and neem bark are mainly due to the ion-exchange mechanism involving combine effect of site binding adsorption and also complexation phenomena. To ensure only adsorptive removal all subsequent experiments were carried out at pH 5.

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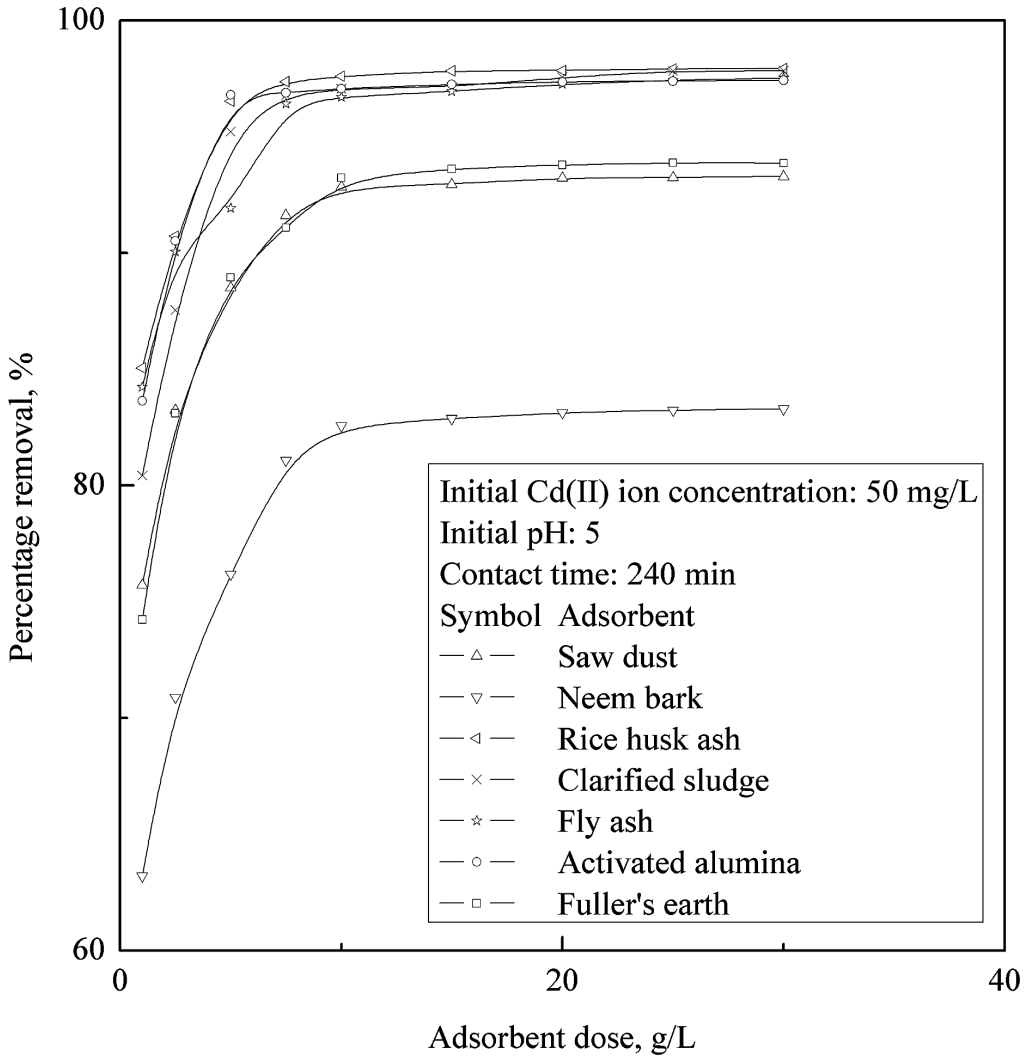
Effects of Initial Metal Ion Concentration on the Adsorption

Figure 8 shows the effect of initial Cd(II) concentrations on the removal efficiency by both the adsorbents. The efficiency of metal ions removal is also affected by the initial concentration of metal ions in aqueous solutions. Removal percentages of Cd(II) from aqueous solution decreases as concentration increases from 3 to 100 mg/L at constant pH. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in the adsorption efficiency (Zouboulis et al. 2002; Kadirvelu and Namasivayam, 2003; Bhattacharya et al. 2006; Naiya et al. 2009a, Singha and Das, 2013).

Figure 8. Variation of the adsorbent dosage on the removal of Cd(II)



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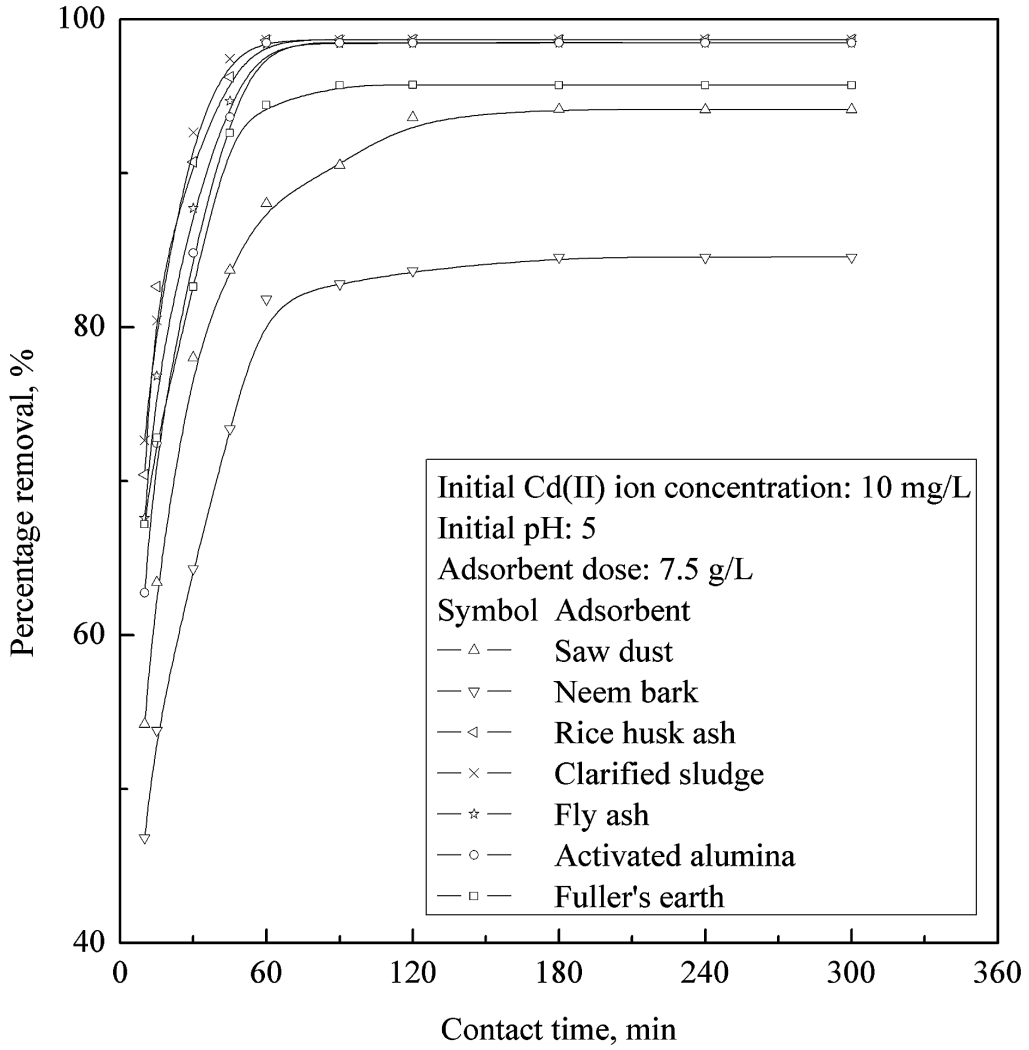
Effects of Adsorbent Concentration on the Adsorbent

Figure 9 illustrates the effect of adsorbent dosage on the adsorption of Cd(II) onto rice husk ash. The removal of Cd(II) was found to increase significantly with an increase in adsorbent dosage from 1–5 g/L. After adsorbent dosage level of 7.5 gm/L the metal ion removed almost remain unchanged. With increase the adsorbent dosages the availability of adsorbent sites and surface area increases hence adsorption increases, i.e., metal ion uptake by the adsorbents increases. For adsorbent dosage of 5 g/L, the incremental metal ion removal becomes very low as the surface metal ion concentration and the solution metal ion concentration comes to equilibrium with each other. For higher adsorbent dosage of 7.5 g/L, the removal efficiency becomes almost constant for the removal of Cd(II) ions onto rice husk ash.

Figure 9. Variation of contact time on the removal of CD (II)



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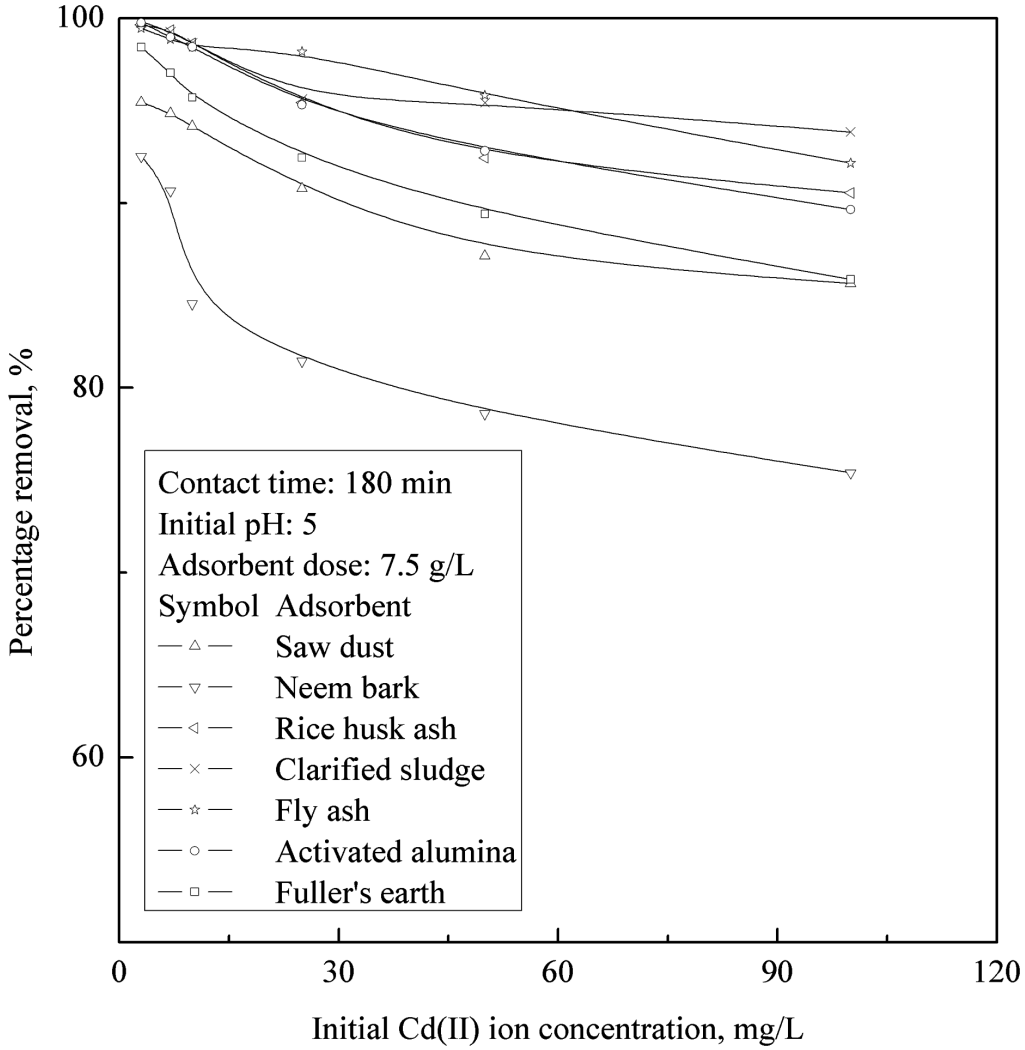
Effects of Contact Time on the Adsorption

Figure 10 shows the variation of contact time on the removal of Cd(II) ions. The effect of contact time for the removal of Cd(II) showed rapid adsorption of Cd(II) in the first 45 min; thereafter, the adsorption rate decreased gradually and adsorption reached equilibrium in about 2 h. Therefore, at 2 h of contact time, the steady state approximation was assumed and a quasi-equilibrium situation was accepted. Accordingly all the batch experiments were conducted for a contact time of 2 h under isothermal and shaking conditions at 120 rpm.

Figure 10. Variation of the initial Cd (II) ion concentration on the removal CD (II)



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ANN PROCEDURE AND PERFORMANCE

Table 5 gives the range of data for ANN analysis. The threshold value for the minimum value of cross-validation MSE was 1×10^{-4}. This value is kept same for analysis using all 3 networks. For the networks that was used for Backpropagation (BP) algorithm (Gradient descent or Momentum), each run was set for a maximum of 32000 epochs. The value of cross-validation MSE were dependent upon the capability of improvement within 10000 epochs, i.e., convergence towards the threshold value, otherwise the training was set to stop.

From the literature servey it is clear that the initial values of α and μ for BP algorithm are not mentioned in some of the papers where these algorithms are successfully used (Übeyli and Güler, 2004; Ozkan et al., 2010; Bonakdari et al., 2011). Although in some papers the values of above mentioned parameters are given (Karnin, 1990; Maier and Dundy, 1998; Udelhoven and Schutt, 2000; Yildiz et al., 2002; Desai et al., 2005; Ho, 2009). From the above literature survey it is clear that the values are

Table 5. Range of data

Measurement Type		Range
Input Parameters	Number of adrorbent	1 to 7
	pH	1 to 8
	Adsorbent Dosage (g/L)	1.0 to 30.0
	Initial Concentration C_o (mg/L)	3.00 to 100.00
	Time T (min)	10 to 300
Output Parameter	Percentage Removal (%)	27.23 to 99.82
Total number of data points		600

Table 6. Optimum numbers of processing elements in the hidden layer for four different transfer functions

Transfer Function in Hidden Layer	Equation	Algorithm	Optimum Number of Processing Elements
Transfer Function 1	$f_{1h}(x) = \tanh \beta x = \frac{e^{\beta x} - e^{-\beta x}}{e^{\beta x} + e^{-\beta x}}$	BP	24
		LM	22
		SCG	20
Transfer Function 2	$f_{2h}(x) = \beta x$ where $\beta x = 1$ *for* $\beta x > 1$, $\beta x = -1$ *for* $\beta x < -1$	BP	25
		LM	15
		SCG	23
Transfer Function 3	$f_{3h}(x) = \beta x$ where $\beta x = 0$ *for* $\beta x < 0$, $\beta x = 1$ *for* $\beta x > 1$	BP	24
		LM	25
		SCG	16
Transfer Function 4	$f_{4h}(x) = \frac{1}{1 + e^{-\beta x}}$	BP	14
		LM	23
		SCG	21

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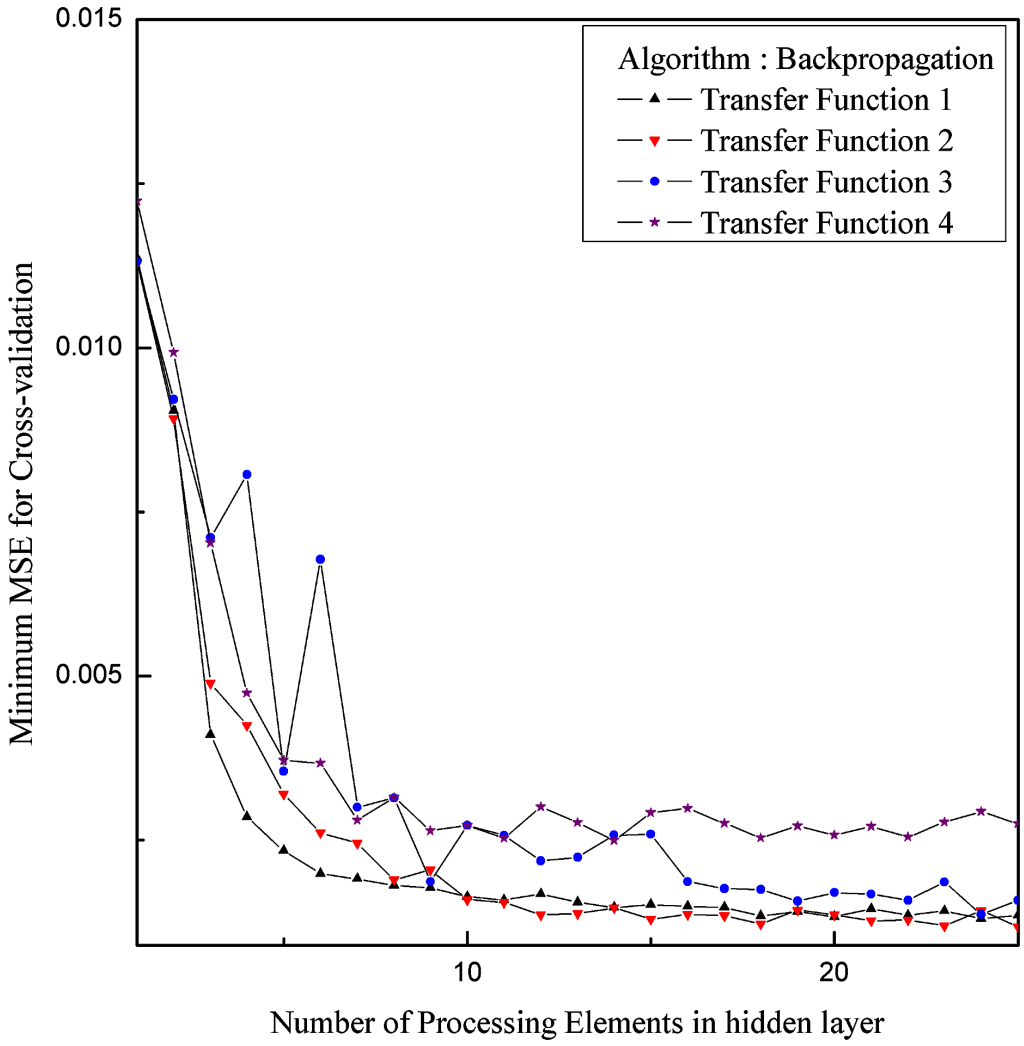
Table 7. Performance of the best neural network on the basis of minimum value of MSE reached during cross-validation

Transfer Function in Hidden Layer	Algorithm		
	Back-Propagation	Levenberg-Marquardt	Scaled Conjugate Gradient
Transfer Function 1	0.001305	0.000629	0.000997
Transfer Function 2	0.001182	0.001279	0.001521
Transfer Function 3	0.001373	0.005997	0.002325
Transfer Function 4	0.002498	0.000763	0.001326

Figure 11. Variation of cross-validation MSE with the number of processing elements in the hidden layer



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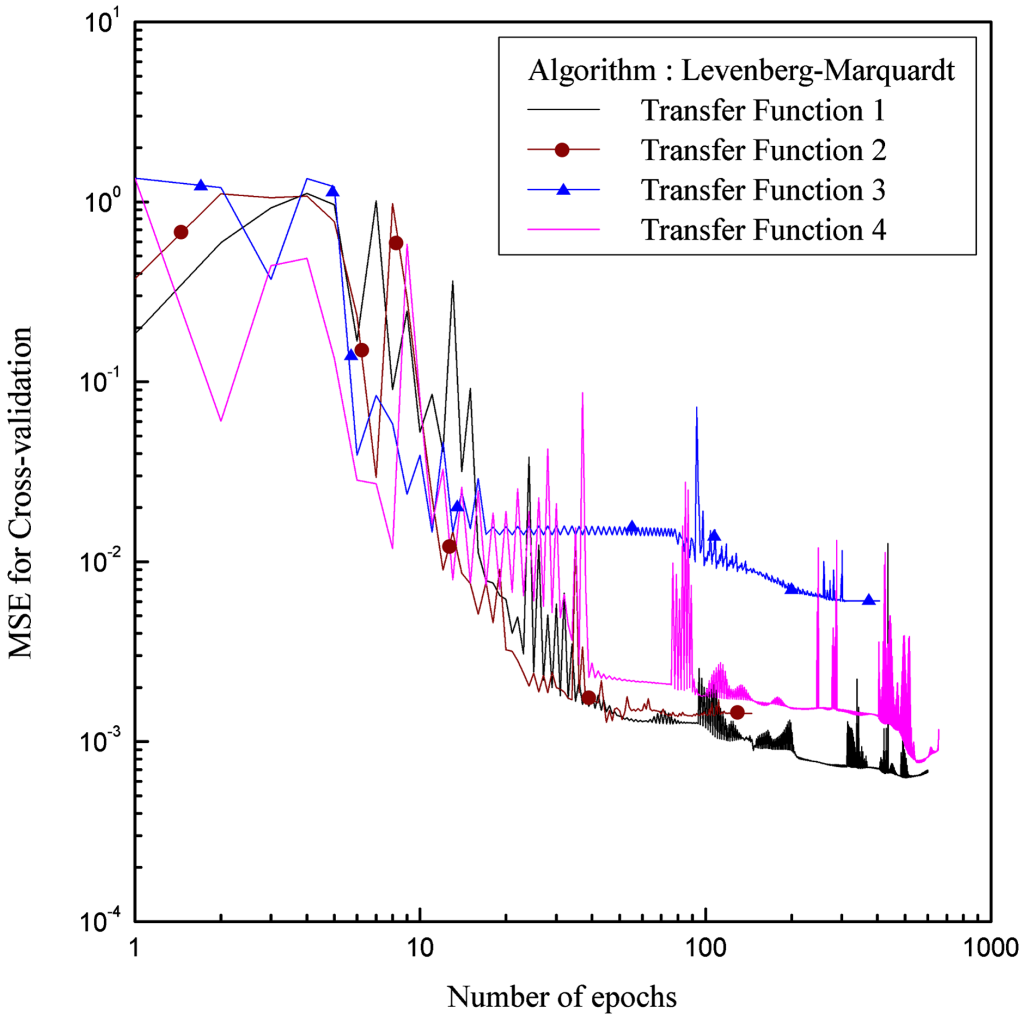
randomly chosen. So it is clear that these values are dependent on the problem it deals with. The initial values of these constant parameters mentioned for training of BP are kept constant throughout this analysis. A few of these values of α and μ for BP algorithm are kept common for this study and the studies by Karnin (1990), Maier and Dundy (1998), Udelhoven and Schutt (2000), Yildiz et al. (2002), Desai et al. (2005) and Ho (2009). So, for the hidden layer of BP network the value of learning rate was 0.7 and momentum coefficient was 1. Similar procedure had been successfully applied in our earlier work (Bar et al., 2010a, 2010b, 2011; Bar and Das, 2011, 2013; Mitra et al., 2014; Singha et al., 2014; Das et al., 2015; Singha et al., 2015).

For network using Levenberg-Marquardt (LM) algorithm each run was set for 1000 epochs. The value of cross-validation MSE were dependent upon the capability of improvement within 100 epochs, otherwise the training was set to stop. Similar type of procedure had been followed in our earlier work (Bar and Das, 2011, 2013; Mitra et al., 2014; Singha et al., 2014; Das et al., 2015).

Figure 12. Cross-validation curve for Levenberg-Marquardt algorithm



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For network using Scaled Conjugate Gradient (SCG) algorithm each run was set for 32000 epochs. The value of cross-validation MSE was dependent upon the capability of improvement within 5000 epochs, otherwise the training was set to stop. Similar procedure have been followed in our earlier work (Bar and Das, 2011, 2013; Mitra et al., 2014).

The determination of optimum value for the number of nodes in the hidden layer was necessary for the best result. This value was determined during training and cross-validation phase (which was done simultaneously) for BP, LM and SCG algorithm respectively. The value of number of nodes for which the MSE of cross-validation is minimum was considered to be optimum. Table 6 presented the optimum value of number of nodes or transfer functions in the hidden layer for the respective transfer functions for which the minimum value of cross validation MSE had been achieved. Table 7 presented the value of the minimum value of cross-validation MSE reached during training. The variation of minimum value of cross-validation MSE with the number of processing elements in the hidden layer for BP network is represented in Figure 11.

A typical presentation of a cross-validation curve for LM algorithm is represented in Figure 12. From the curve it can be observed that for transfer function 1 and 2 the value of cross-validation MSE had

Table 8. Performance of the different algorithms for prediction of concentration by the optimized neural network for different transfer functions in case of final prediction

Transfer Function in Hidden Layer	Measurement Type	Algorithm		
		Back-Propagation	Levenberg-Marquardt	Scaled Conjugate Gradient
Transfer Function 1	AARE	0.019493	0.017936	0.020685
	SD (σ)	0.017946	0.027100	0.025833
	MSE	17.87191	23.54199	21.83176
	CCC (R)	0.995897	0.994052	0.994594
	χ^2	2.725506	3.821059	3.710545
Transfer Function 2	AARE	**0.019347**	0.026108	0.020649
	SD (σ)	**0.015800**	0.029897	0.018120
	MSE	**16.86962**	33.58132	19.01515
	CCC (R)	**0.995323**	0.991533	0.995132
	χ^2	**2.450078**	5.540861	2.837256
Transfer Function 3	AARE	0.020815	0.035238	0.026028
	SD (σ)	0.021613	0.039434	0.024704
	MSE	28.96022	65.30535	40.44909
	CCC (R)	0.992513	0.982812	0.988752
	χ^2	3.929253	9.635237	5.343233
Transfer Function 4	AARE	0.020162	0.021813	0.018880
	SD (σ)	0.022263	0.024194	0.018796
	MSE	27.78813	24.59610	19.18790
	CCC (R)	0.992742	0.993727	0.994805
	χ^2	3.872711	3.848565	2.735927

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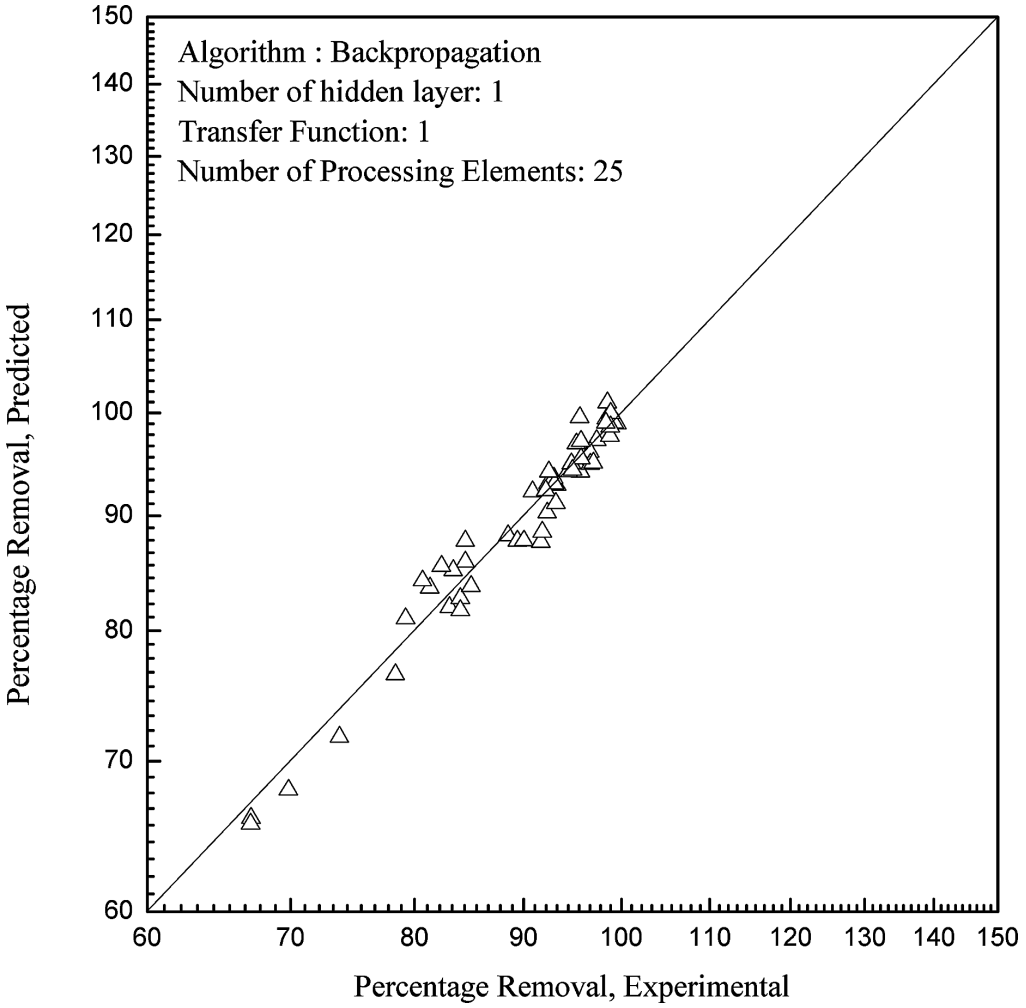
Figure 13. Comparison between the Experimental Data to be predicted from ANN



increased near the end of termination of training, i.e., the value of MSE increased in the last 100 epochs and showed no improvement during that period. For transfer function 3 and 4 the value of cross-validation MSE remained constant for the last 100 epochs, so the training was terminated.

Table 8 gives the comparison of all the statistical error parameters related to final prediction. The accuracy is evident from the observation of the low values of various statistical parameters related to the error, e.g., AARE, SD (σ). In all cases the values of R, i.e., cross correlation coefficient (CCC) were found close to unity, i.e., 0.99 and above. To draw conclusion of all the results the χ^2 test was conducted and is represented in Table 8.

The observation of all the results of the χ^2 test from the Table 8 it is clear that the ANN model with Backpropagation algorithm, using a hidden layer with transfer function 2 and 25 processing elements gives better predictability of the percentage removal. Thus, the successful prediction capability was understood from Figure 13 which is the comparison between the values of percentage removal of experimental and ANN prediction.

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CONCLUSION

The sorption of Cd(II) ion onto different adsorbents in batch mode are reported. Effects of different operating parameters on the removal efficiency are investigated. We have developed an ANN model for prediction of percentage removal of Cd(II). A multilayer perceptron with backpropagation and Levenberg-Marquardt algorithm and four different standard transfer functions in a hidden layer and a linear output function has been used for all cases. The ANN model with Backpropagation algorithm, using a hidden layer with transfer function 2 and 25 processing elements gives better predictability of the outlet concentration.

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APPENDIX: NOMENCLATURE

C_o: Initial Cd(II) concentration (mg/L)
C_t: Cd(II) concentration at time t (mg/L)
m_s: Amount of adsorbent added in g
N: Number of data points
q_t: Amount (mg) adsorb per g of adsorbent

R: Cross correlation coefficient, $R = \dfrac{\sum_{i=1}^{N}\left(x_i - \overline{x}\right)\left(y_i - \overline{y}\right)}{\sqrt{\sum_{i=1}^{N}\left(x_i - \overline{x}\right)^2 \sum_{i=1}^{N}\left(y_i - \overline{y}\right)^2}}$, dimensionless

V: Volume of the solution in ml
x: Experimental value of % removal of Cd(II)
y: ANN predicted value of removal of Cd(II)

MSE: Mean Squared Error, $\frac{1}{N}\sum_{i=1}^{N}\left(x_i - y_i\right)^2$, dimensionless

AARE: Average Absolute Relative Error, $AARE = \frac{1}{N}\sum_{i=1}^{N}\left|\dfrac{\left(y_i - x_i\right)}{x_i}\right|$, dimensionless

Greek Letter

χ^2: $\chi^2 = \sum_{i=1}^{N}\dfrac{\left(x_i - y_i\right)^2}{y_i}$, dimensionless

σ: $\sigma = \sqrt{\sum_{i=1}^{N}\dfrac{1}{N-1}\left[\left|\dfrac{\left(y_i - x_i\right)}{x_i}\right| - AARE\right]^2}$, dimensionless

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Chapter 68
Occurrence and Treatment of Micropollutants in Landfill Leachate

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ABSTRACT

Micropollutants have emerged as a new challenge to the scientific community over the past decade. This chapter discusses the occurrence of various micropollutants in landfill leachate. Phthalic acid esters (PAEs) are one of the most investigated compounds in landfill leachate and are therefore given special focus in this chapter. The potential treatment options for these micropollutants are discussed with relevance to the estrogenicity potential of micropollutants. The potential of leaching of micropollutants from landfill sites is discussed to emphasize on the requirements of appropriate liners to avoid such exposure to the surrounding environment. Biological treatment in particular membrane bioreactors have been successfully used to remove some of the micropollutants. Advanced oxidation processes such Fenton and photo-Fenton have limited application reported in literature whereas other physic-chemical processes such as coagulation and adsorption have been demonstrated to be effective in the removal of micropollutants.

INTRODUCTION

Increasing population growth, changes in social and resource-use habits, and significant industrial and technological progress have led to an increase in the generation of municipal and industrial solid waste worldwide (Ojeda-Benítez & Beraud-Lozano, 2003; Renou et al., 2008). Landfills are one of the most affordable and acceptable means of final disposal of solid waste worldwide. Solid waste in a landfill is degraded by both aerobic and anaerobic processes. Once waste is placed in a landfill, it undergoes many physical, chemical and biological processes. These processes lead to production of landfill leachate and gas. Landfill leachate is a complex mixture with markedly varying composition depending largely on

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the type of waste and age of the landfill. Leachate production poses serious environmental concerns such as pollution of groundwater and surface water if not properly managed, collected and treated. These concerns are particularly serious, where waste is deposited in unlined landfills (Umar, 2010).

Landfill leachate is generally very high in organic matter (both biodegradable and refractory to biodegradation), with humic-like matter making up an important group, as well as ammonia–nitrogen, heavy metals, chlorinated organic and inorganic salts. Although much lower in concentration (μg/L to ng/L) when compared with conventional contaminates, micropollutants constitute an important group of contaminants in landfill leachate. Over the last few decades, there has been an increasing concern on their occurrence due the increasing concentration originating from a wide range of sources including pharmaceutical, chemical engineering and personal care product industries in rivers, lakes, soil and groundwater. Micropollutants are subjected to various processes such as distribution between different phases, biological and abiotic degradation in environment (La Farre et al., 2008). These processes contribute to their elimination and affect their bioavailability. The role of the aforementioned processes in micropollutants' fate depends on their physico-chemical properties (polarity, water solubility, vapor pressure) and the type of the environment (natural or mechanical), where the micropollutants are present (groundwater, surface water, sediment, wastewater treatment systems, landfill leachate, drinking water facilities) (Virkutyte et al., 2010). As a result, different transformation reactions can produce metabolites that often differ in their environmental behavior and ecotoxicological profile from the parent compounds. Micropollutants may include two classes of contaminants: (1) legacy contaminants of which toxic effects have been established, and control measures have been developed; (2) contaminants of emerging concern that are not currently regulated and are thought to have potential threats to environmental ecosystems or human health and safety (La Farre et al., 2008).

Persistence of micropollutants in the groundwater down gradient of landfills has been reported by in various studies (Barnes et al., 2008; Buszka et al., 2009). In fact, landfill leachate contaminated groundwater had been shown to have the highest median concentrations of micropollutants (Lapworth et al., 2012). As a result, landfills have been recognized as one of the primary sources of contamination in groundwater and surface water (Barnes et al., 2008; Befenati et al., 2003; Buszka et al., 2009; Holm et al., 1995; Stuart et al., 2012). Pharmaceutical and personal care products (PPPCs) and endocrine disrupting compounds are a great concern with regard to landfill leachate as these compounds have the potential to contaminate both surface and ground water. Because pharmaceuticals are biologically active substances designed to cure or prevent diseases, they can interfere with biological systems and their toxic effects can affect every hierarchical ecological level: subcell, cells, organs organisms, populations, ecosystems, and ecosphere (de Witte et al., 2011). Endocrine disrupting compounds disrupt the endocrine system of aquatic biota (multiple-appendaged amphibians, feminization of fish, etc.) (Yang et al., 2014). Recently, evidence from field research has indicated adverse reproductive and developmental effects in wildlife (Kidd et al., 2007).

Treatment of landfill leachate is therefore, an important part of leachate management strategy. Several physicochemical and biological techniques are used for the treatment of landfill leachate, such as coagulation, flotation, chemical precipitation, adsorption, membrane filtration and various biological processes (i.e., sequencing batch reactors, anaerobic sludge blanket) (Garcia-Lopez et al., 2014; Ince et al., 2010). A combination of physicochemical and biological processes is generally needed to treat landfill leachate to an acceptable level. Conventional treatment approaches can be ineffective for the treatment of micropollutants. As a result, there is an increasing interest in alternative novel approaches that are efficient in removing such toxic compounds and to remove potential estrogenicity. A combination

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of conventional and novel processes is in particularly, promising considering the increasingly stringent regulations related to quality of treated leachate prior to discharging to receiving waters. The objective of this chapter is to provide an assessment of the presence of micropollutants in landfill leachate and to look into the effectiveness of various methods for their removal.

BACKGROUND

In recent decades, the types of waste materials deposited in landfills have changed, mainly as a result of higher demand and better quality of consumer products. For example, batteries, paints, oils, electrical products and micropollutants that are potentially deposited at landfills contain additives that can negatively impact the environment and human health (Eggen et al., 2010). Micropollutants in landfill leachate include a variety of organic contaminates including compounds used in household and industrial applications and consumer products that include fecal and plant sterols, food additives, soaps and detergents, solvents, cleaning agents, fire retardants, plasticizers, perfumes, pesticides and pharmaceuticals (Andrews et al., 2012). Their presence in landfill leachate can be a consequence of the direct use of these compounds and their successive discharge or their leaching from discharged products (Loffredo et al., 2014). Pharmaceutical compounds may occur in concentrations of approximately 8.1 mg/kg in typical MSW (Musson & Townsend 2009). Having been discarded in landfills, micropollutants may be degraded/metabolized, adsorbed to solids, or dissolved in leachate (Musson and Townsend 2009).

Leaching of organic micropollutants from landfills to groundwater and/or disposal to surface water is a an important environmental problem, considering these compounds are potentially toxic, estrogenic, and carcinogenic to both terrestrial and aquatic organisms (Cozzarelli et al. 2011; Huset et al. 2011; Matejczyk et al. 2011). Some studies have reported that mixtures of dilute concentrations of micropollutants in water may deleteriously affect human health, as had been previously shown for aquatic biota (Sharpe & Skakkebaek 1993; Lye et al. 1999; Pomati et al. 2006; Tillitt et al. 2010).

Although most modern landfills have leachate collection and pumping systems to collect leachate into lined holding pits or lagoons, leaks through liners, caps, and leachate collection systems could lead to some of its escape from containment systems into the surrounding environment (Andrews et al., 2012). Furthermore, leachate collected in containment systems generally is drained into sewer lines that discharge to municipal Wastewater Treatment Plants (WWTPs). As existing WWTPs were not designed to remove micropollutants, varying proportions micropollutants could be discharged with treated waste water back into the receiving streams (Ternes 1998; Snyder et al. 2007).

Understanding the occurrence and removal of micropollutants in wastewater and develop effective ways to safe levels is critical in assessing their environmental and public health risk and determining safe levels. As the reclamation and reuse of a range of wastewaters is an emerging approach to mitigate the stress from water scarcity in many regions of the world, one of the main concerns in water recycling is the risk resulting from micropollutants at trace concentrations. As a result, there is now a strong need for the enhanced removal of micropollutants using alternative approaches which are efficient and cost effective.

One of the major limitations in determination of trace organic contaminants has been the difficulties in analyzing these compounds considering their very low concentration. This has been more relevant to complex matrices such as landfill leachate. However, recent analytical advancements have now made it possible to detect compounds at very low level to be determined in most wastewater matrices. Although landfill leachate has been extensively investigated for the presence and removal of dissolved organic

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carbon (DOC), ammonium, methane, and heavy metals, there is a limited data on the type and concentration of micropollutants present in landfill leachate. Consequently, there is little data available on their removal from landfill leachate using conventional and novel approaches.

Occurrence of Range of Micropollutants in Landfill Leachate

The U.S. Geological Survey recently conducted the first national assessment of the range of micropollutants in landfill leachate in United States (Masoner et al., 2014). Leachate was collected form 19 active landfill sites and analysed it for 202 chemicals across a wide range of uses, including pharmaceuticals, hygiene products, home-use chemicals, pesticides, plastics etc. Out of those, a total of 129 compounds including 62 prescription pharmaceuticals, 23 industrial chemicals, 18 nonprescription pharmaceuticals, 16 household chemicals, 6 steroid hormones, and 4 plant/animal sterols were detected in landfill leachate. Concentration of the chemicals found varied widely. Steroid hormone concentrations generally ranged from 1 to 100s ng/L, prescription and non-prescription pharmaceuticals concentrations generally ranged from 100 to 10,000 ng/L, whereas home-use and industrial chemicals ranged from 1,000 to 1,000,000s ng/L.

Organic compounds identified by GC-MS full scan analysis of leachates from three landfills (landfill A, B, and C) was carried out by Eggen et al. (2010). They classified organic compounds into substance groups to facilitate interpretation of leachate composition. The non-target analysis indicated hundreds of compounds per sample of which, about 80% could be classified into substance groups. The authors performed qualitative and semi-quantitative overviews on the substances released and transported via the landfill leachate. Total organic load of leachate samples collected from landfills B and C was approximately 4 and 1.5 times higher than those from landfill A, respectively. At landfill A, leachate of the fresh active part releases about 10-fold more organic substances than leachate from the old, inactive dump. The authors also identified chemicals in the landfill and their transport downstream of a sandy aquifer was reported at landfill A. The amount of organic substances decreased in the wells downstream of the landfill, although 100 m downstream was at the same level as active part. In addition to variation in the total organic content, the composition of pollutant mixtures was different for each site and also between samples at landfill A. The ratio of PAHs to cycloalkanes, alkanes, and iso-alkanes could indicate the degradation potential in landfills. The highest proportion of alkanes was measured in leachates from landfill C and in 50 m downstream at landfill A. In general, these indicate different sources of waste and probably different biodegradation potential of the landfills. The proportion of cyclic or unsaturated hydrocarbons was reported to be high in leachates from landfills B and C.

Alkylated phosphates, both chlorinated and non-chlorinated, were found in all leachate samples (approximately 2–10% of total organic content) and triethylphosphate and tris(chloropropyl)phosphate (TCPP) were detected in all leachates samples, except in the operational part of the landfill A (Eggen et al., 2010). Tri(2-chloro-ethyl)phosphate (TCEP) and tris(1-chloro-2-propyl) phosphate (TCPP), were reported in landfill leachate by several other authors (Barnes et al., 2004; Paxéus, 2000; Schwarzbauer et al., 2002). According to these authors, the TCEP, TCPP and Tri-iso-butylphosphate were found in ranges of 220-240,000, 4000–50,000 and 110,000–350,000 ng/L, respectively.

Some of the widely used insecticides such as N,N-diethyl toluamide (DEET), benzothiazole, and N-butyl benzenesulfonamide (NBBS), were reported in leachate samples by several authors (Barnes et al., 2004; Paxéus, 2000; Schwarzbauer et al., 2002; Welander, 1997). The polar properties of these substances with log K_{ow} (ratio of the concentration of a chemical in n-octanol and water at equilibrium at a specified temperature) values of 2.2 (DEET), 1.99 (benzothiazole), and 2.1 (NBBS) (Westerhof et

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al., 2005), contribute to their spread in aqueous environment. For example, while NBBS is a naturally occurring substance that is used commercially as plasticizer in the polymerization of polyamides and has previously been shown to be neurotoxic (Strong et al., 1991), DEET is an insect repellent and is frequently detected in leachates at µg/L level (Eggen et al., 2010). NBBS has also been measured in landfill leachates at µg/L range (Welander, 1997) and standardized OECD tests have classified this compound as persistent. Considering the polarity of TCPP with log K_{ow} 2.59–3.33 (OECD), TCEP with log K_{ow} 1.4, DEET (2.2) and NBBS (2.1), these compounds are not expected to bioaccumulate in the environment, however their recalcitrant nature and high polarity render them potentially readily transportable through conventional landfill treatment systems.

Perfluorinated compounds (PFCs) have a widespread application in a myriad of products, including household cleaning agents, carpets, textiles, paper coatings, cosmetics, fire-fighting foams and packaged-food containers (Hekster et al., 2003). Presently, little data on their occurrence in landfill leachate is available, however, some studies have shown that landfill leachate may represent a significant source of PFCs (Bossi et al., 2008; Kallenborn et al., 2004; Woldegiorgis et al., 2006; Busch et al., 2010). Contrary to many persistent organic pollutants with a medium to high hydrophobicity, many PFCs are mainly found in the water phase (Schultz et al., 2006), and efficient removal of these compounds becomes challenging during leachate treatment (Eggen et al., 2010). Quantitative analyses of PFCs in water and particle phases were performed for leachates from two landfills and sediment samples from another landfill by Eggen et al. A comparison of the concentrations of PFCs measured in 2004 and 2006 showed that their concentration was generally greater in 2006, where the majority of PFCs were found in the aqueous phase. In the 2004 leachates, perfluorooctanoic acid (PFOA) was the predominant compound with concentration respective ranges of 23–118 and 5.8–157 ng/L in water and particle phase.

In a study by Busch et al. (2010), the sum of PFCs was in the range of 31–12,819 ng/L (average 5777 ng/L) in untreated leachate samples, 15–129 ng/L (average 42 ng/L) in reverse osmosis treated leachate, 9–4079 ng/L (average 723 ng/L) in active carbontreated leachates (n=8), 621 and 1257 ng/L (n=2) in nanofiltrated leachates, 1992 and 4610 ng/L in wet air oxidation treated leachates, and 4023 and 8059 ng/L in biologically treated leachates. Polycyclic musk compounds are used in various household products and cosmetics. The occurrence of polycyclic musk compounds in landfill leachate was investigated by Eggen et al. (2010). The authors reported the highest concentration of polycyclic musk compounds in leachates from the closed and vegetated part of the landfill with concentration of 482,000 ng/L in the water phase.

Bisphenol A (BPA), also known as 2,2-bis-(4-hydroxyphenyl) propane or 4,40-isopropylidenediphenol, is an endocrine disrupting compound (EDC) that has been widely studied due to its extensive use in making polycarbonate plastic and epoxy resins, which are used in polycarbonate baby feeding bottles and epoxy food-can linings. BPA has been shown to have some similarity of chemical structure with estrogen, and exhibits affinity with estrogen receptors. BPA has been classified as an EDC by the USEPA (1997) and is found in a wide range of aquatic environments. BPA has also been reported in landfill leachate of 7 out of the 10 landfill sites by Yamamoto et al. (2001) with concentrations ranging from 1.3 to 17,200 µg/L. The mean concentration of BPA in that study was 276 µg/L which is in agreement with that reported by Boonnorata et al. (2014). However, Kalmykova et al. (2013) reported a lower concentration (up to 107 µg/L) of BPA than aforementioned studied.

Li et al. (2014) investigated the presence of polybrominated diphenyl ethers (PBDEs; additive flame retardants) at 4.0–351.2 ng/L level, with an average of 73.0 ng/L in landfill leachate in a city in North China. The authors reported that BDE-209 dominated the congeners in most of the samples, followed

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by BDE-47 and BDE-99. Greater PBDEs concentrations were reported in leachate from young landfill sites located in the urban area. The authors performed a Pearson correlation analysis which demonstrated a potential dependence of the concentration of PBDEs on landfill age, suspended solids and DOC concentration.

Phthalic Acid Esters (PAEs)

Phthalic acid esters (PAEs) can be highly concentrated in landfill leachate (Schwarzbauer et al., 2002) and are one of the most extensively investigated micropollutants in landfill leachate. Phthalates has been detected in leachates from landfills in several studies (Table 1). As noted in Table 1, a wide range in the concentration of PAEs was reported ranging from 0.10-470 µg/L. PAEs are classified as endocrine disrupting compounds that are known to adversely impact the reproductive, neuro developmental, and immune system of both humans and wildlife. Dissolved organic matter (DOM) facilitated transport of PAEs is an important transport mechanism from solid waste (Bauer & Herrman, 1997). The distribution of three PAEs including diisobutylphthalate (DIBP), di-n-butylphthalate (DnBP) and bis(2-ethyl) hexylphthalate (DEHP) in humic acid (HA), fulvic acid (FA) and hydrophilic fractions (those having an affinity to water and are usually charged or have polar side groups to their structure) of leachates from sanitary or bioreactor landfills was evaluated by Zheng et al. (2007). The results showed that the PAEs were bound mainly to the HA fraction in leachate, irrespective of landfill age or leachate recirculation. Molecular weight of DOM correlated well with PAEs partition. Considering the presence of phenolic, carboxyl or amide groups in DOM fractions, the interactions between PAEs and leachate DOM were expected to be mainly due to hydrogen bonding. The peptide groups in the HA fraction was likely explanation of the strong affinity of PAEs for HA. The fluorescence excitation-emission-matrix spectra demonstrated that the hydrophilic fractions shared similarities with HA-like substances with regard to their molecular structure, partly explaining why PAEs exhibited a clear sorption to the hydrophilic fractions.

Another study conducted by Xiaoli et al. (2010) showed that the association of humic substances (HS) with PAEs depends greatly both on the properties of the PAEs and the source of HS. Greater association of DnBP, which has a high log K_{ow} and low water solubility suggests that non-specific hydrophobic interactions between PAEs and HS could have an important role in their abiotic association. The HS, with higher aromatic content and a larger molecular weight, has a strong association with DnBP, indicat-

Table 1. Concentration of various phthalate esters in landfill leachate

Compound	Concentration (µg/L)	Reference
bis (2-ethylhexyl) phthalate	<1.0-23	Kalmykova et al. (2013)
bis (2-ethylhexyl) phthalate	180	Rocha et al. (2013)
bis (2-ethylhexyl) phthalate	293	Boonnorata et al. (2014)
Diethyl phthalate	<0.10-22	Kalmykova et al. 2013
Diethyl phthalate	130	Boonnorata et al. (2014)
Di-n-butyl phthalate	<0.10-1.8	Kalmykova et al. 2013
Di-n-butyl phthalate	275	Boonnorata et al. (2014)
Di-n-butyl phthalate	470	Rocha et al. (2013)

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ing that the hydrogen-bonding between the H-donating aromatic groups of HS with the H-acceptors in the PAE molecules may be involved in the association reaction between PAEs and HS. Occurrence of DEHP, DBP, and di-ethyl phthalate (DEP) (grouped as benzenedicarboxylic acid esters and contributing 5–20%) were detected in at least three leachate samples collected from three different landfill sites.

Potential of Leaching of Micropollutants from Landfill Sites

In addition to the micropollutants in leachate produced, there is a strong potential of the contamination of the groundwater and reservoirs due to their leaching specifically in the vicinity of landfills. This problem is particularly severe in countries where solid waste is landfilled or has been landfilled without separation/pre-treatment as this could result in enhanced release of contaminants, posing potential contamination of the surrounding environment.

Several antibiotic compounds (e.g., sulfamethoxazole, lincomycin, and erythromycin) have been detected in groundwater in Europe and North America, with maximum concentrations in the range of 5.7–2×10^3 ng/L (Lapworth et al., 2012; Peng et al., 2014). Moreover, a variety of industrial chemicals (e.g., detergents, fire retardants, and plasticizers), pharmaceuticals and personal care products (PPCPs) (e.g., anti-inflammatories, β-blockers, drugs of abuse, antiseptics, preservatives, and sweeteners) and their metabolites have been observed in groundwater (Lopez-Serna et al., 2013; Loos et al., 2010; Osenbruck et al., 2007). The occurrence of various PPCPs including antibiotics, azole anti-fungals, non-steroid anti-inflammatory drugs, lipid regulators, parabens, antiseptics, and bisphenol A, was investigated in groundwater and reservoirs in the vicinity of two municipal landfills in the metropolis of Guangzhou, South China by Peng et al. (2014) Dehydroerythromycin, sulfamethoxazole, fluconazole, salicylic acid, methylparaben, triclosan, and bisphenol A were the mostly frequently detected PPCPs in the groundwater at low ng/L levels. Lapworth et al. (2012) found that landfill leachate contaminated groundwater had the highest median concentrations of a range of emerging organic contaminants.

The pharmaceuticals, paracetamol, phenazone, and gemfibrozil were not detected in any of the samples in a study conducted by Eggen et al. (2010), while the non-steroidal anti-inflammatory drug (NSAID), ibuprofen, was detected in all leachate samples. The highest ibuprofen concentration of 166,624 ng/L, was measured in leachate from the inactive part of the landfill, decreasing to 96.9 ng/L at inlet to treatment plant. Naproxen, another NSAID, was measured in the leachate from the active part of the landfill at a concentration of 282 ng/L. Compared to ibuprofen, the lower concentration level of naproxen probably reflects a lower deposition volume and/or a faster degradation with shorter half-life (9–14 days) compared to ibuprofen (32 days) (Araujo et al., 2009; Tixier et al., 2003). The neuroleptic drug carbamazepine applied as an anti-epileptic drug and anti-depressive was measured at trace concentration of 8.6 ng/ L in the active phase of the landfill and at inlet to the treatment plant at 0.8 µg/L. Despite these trace levels, carbamazepine is one of the most distributed drugs in the environment (Clara et al., 2004; McClellan & Halden, 2010; Zhang et al., 2008). Due to its persistence and semi-polar properties, carbamazepine can reach groundwater and has been detected in drinking water (Donn et al., 2008).

The concentration of polycyclic musk compounds was reported to decrease downstream of the landfill. Considering their more hydrophobic properties (HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran) log K_{ow} 5.9, AHTN (6-acetyl-1,1,2,4,4,7-hexamethyltetraline) log K_{ow} 5.7) (Balk & Ford, 1999), these polycyclic musk substances are adsorbed on surfaces of suspended matter and detected in both the water and particle phases. The particle-bounded concentration of musk, presented as the sum of AHTN and HHCB, at active part and 200 m downstream of landfill

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was 9.6 and 17.9 ng/L, respectively. The corresponding water phase concentration was 6.5 and 3 ng/L, respectively. The authors inferred that it indicated transportation of these compounds via both water and particle phases through the sandy aquifer of the landfill. The particle-bound musk contribution in leachates from another landfill, taken at the discharge of the WWTP drainage system, was 27 ng/L. The relatively lipophilic HHCB has been observed in the range of 43–63 mg/kg dry weight sewage sludge in previous studies focusing on the environmental fate of musk compounds (Carballa et al., 2007).

Treatment of Micropollutants in Landfill Leachate

The current scenario related to the occurrence of micropollutants in the receiving waters requires new approaches for their treatment. Unfortunately, conventional wastewater treatment plants are designed to deal with bulk substances that occur regularly and in large quantities (primarily organic matter and the nutrients, i.e., nitrogen and phosphorus). Micropollutants are however, entirely different due to their unique characteristics and behavior in the treatment plant and are not generally eliminated during the treatment. Moreover, their concentration is very low compared with conventional contaminants making them less amenable to elimination. Thus, new measures need to be taken to reduce for their reduction or complete elimination from water and wastewater.

Membrane Bioreactors

A recent study by Boonnorata et al. (2014) investigated the removal of BPA, 2,6-di-tert-butylphenol (2,6-DTBP), 2,6-di-tert-butyl-4methylphenol(BHT), di-ethyl phthalate (DEP), di-butyl phthalate (DBP) and bis-(2-ethylhexyl) phthalate (DEHP) in municipal solid waste landfill leachate using two-stage membrane bioreactor (MBR) in a long term operation of 500 days. These contaminants were effectively removed in both anoxic and aerobic conditions, however, greater removals were obtained under aerobic conditions. The predominant removal mechanism of removal of investigated compounds was biodegradation with removal of up to 99.5%, 99%, 99%, 98%, 97% and 96% for BPA, 2,6-DTBP, BHT, DEP, DBP and DEHP, respectively. Chemical properties of the leachate were considered the main factor affecting the removal efficiency of contaminants. Among the investigated compounds, BPA, 2,6 DTBP, DEP are relatively hydrophilic, their biodegradation rate was higher. The molecular structure of DHEP is more complex and pre-treatment by adsorption and downstream biological treatment could be an effective way of removing such compounds.

Yiping et al. (2008) used anaerobic-membrane bioreactor in order to remove organic micropollutants that were present in the landfill leachate effluent. In their study, 17 organo-chlorine pesticides (OCPs), 16 polycyclic aromatic hydrocarbons (PAHs) and technical 4-nonylphenol (4-NP) were investigated and they found that 4-NP compound were removed by the MBR whereas OCPs and PAHs were mainly removed by the anaerobic process. An overall removal of 94% of OCPs, 77% of 4-NPs and 59% of PAHs was reported by the authors.

A study conducted by Wintgens et al. (2003) investigated two different landfill leachate treatment plants with a variety of process configurations. The xenoestrogenic substances, namely, nonylphenol and bisphenol A were detected in high µg/L-ranges in raw landfill leachate. MBR was capable of removing more than 80% of the nonylphenol load and the final concentrations were reported to range between 1–12

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µg/L nonylphenol and 3–30 µg/L bisphenol A, respectively. The authors reported that reverse osmosis was less effective for the removal of both nonylphenol and bisphenol A than MBR with downstream polishing stages like nanofiltration and activated carbon adsorption.

Fenton and Photo-Fenton

Rocha et al. (2013) identified more than 40 organic compounds in landfill leachate including benzene (0.09±0.07 mg/L), trichlorophenol (TCP) (0.18±0.12 mg/L), phthalate esters DnBP (0.47±0.01 mg/L), Butyl benzyl phthalate (BBP) (0.36±0.02 mg/L), DEHP (0.18±0.01 mg/L), among others and investigated their removal using solar photo-Fenton oxidation process. Toluene, pentachlorophenol, dimethyl phthalate, diethyl phthalate, and Di-noctyl phthalate were not detected in any of the samples. After treatment, TCP decreased to below the detection limit whereas the benzene concentration increased approximately three fold. Oxidation of 3 phthalate esters namely DnBP, BBP, and DEHP by the solar photo-Fenton process was demonstrated the process to be very efficient for the treatment of DnBP with a reduction of 77% however the reduction of BBP was low (17%) whereas no reduction of DEHP was observed. Overall, the solar photo-Fenton process was considered to be very efficient for the treatment of sanitary landfill leachates, leading to the complete elimination of 24 of the detected micropollutants to levels below their respective detection limits and low to significant abatement of seven other organic compounds, thus resulting in an increase of the leachate biodegradability.

There are limited studies conducted using the Fenton-based processes for the removal of micropollutants from landfill leachate. In addition to the limited investigation of the Fenton and related processes (photo-Fenton, electro-Fenton), there is no data on the types of breakdown products that could form during these treatments. Determination of by-products is significantly important considering some of those by-products are even more toxic than the parent compounds raising concerns related to the toxicity of treated leachate.

Adsorption

Activated carbon is the most commonly used adsorbent for industrial applications, particularly for the elimination of organic compounds from aqueous solution due to its chemical and textural properties (Alslaibi et al., 2013; Ocampo-Pérez et al., 2012). Adsorption on activated carbon has been recommended by the US Environmental Protection Agency as the best available technology for removing non-biodegradable toxic organic compounds from drinking water and industrial wastewater (USEPA, 1997). One of the important aspects of the adsorption processes considering the treatment plant design is the adsorption kinetics (Alslaibi et al., 2014). The overall adsorption rate of phthalic acid, BPA, diphenolic acid, 2,4-dichlorophenoxy-acetic acid, and 4-chloro- 2-methylphenoxyacetic acid on two commercial activated carbons was studied by Ocampo-Pérez et al. The authors used pore volume and surface diffusion model (PVSDM) diffusional and a kinetic model. The PVSDM model considers external mass transport, intraparticle diffusion, and adsorption on an active site whereas the concentration decay data were interpreted by using kinetics models. The PVSDM model satisfactorily fitted the experimental data of adsorption rate onto activated carbon. The contribution of pore volume diffusion represented greater than 92% of intraparticle diffusion, implying that the pore volume diffusion was the controlling mechanism of the overall rate of adsorption and role of surface diffusion could be neglected. Although

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both diffusional models and kinetic models successfully fitted the adsorption rate experimental data, the authors recommend the use of diffusional models, since the assumptions were closer to the real adsorption process, than those of kinetic models.

The sorption and degradation of petroleum hydrocarbons (PHCs), alkylphenols, BPA, phthalates and PAHs in landfill leachate was investigated by using peat, sand and GAC filters by Kalmykova et al. (2014). It was reported that the removal of the sand filter was insufficient to meet water quality standards. However, sand filter was proposed as a necessary pre-treatment for the precipitated iron to avoid saturation of the filter material and to improve the removal of PAHs and PHCs in peat and GAC filter. Pyrene and DEHP were reported to be removed to a similar extent by sand and GAC filters, whereas the removal efficiency of the higher alkanes was lower for peat and GAC filters. The general trend revealed that PHCs were the most difficult compounds to remove, which was attributed to the colloid-facilitated transport from the peat filter and desorption from the GAC filter.

Coagulation

Coagulation is rarely investigated for the removal of micropollutants which predominantly relates to the ineffectiveness of coagulants to satisfactorily remove such compounds. Six PAEs, namely dimethyl phthalate (DMP), di-ethyl phthalate (DEP), DBP, BBP, DEHP, and di-octyl phthalate (DOP), are listed as priority pollutants by the US Environmental Protection Agency. The removal of these six PAEs by coagulation was evaluated from fresh and partially stabilized landfill leachate by Zheng et al. (2009). The PAEs were partly removed from fresh and partially stabilized landfill leachates (about 30% and 50%, respectively) by coagulation. The PAEs removal efficiencies in the fresh leachate were similar to the reduction of dissolved organic matter (DOM) measured as TOC and relative to the hydrophobicity of PAEs. The humic substances in the partially stabilized leachate facilitate the PAEs removal in a CF process. However, more studies are required to investigate the removal of micropollutants considering coagulation as the most widely and commonly used pre-treatment method in landfill leachate treatment. The use of novel coagulants ($TiCl_4$) and electrocoagulation are potential alternatives to traditional coagulation approaches for the removal of trace contaminants.

Estrogenicity of Landfill Leachate

There is increasing concern about the environmental effects of oestrogens and xenoestrogens that end up in receiving waters (Daughton, 2009). Estrogenic activity of municipal waste landfill leachate was investigated using a reporter-gene-based bioassay with a human breast-cancer-derived cell line (MVLN cells) by Coors et al. (2003). The leachate was processed using two different membrane processes operating in parallel. One process consisted of aerobic biological degradation, ultrafiltration, and downstream adsorption onto activated carbon. The second process used reverse osmosis treatment of the raw leachate. The efficacy of these two processes in removing estrogenicity was compared. Although both treatments removed more than 97% of the estrogenic activity, calculated as estradiol equivalents (EEQs), the treatments were not equally effective; after adsorption onto activated carbon, no estrogenicity was detected, whereas concentrated effluent of the reverse osmosis treatment elicited an estrogenic response in the bioassay potentially due to accumulation of contaminants in the brine. Chemical analysis revealed that bisphenol A was responsible for the majority of the estrogenic response in the raw and treated landfill leachate.

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An in vitro test based on recombinant yeast strains transfected with genes for the human estrogen receptor was adapted to study the occurrence estrogenic and antiestrogenic substances in six Swedish landfill leachates (Svenson et al., 2009). The authors measured the antiestrogenic effects as inhibition of the estradiol induced response with the human estrogen receptor α, and quantified by comparison with the corresponding inhibitory effects of a known antiestrogen, hydroxytamoxifen. The results revealed that the estrogenicity was within the range of that determined in domestic sewage effluents, from below the limit of detection to 29 ng estradiol units/L. Antiestrogenicity was detected in some of the landfill leachates and ranged between 38 and 3800 µg hydroxytamoxifen equivalents/L. Fractionation of leachate revealed that estrogenic compounds were located in two dominant fractions. BPA, estradiol, and ethinylestradiol accounted for the estrogenic activity in extracts of leachates.

CONCLUSION

Emerging compounds identified in landfill leachate include a range of chlorinated alkylphosphates including the possible carcinogenic flame retardant (TCPP), the neurotoxin plasticizer (NBBS), the insect repellent (DEET), PFCs, pharmaceuticals and personal care products such as the NSAIDs (ibuprofen and naproxen) and polycyclic musk compounds. Analysis of micropollutants is becoming increasingly important as well as prevalent and increasing studies have reported their occurrence in landfill leachate. In addition to analyzing the landfill leachate, there is a strong need of future research to correlate the landfill leachate and micropollutants occurrence in the nearby aquatic environments. Despite the contribution of estrogenic load on the aquatic environment seems to be low for treated leachate when compared with that of sewage treatment works, the high estrogenic activity in raw landfill leachate stresses the necessity for the appropriate treatment to minimize such hazards. Long-term fate of micropollutants in landfill leachate has not been extensively studied which is critical considering the recalcitrant nature of some of the micropollutants. Long-term studies of changes with regard to changes in microbial structure and function in environments downgradient of landfills could provide insight into the potential hazards associated with landfill leachate.

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Chapter 69
Green Information Technology Usage:
Awareness and Practices of Philippine IT Professionals

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ABSTRACT

Green information technology is resource efficient and effective consumption through the use of IT infrastructures to address environmental sustainability. This study aims to understand the level of awareness and practices of IT professionals towards GIT in organizations. A survey questionnaire was used, the study found that participants have a high awareness and practices of Green IT covering the efficient use of computing resources, energy conservation in an office environment, responsible disposal of electronic wastes, and demonstrate an individual contribution and commitment to GIT adoption practices in organizations. The study also found that male IT professionals have better awareness of GIT in organizations. The awareness and practices of IT professionals in GIT offers direction for organizations to strategically integrate GIT within their core business objectives and activities to attain environmental sustainability. Practical and theoretical implications are presented.

1. INTRODUCTION

Green IT is the study and practice of environmentally sustainable computing in organizations. It is an approach to address the growing environmental challenges resulting in detrimental effects to natural resources, increased carbon emissions, and leads to global warming (Bengtsson and Ågerfalk, 2016). These problems are associated with business activities heavily relying on the use of IT. Thus, it resulted in the inception of Green IT (GIT). The goal of GIT is to achieve resource-efficient and low-carbon business activities to minimize its impact on the environment (Loeser et al., 2017. Therefore, GIT remains a significant area of both research and practice.

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Previous studies suggest that knowledge of new technology is critical to further technology adoption in organizations (Jenkin et al., 2011; El Idrissi and Corbett, 2016). It is also necessary to understand the role of professionals in the adoption of GIT in organizations and become an integral element of their work culture. Recent information technology (IT) infrastructure spending is crucial to achieving business performance (Chuang and Huang, 2016), however, as this grows, behavioral change among IT professionals is perceived significant to achieve sustainable use of computing resources (Murugesan and Gangadharan, 2012). Therefore, IT professionals have an important role to play in achieving environmental sustainability through their awareness of and practices in GIT in organizations.

The immense perspective to establish the practices of IT users helps to achieve environmental sustainability. More recently, GIT is a global issue for various industries. However, it is also growing concern in developing countries in which lacking educations is observed. The developing countries have been slow in recognizing environmental sustainability concerns and challenges (Hernandez and Ona, 2016; Chugh et al., 2016) in comparison to developed countries with advanced strategies, policies, and technology implementations on GIT. Therefore, developing countries have a significant role to play in GIT adoption (An Hign et al., 2017). It also calls for an urgent introduction to GIT, and take essential actions to engage and increase awareness of employees in organizations.

To date, studies on exploring the awareness of employees in GIT and practices are mostly focused in developed countries. However, a handful of studies investigating this phenomenon in developing countries such as the Philippines is not evident in the literature. Considering the growing economy and population of the country, therefore, this study attempts to fill this gap and offer new insights on GIT awareness and practices of IT professionals, which could be integrated as part of IT professionals' roles in achieving environmentally sustainable work practices in organizations.

This study aims to present the findings of a survey that explores the environmentally sustainable practices by Philippine IT professionals. To attain the goal of the study, a survey was used to determine the level of awareness and practices in GIT among IT professionals. The remaining parts this research covers the following sections: (2) discussions on the roles of IT professionals in environmental sustainability and overview of the Philippine IT industry, (3) discussion of the research method and considerations in adopting a survey instrument, (4) the results of the study and presentation of findings, (5) discussion of the theoretical and organizational contributions and lastly (6) the conclusions and research limitations are discussed.

2. LITERATURE REVIEW

2.1. Overview of the Philippine IT Industry

As of 2016, the total IT companies in the Philippines was at an average of 646 with different business activities supporting local and international customers (IBPAP, 2016). Moreover, the IT sector continues to grow due to the international demands and developing economies. In 2015, the IT sector posted USD 22 billion in revenues, thus, making it the second largest source of income in the Philippines (Magkilat, 2015) and accounts for 9% of the gross domestic product in 2016 (IBPAP, 2016). The IT sector labor market and productivity increased by 1.2 million direct jobs. The stable growth of the IT sector is attributed to the foreign direct investments, the numerous expansions and projects in the past five years (Manning et al., 2016). Recently, the IT sector encourages partnership with government agencies

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and academe to harness research and development (Hernandez and Ona, 2015), co-develop industry champions and participate in environmental sustainability programs. Similarly, the IT sector embarked to greener business activities such as GIT as one of the focus areas for rapid growth and sustainability (Department of Information and Communications Technology, 2016). Specifically, the professional associations and organizations in the IT sector developed GIT roadmap and strategy together with the design of guidelines on its implementation (Hernandez and Ona, 2016). Overall, through GIT, the IT sector contributes to achieving a more sustainable business and environment.

2.2. Roles of Information Technology Professionals in Environmental Sustainability

The Philippines Information Technology-Business Process Management (IT-BPM) sector experience sustained growth in the last five years (Department of Information and Communications Technology, 2017), however, as an indirect result, greengas house emissions and energy consumption continuously rise (Department of Science and Technology, 2013). These results contribute to the long term environmental degradation. Thus, organizations in the Philippines proactively adapt to GIT and sustainable practices as IT infrastructure continues to grow (Komatsuzaki, 2016) in many industries. Santiago (2013) reported that GIT and sustainability initiatives spending in the Philippines would reach USD 2.5 billion by year 2020. It manifests the gap in GIT and sustainability adoption and slower as compared to other developing countries as Philippine organizations lack strategic directions and approaches to further GIT adoption (Deloitte, 2015). Moreover, major problems and issues confronting the Philippines on sustainable environment from an IT perspective covers (a) rising electronic waste (Terazono et al., 2017), (b) ignorance (Roumasset et al., 2016), rising energy costs (Roxas and Santiago, 2016), (d) increasing carbon footprint (Holden et al., 2017), and depletion of natural resources (Khan et al., 2016).

These problems prompt serious threat to environmental sustainability, public health and safety, thus, a strategic approach is necessary to address these problems (Lee et al., 2013; Khor et al., 2015; Terazono et al., 2017). The establishment of GIT based strategic business approach, guidelines, integration of IT infrastructure, and systems are critical in the primary business procedures of an organization to achieve resource-efficiency and effectiveness and reduce environmental footprint (Montabon et al., 2016). The goal of GIT is to address technology inefficiencies essentially, focus on searching for available best options, and more effective strategies. Environmental sustainability may be referenced alongside different measures, but, in the perspective of GIT, it is commonly concentrated in the reduction of energy consumption in the entire business lifecycle (Deng and Ji, 2015), decreasing greenhouse gas emissions, better environmental knowledge and governance (Mithas et al., 2010), the usage of technology efficient equipment, and electronic waste reduction from IT industry (Luthra et al., 2014). Prior works proved that GIT adoption reduces costs (Tseng et al., 2013; Harmon and Auseklis, 2009; Chitra, 2011). It can also increase profit by 45% of organizations (Gullo and Haygood, 2010). Considering GIT adoption is an essential aspect in addressing sustainability associated concerns. Similarly, Hilty and Aebischer (2015) stated that IT use can positively persuade environmental concerns. However, the beneficial outcomes of GIT adoption were recognized concerns worthy of further investigation.

Disposal of IT waste responsibly is a significant measure towards encouraging environmental sustainability (Afroz et al., 2012). Electronic waste can come from used and damage electric and electronic devices that reached the end of life. The IT industry contributes 36% of electronic wastes generated in the Philippines (Terazono et al., 2017). Thus, electronic waste is now a major concern both in quantity

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and toxicity in nature (Li et al., 2017). Most organizations and households are unaware of responsible electronic waste disposal schemes, except for firms with in-placed waste management policies (Yoshida et al., 2016). In support of this growing problem, managerial support and commitment, and organizational culture hinder environmentally friendly practices (Zaman and Sedera, 2016). Therefore, investigating the practices of IT professionals as well as organizations perspective with the sustainable environment could promote responsible electronic waste disposal within the IT industry.

The IT industry generates nearly 740 million metric tons of carbon emissions annually (Gelenbe and Caseau, 2015) in which carbon footprint also increases (Kanemoto et al., 2016). Hence, IT professionals can take the initial step to reduce carbon footprint in their organizations. The continuous growth of IT industry in the Philippines has led to the growing IT practitioners in the industry. The Philippines employs nearly 1.2 million of IT professionals working in IT-BPM industry (Hernandez and Ona, 2015). Considering the growing number of employees, it is essential to introduce awareness on GIT practices as to further GIT adoption in organizations (Hernandez and Ona, 2016). The IT industry is largely consuming energy and engaged in maintaining related products in various sectors (Hernandez and Ona, 2016). Hence, the practices IT employees adopt can have implications on environmental sustainability. The behaviors of IT employees also constitute an essential enabler on sustainable environmental practices. Moreover, GIT awareness emerged significantly in different industries (Makela and Luukkainen, 2013). Given the employees' awareness of GIT, it signifies a real foundation of change in behaviors with a greater focus on environmental sustainability (Baggia et al., 2017). Employees can take action and influence others to adopt GIT practices by changing some of their existing IT activities (Gan et al., 2017). However, GIT adoption practices are limitedly discussed in the literature (Loeser et al., 2017). It presents the necessity to adopt further GIT practices through the IT professionals' uptake through their knowledge and ability to apply these practices. Hence, investigating the level of sustainable computing knowledge remains an important aspect of information systems research and practice.

A key driver of sustainability investments within firms was employees' knowledge, support, and commitment towards sustainable computing practices (Yang et al., 2017). Front liners including employees and managers were considered crucial in adapting to sustainable computing activities (Al-Shemmeri and Naylor, 2017). Molla et al. (2014) in their study of IT professionals found that more concerns were focused on rising environmental challenges and their positive perspective about GIT. It was also concluded that it professionals were gradually changing their behaviors on GIT through paper-saving activities, however, in doubt of firm's awareness, practices, and policies on GIT. In a study of Philippine IT professionals to determine the significance of environmental issues, 35 percent of the respondents indicated that environmental sustainability was incorporated into their business activities (Hernandez and Ona, 2016). However, GIT is missing from the employees' perspective. Conversely, there were some sustainability practices covering switching off unused computers (Hernandez and Ona, 2016) and 3R (recycle, reuse, reduce) (Widjaja et al., 2011; Terazono et al., 2017), reducing the brightness of desktop displays (Chow and Chen, 2009), and common understanding about sustainable computing practice (Watling and Zhou, 2011) as well as reducing printed business documents.

The main point of the literature review highlights the concerns on sustainable computing activities. These issues and challenges were investigated comprehensively, thus, mostly conducted in developed nations, covering small to large scale organizations (Weng and Lin, 2011; Zailani et al., 2014; Abdullah et al., 2014; Cuerva et al., 2014, Lim et al., 2015), however, as stated in the introduction, a handful of studies have been available in the literature exploring the environmentally sustainable practices of IT

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professionals in the Philippines. Hence, this research explores on both awareness and practice as there is little work in this area despite the critical roles of IT practitioners in the design, manufacturing, use, and disposal of IT infrastructure and related systems.

Finally, this study aims determine the green behaviors (Jenkin et al., 2011) of IT employees (Murusegan and Gangadharan, 2012) in a developing country perspective (Lee et al., 2013), by specifically exploring awareness (Chuo and Chuo, 2012) and practices in GIT (Seidel et al., 2010). Figure 1. presents the awareness of and practices in GIT of Philippine IT professionals. The components identified were from the previously discussed literature review in the section.

3. METHODOLOGY

The purpose of this research is to determine the level of awareness and practices of Philippine IT professionals towards GIT. The succeeding sub-sections discuss the survey questionnaire, demographic profile of the participants and data collection activities. This study used a validated survey questionnaire from the literature with three sections and sixteen items (Chugh et al., 2016). The questionnaire uses Likert's scale using a five-point scale for awareness and GIT practices with categories such as (a) demographic information, (b) awareness of environmental sustainability and (c) environmentally sustainable practices adopted by respondents and their organizations.

The survey questionnaire was distributed to thirty-eight firms of different sizes. The respondents were invited to participate through an email sent to the firm's IT manager containing the web survey link. The data was gathered from October – December of 2016. The survey was distributed to IT professionals as they were considered as knowledge workers (Gullo and Haygood, 2010) and were involved in GIT practices at the professional and individual level. The IT professionals were also considered as they were users and driver of GIT initiatives. Purposive and snowball techniques were used to ensure that the respondents were only IT professionals of different participating organizations. The IT managers were requested to distribute the survey to the selected IT professionals and encourage them to submit a completed survey. However, the identities of the respondents were not solicited from these organizations.

The survey questionnaire was sent through email with 108 completed survey received and only 104 were considered usable. Considering the exploratory and initial research on environmental sustainability awareness and practices, this study analyses IT employees' awareness regarding GIT practices from a chosen group of thirty-eight companies. It is considered that the selected group of IT professionals was valid representatives of the IT sector in the Philippines. The demographic characteristics of the IT professionals are presented in Table 1.

4. RESULTS AND DISCUSSION

Table 2 presents the mean score of the survey among all age groups; the results indicate that age group thirty-five and older are more aware of emissions and implications to the environment. Likewise, they perceived greater importance in renewable resources and understanding on electronic waste. Also, the results indicate age group thirty-five and older have higher agreement on their responsibility to act on environmental issues. However, age group twenty to twenty-four have a higher awareness of the increasing costs of energy use of IT equipment, and consistent on turning off computers after office hours.

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Figure 1. Green IT awareness and practices of Philippine IT professionals

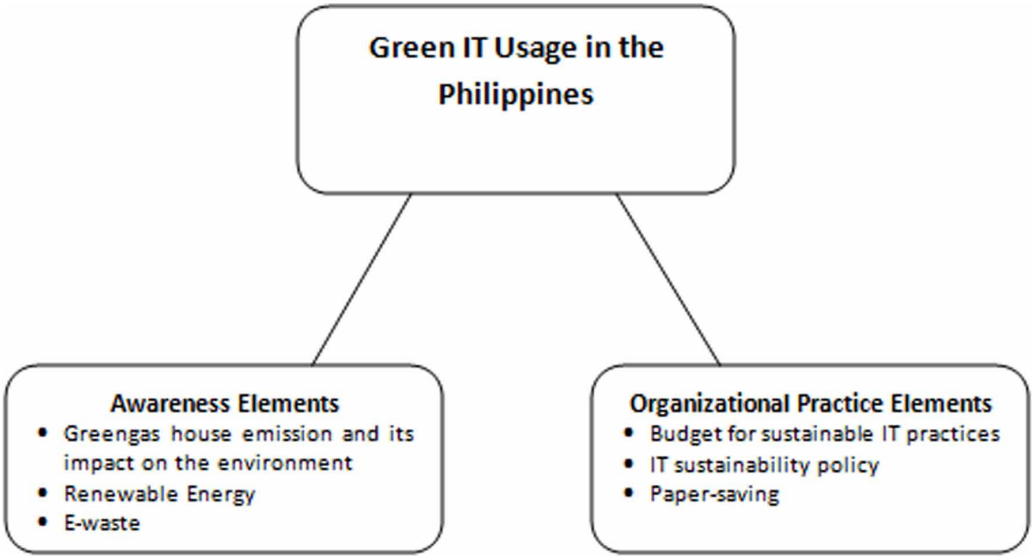

Table 1. Demographic profile of IT professionals

Characteristics	N (%)
Age – Group	
20-24 25-29 30-34 35 and older	15 (14.42%) 41 (39.43%) 26 (25%) 22 (21.15)
Gender	
Male Female	79 (75.96%) 25 (24.04%)
Number of Employees in the Firm	
Less than 1000 More than 1000	48 (46.15%) 56 (53.85%)

Meanwhile, all age groups have almost similar awareness in switching-off lights. The results also show that thirty-five and older have noted that their organizations have sustainability policy, and employ an in-charge for sustainable practices, and put emphasis on paper-saving activities.

Based on the results of the survey (see Table 3), the comparison between male and female groups has little difference in most of the items. Both male and female groups have similar agreement on shutting down of computers when not used in their firms, allocates budget for sustainable IT practices, and highlights paper-saving activities. The male group had a higher awareness of renewable resources, considers individual responsibility on sustainable environment challenges including electronic waste disposal, switching-off lights, and energy use of equipment. The male group also recognized the relevance of sustainable ICT guidelines and considered designating a member of the organization to further GIT

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Table 2. Comparison of the mean score among age groups

Statement	Age Group				
	20-24	25-29	30-34	35 and Older	Average
I am aware of greenhouse gas emissions and its impact on the environment	3.4	3.3	3.5	3.6	3.5
I am aware of renewable energy	3.3	3.7	3.5	3.8	3.6
I have knowledge of e-waste	2.6	3.1	3.2	3.4	3.1
I take responsibility to assist in making a difference on environmental issues, for instance, energy consumption and e-waste disposal	3.1	3.2	3.5	3.7	3.4
I am aware of the increasing cost of energy consumption in desktop computers	3.3	3.1	3.3	3.2	3.2
I shut down my personal computer after work day.	3.6	3.2	3.1	3.1	3.3
I switch-off lights when not be used.	3.5	3.7	3.5	3.5	3.6
My company provides budget for sustainable IT practices	3.0	3.5	3.3	3.5	3.3
My company has an IT sustainability policy	3.1	3.3	3.2	3.5	3.3
My company has a dedicated person responsible for ICT sustainable practices	3.5	3.4	3.5	3.6	3.5
My company highlights paper-saving	3.3	3.6	3.4	3.7	3.5

practices. Therefore, it could be explained that male professionals observed better understanding and awareness of sustainable environmental practices and proactive behavior. Overall, GIT practices among female and male groups were similar within the organizations involved in this study.

The results of the survey present (see Table 4) the comparison between two groups: organizations with less than one thousand employees and organizations with more than one thousand employees. Overall, organizations with less than one thousand professionals have lower GIT practices covering (a) greenhouse gas emission, (b) consideration of renewable resources, (c) electronic waste understanding,

Table 3. Comparison of the mean score among the genders

Statement	Gender	
	Male	Female
I am aware of greenhouse gas emissions and its impact on the environment	3.7	3.5
I am aware of renewable energy	3.8	3.4
I have knowledge of e-waste	3.6	3.2
I take responsibility to assist in making a difference on environmental issues, for instance, energy consumption and e-waste disposal	3.3	3.5
I am aware of the increasing cost of energy consumption in desktop computers	3.5	3.3
I shut down my personal computer after work day.	3.9	3.3
I switch-off lights when not be used.	3.7	3.4
My company provides budget for sustainable IT practices	3.3	3.3
My company has an IT sustainability policy	3.8	3.2
My company has a dedicated employee responsible sustainable IT practices.	3.8	3.6
My company highlights paper-saving	3.5	3.5

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Table 4. Comparison of the mean score among different size of organizations

Statement	Size of the Organization	
	Less than 1000 Employees	More than 1000 Employees
I am aware of greenhouse gas emissions and its impact on the environment	3.1	3.4
I am aware of renewable energy	3.1	3.5
I have knowledge of e-waste	3.0	3.2
I take responsibility to assist in making a difference on environmental issues, for instance, energy consumption and e-waste disposal	3.1	3.7
I am aware of the increasing cost of energy consumption in desktop computers	3.0	3.4
I shut down my personal computer after work day.	3.1	3.5
I switch-off lights when not be used.	3.3	3.9
My company provides budget for sustainable IT practices	3.1	3.4
My company has IT sustainability policy	3.1	3.4
My company has a dedicated employee responsible sustainable IT practices.	3.5	3.4
My company highlights paper-saving	3.2	3.8

(d) individual responsibility and contribution to addressing environmental challenges, and (e) issues on the rising energy use of IT equipment. It is also observed that most of these organizations have a lower budget for IT practices, sustainability policy. The results also indicate that organizations with more than one thousand employees have an emphasis on the importance of switching-off lights, and paper-saving activities as an element of sustainable practices as compared to smaller organizations.

5. THEORETICAL IMPLICATIONS

This paper provides a significant contribution to the Green IT literature. First, it is evident that a handful of studies are available investigating the awareness and practices on environmental sustainability among Philippine IT professionals. Prior studies were essentially persistent to understanding the factors and practices on applying information technology to enhance corporate environmental sustainability (Hernandez and Ona, 2015), however, lacks further exploration on understanding employees' perception regarding their role in sustainability through GIT adoption. This study offers new insight on the awareness, perception, and practices of Philippine IT professionals towards sustainability. The results of the survey suggest that 89% percent have good or very good awareness regarding emissions and its environmental impacts. This understanding relates to firms attempts to adapt to sustainable environmental programs. Likewise, if employees are aware of GIT practices, then, these could be more adopted by the IT professionals and become optimistic to further GIT efforts (Mariani and Imam, 2012).

Second, a handful of studies on GIT practices in developing countries, such as the Philippines, in which IT spending by firms constantly increased. To the date, the IT industry of the Philippines constantly contributes to carbon emissions due to the increasing investments in IT infrastructure. Investigating the Philippine IT professionals GIT practices can offer essential perspectives that can assist in developing

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much significantly needed GIT practices for Philippine IT organizations. A study suggests that knowledge of IT professionals on GIT practices contributed to addressing environmental issues (Molla et al., 2014). It also suggests that sixty-nine percent of respondents had a fair, good or very good awareness to make a difference on the environment.

Third, male employees exhibited higher awareness and understanding of sustainable environment challenges and their responsibility towards addressing these concerns. Nonetheless, both male and female groups have largely similar adoption of environmentally sustainable practices. These findings are in contrast with Molla et al., (2014) which found both male and female groups were similarly aware of GIT practices, and its significance to attaining environmental sustainability.

The results of the survey also indicate that nearly fifty percent of the respondents signified concern in the increasing resources needed for desktop and server energy consumption. The rising electricity cost is a result of suppliers' imposition of additional electricity charges. However, there is an extent of reducing these costs through environmentally sustainable practices through shutting down of computers when unused and switching off lights after working hours. It is expected that firms must design relevant policies and guidelines to further GIT adoption. However, these organizations need to be GIT champions to spur the adoption of these practices by the employees (Antonioli et al., 2013). However, the results indicate that only forty nine percent of the respondents had dedicated an employee to oversee GIT practices within their organizations. Assigning a dedicated employee could further improve GIT adoption practices among IT professionals in organizations.

To date, the Philippine spending on GIT is not yet formalized as part of the national budget (DTI, 2017). This situation also reflects the commitment of organizations to allocate financial budget for GIT adoption, however, the results also indicate an average of 3.4 mean score which suggests that a few organizations in the Philippines have allocated budget to further the adoption of GIT. Therefore, lacking budget is a major concern in some organizations in the Philippines. However, the results also indicate that only seventeen percent disagreed that their organizations have allotted budget to support GIT efforts. It reflects that firms may have allocated some budget, however, but these were not promoted effectively within the firms. Hence, requires a new way to encourage budget spending to adopt these GIT practices continuously.

This research opens new opportunities for employees to further GIT adoption within organizations. It also emphasizes the need to develop a framework to apply GIT practices. Lastly, this paper offers new insight into the awareness of Philippine IT professionals on GIT adoption. This work will build on the growing appreciation of firms on GIT adoption as an area of research and practice of environmental sustainability within organizations. The outcomes of the research could be used to promote the proactive participation of employees on GIT practices, therefore, as this research considered a multidimensional construct of investigating Philippine IT professionals practices and awareness level of GIT, and support future researches in this area.

5.1. Organizational Implications

The study suggests that IT professionals employed in large firms in the Philippines have better awareness and knowledge of GIT practices. The findings of this study are consistent with Ansari et al. (2010) about GIT awareness and practices in Bangladesh. Although organizations aim to adapt to GIT practices, however, employees need sufficient knowledge to adopt and may lead to better participation. Hence,

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small organizations need to provide capacity building and education programs to their employees on GIT adoption including awareness in carbon emissions, responsible electronic waste disposal, and use of information systems to integrate roles in GIT adoption practices.

The role of an economic, social and environmental partnership is critical to the success of GIT adoption in firms (Stankeviciute and Savanneviciene, 2013). Although capacity building equips employees about GIT adoption, it cannot always assure individual participation. Previous studies suggest that culture and individual's attitude remains a barrier and hinder GIT adoption. The study of Gholami et al. (2013) found that managers have an important role to play in adapting to GIT practices. Similarly, the lack of managerial support becomes a significant barrier to the successful GIT adoption in organizations (Buchalcevova and Gala, 2013). Prior studies suggest that innovative culture is attained from top managers to entry level employees, hence, senior managers attitude and ability to persuade employees on GIT practices (Guerci and Pedrini, 2014; Robbins et al., 2014). Certainly, there is the potential of changing the firms' culture and modify individual's actions (Robbins et al., 2014) by developing appropriate GIT guidelines. Conversely, it requires better managerial support, commitment, and responsibility. Organizational policies can spur positive actions to managers going to the staff to motivate them to proactively contribute to sustainable business and environment improvements (Guerci and Predini, 2014).

Despite the implementation of policies, procedures, and facilities to further GIT adoption in organizations, this study also found the lacking budget allocation towards GIT practices, which also come backs with managerial support and behavior. Also, rewards and incentive systems can play a critical role in employees' behavior to continue adopting GIT in organizations (Lim et al., 2013). Likewise, rewards and incentive programs can result in positive implications on enhancing employees' participation in GIT adoption. Interestingly, the results of the survey indicate an equal awareness of GIT adoption and knowledge on sustainable practices among age groups. However, Philippine IT professionals thirty-five and older had better knowledge and awareness of GIT practices and responsibility on environmental issues. This finding is consistent with Molla et al. (2014). Nevertheless, it is an important finding that younger IT employees in developed countries such as Australia are involved with GIT adoption activities than older IT employees.

6. CONCLUSION AND FUTURE WORK

GIT adoption practices play a critical role in spurring environmental performance, however, may not warrant positive outcomes. Conversely, this can be attained by developing appropriate policies and education program aiming to improve the rate of participation and roles of employees, thus, achieving the goals of environmental sustainability. Prior studies found the significance of individual's understanding can influence in enhancing the rate of participation towards GIT. Hence, it presents the necessity to determine the awareness level that can be useful to develop strategic approaches for engaging employees to implement environmentally sustainable business activities. This study is the first to offer insights on exploring the awareness and environmental sustainability of IT employees in the Philippines and presented deeper understanding and perception regarding GIT adoption practices. The insights presented from this research can offer direction in encouraging and developing practices to sustain GIT adoption in Philippine IT organizations.

This study used a survey to understand the awareness level on GIT adoption practices of Philippine IT professionals. The findings suggest conclusion which can be valuable to firms in designing strategies, guidelines, programs, are presented. First, this study found that IT professionals aged thirty-five

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and over have a higher understanding of environmentally sustainable practices as compared with other age groups. Significantly, employees aged twenty to twenty-four have lower awareness of GIT practices. The awareness gap between age groups can be explained through the length of stay and experience in IT and their organizations.

This study also offers new insights on GIT practices to achieve environmental sustainability and also recognize the need for further research. Furthermore, IT professionals with prior understanding in regards to GIT adoption can significantly contribute by introducing changes and encourage other employees to adopt by sharing and communicating their positive experience, insights, and outcomes. Also, promote the significance of adopting to GIT practices to attain environmental sustainability within their peers. The study also found that male IT professionals had better awareness on environmentally sustainable practices. However, both male and female groups had a largely similar adoption rate of GIT within their firms.

Lastly, organizations with one thousand IT professionals and above have advanced awareness on the sustainable environment compared to smaller firms. It is also found that firms with one thousand IT professionals have a greater emphasis on shutting down of unused computers, switching off lights and paper-saving initiatives as part of their sustainable environmental practices as compared to smaller organizations involved in this study. This work suggests that smaller organizations are laggard in GIT practices education drive, as employees are the asset of the firms. Therefore, it is necessary to provide sufficient education for them to realize the potential and beneficial outcomes of adopting to environmentally sustainable practices.

Although this study offers new insights about the awareness of Philippine IT professionals on environmentally sustainable practices, this study is not also free from limitations. First, the study only covered Philippine IT professionals, which lacks a global opinion. Hence, the findings and suggestions from this study are only applicable to Philippine IT firms or countries with similar characteristics. This research suggests further studies on exploring the knowledge of IT professionals in several developed and developing countries. Second, this study is based on a survey of respondents of only in IT organizations, future studies can deal with a large number of respondents across sectors and industries in which different insights can be obtained and can assist in designing new strategies and policies to achieve a low-carbon economy, thus, resulting in sustainable business and environment. Finally, exploring the experience of IT professionals through qualitative studies could further reveal meaningful insights in GIT adoption in organizations.

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Chapter 70
Revisiting the Conflicts between 'Environmental Taxes vs Standard' in the Context of International Trade:
The Role of Waste Recycling

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ABSTRACT

The present paper throws light on the famous "tax versus standard" debate in the sphere of environmental economics by using general equilibrium framework and tries to examine which of the two, i.e., tax or standard is the better way to deal with pollution. It has done so in the presence of a waste recycling sector which is the unique feature of it and has shown the impact of tax and standard separately on different polluting and non-polluting sectors of the economy. The study has developed a unique as well as an interesting result that in the presence of a waste recycling sector in the economy, both pollution tax and environmental standard have the same impact.

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1. INTRODUCTION

Over the last two and a half decades, perhaps the most relevant, worrying and most thought over issue worldwide has been global warming and the root cause of it, environmental pollution and how to deal with it for the sake of saving this planet. There may be no wrong in saying that an upsurge in the population growth and an urge for rapid development have contributed to the present scenario of environmental degradation. But the need for development cannot be denied either considering the fact that over two third of the population worldwide still belongs to developing economies. In order to become developed, it is necessary to fasten the production process and other economic activities and here lies the tragedy of the poor nations because such activities are contributing to the devastating environmental pollution. For sustainable development, it is therefore necessary to adopt proper measures that can continue the production process yet do not create pollution to an extreme level. The measures which are available to the controlling authority for dealing with pollution have given birth to the famous debate of environmental economics: "tax versus standard", that is, the authority can either impose tax on the polluting industries or they may reduce the maximum allowable level of pollution for the sake of environment. Developed countries, with their good capital base, have started using those technologies that will not create pollution. This technology may be referred to as "green technology" or "green capital." Developing nations, mostly, do not even possess such technology for being poor. Therefore, they either cannot use such sophisticated technology or even if they can, they use it in selected; few areas, not in all sectors of the economy because of lack of capital. Developing economies largely either imposes tax or restricts the emitting level and, if possible, uses "green technology" in very few areas.

Green technology generally enters in developing economies through the inflow of foreign capital or foreign investment and in the presence of globalization[1] this trend is expected to grow where a developing nation would come across foreign entrepreneurs possessing pollution free technical knowhow. So the use of "green technology" in a developing nation initiates mainly through foreign investment. There are empirical evidences in support of this argument.[2]

One more important aspect that has gained momentum and earned respect in the modern world is the recycling and reusing a product. During the production process, there may be few things which become obsolete but there may be few things which may be re-used and may be given the shape of another product through the process of recycling. Recycling is the process of separating, collecting and remanufacturing or converting used or waste products into new materials. The recycling process involves a series of steps to produce new products. Recycling helps to extend the life and usefulness of something that has already served its initial purpose by producing something that is useable. Recycling has a lot of benefits and importance not only to us humans but especially to our planet. Recycling is very important as waste has a huge negative impact on the natural environment. A few of these impacts are:

1. Harmful chemicals and greenhouse gasses are released from rubbish in landfill sites. Recycling helps to reduce the pollution caused by waste;
2. Habitat destruction and global warming are some the effects caused by deforestation. Recycling reduces the need for raw materials so that the rainforests can be preserved;
3. Huge amounts of energy are used when making products from raw materials. Recycling requires much less energy and therefore helps to preserve natural resources.

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Recycling is essential to cities around the world and to the people living in them because we have no space for waste. Our landfill sites are filling up fast. Recycling reduce financial expenditure in the economy. Making products from raw materials costs much more than if they were made from recycled products. It also preserves natural resources for future generations.

Presently in India, about 960 million tonnes of solid waste is being generated annually as by-products during industrial, mining, municipal, agricultural and other processes. Of this, 350 million tonnes are organic wastes from agricultural sources; 290 million tonnes are inorganic waste of industrial and mining sectors and 4.5 million tonnes are hazardous in nature. There are many evidences that output or may be wastage of one sector is used by that sector or by a different sector to form a new product.[3] So the dirty goods[4] may contribute to the formation of pollution free goods. But the process of recycle and re-use needs the presence of sound, advanced technology which again generates the necessity of 'green technology".

The main motivation behind this study generates from the fact that there are only a few empirical works are there on the issue of pollution control through pollution tax or setting standard. From the theoretical angle, also there are only few works to mention and even in this regard perhaps no work has been done by comprising the famous debate of "tax versus standard" in the presence of recycling sector in a general equilibrium framework. The only exception in this regard is the work by Gupta (2012). He has examined the trade-off between tax and standard in a general equilibrium framework. This model helps us in understanding the inter-sectoral linkages and also to examine whether there is actually any trade-off between tax and standard in the presence of recycling.

This study is based on a small open economy general equilibrium structure that has been used by several authors for dealing with environmental and trade related issues.[5] The present study considers the impact of both pollution tax as well as setting environmental standard by regulating the level of emission in the presence of a recycling effect. The concept of green capital is also incorporated without categorising the different sectors of the economy into formal or informal sectors.

The paper is organised in the following sub sections. Section 2 considers the basic model. Comparative static analysis is done in section 3. Finally, the concluding remarks are made in section 4.

2. THE BASIC MODEL

We consider a small open economy with four sectors: a sector that requires no green capital and they need not recycle wastes (sector X), the sector which requires green capital to recycle wastes (sector Z), the polluting-manufacturing sector (sector Y) and the fourth sector is the waste-generating, non-traded intermediate good sector (sector V)[6]. This sector also uses green-capital. Its output is independent of the output of sector y. Wastes are generated by sector y during the process of producing its own output and by sector v from solid wastes of the community or from consumers. As sector v uses green capital, the wastes generated by this sector are all recycled by sector Z. In other words, as sector V uses green capital, the wastes generated by this sector are not harmful for the economy as they can always be used for the purpose of recycling. Sector X and sector Z together can be considered as "non-polluting" sectors within the economy. The assumption of small open economy implies that apart from the non-traded sector v, for all other sectors the product prices are fixed as the economy is a price-taker in the in the international market.[7] Production function in each sector exhibits constant returns to scale (CRS), variable co-efficient technology and diminishing marginal productivity to the variable factors. Sector x and

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Sector Y use traditional capital, K, which is perfectly mobile between these two sectors. Sector z and sector V use much advanced, sector-specific "green capital" K_G which is perfectly mobile between these two sectors. The use of K_G by these two sectors implies the use of better, advanced, non-polluting technology by these sectors. Labour is assumed to be perfectly mobile among all the four sectors. Sector X and Sector V employ labour at a fixed wage rate $\bar{w}$ .The remaining workers are used by the other two sectors, that is, sector Y and sector V, at the competitive wage rate w, which is assumed to be flexible and lower than $\bar{w}$. The workers who fail to get a work in sectors x and sectors z are absorbed in sectors y and v. So, there exists full employment in the labour market. The product of sector x is regarded as a numeraire and its price has been set equal to unity. A pollution tax α is imposed on per unit of output of sector y, which is the polluting-manufacturing sector.

The following notations are used in the formal presentation of the model:

a_{Li} = Labour-output ratio in the i-th sector, i = x,y,z,v

a_{Ki} = Capital-output ratio in the i-th sector, i = x,y,z,v

P_i = Price of the product of the i-th sector, i = x,y,z,v

w = Competitive wage rate of sector y and sector v

$\bar{w}$ = Fixed wage rate of sector x and sector v

X = Output of sector x

Y = Output of sector y

Z = Output of sector z

V = Output of sector v

r = Rate of return on traditional capital

R = Rate of return on green capital

L = Total endowment of labour in the economy

K = Total endowment of traditional capital

K_G = Total stock of green capital

α = Tax rate on per unit of output of sector y

Ω = Maximum allowable pollution

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λ_{ji} = Use of j-th factor by i-th sector with respect to total factor endowment (j=L,K; i=x,y,z,v)

θ_{ji} = distributive share of the j-th input in the i-th sector

2.1. Equational Structure of the Model

The competitive equilibrium conditions of the four sectors are given as:

$$\bar{w}\, a_{LX} + r\, a_{KX} = 1 \tag{1}$$

$$w\, a_{LY} + r\, a_{KY} = P_Y - \alpha = P_Y' \tag{2}$$

$$\bar{w}\, a_{LZ} + R\, a_{KZ} + P_V a_{VZ} = P_Z \tag{3}$$

$$W a_{LV} + R a_{KV} = P_V \tag{4}$$

The relationship between the waste-generating intermediate sector v and waste recycling sector z is given as:

$$a_{VZ} Z = V \tag{5}$$

Mobility of traditional capital between sectors x and sector y is given as:

$$a_{KX} X + a_{KY} Y = K \tag{6}$$

Full employment condition of the labour market is given by:

$$a_{LX} X + a_{LY} Y + a_{LZ} Z + a_{LV} V = L \tag{7}$$

The mobility of green capital between sector z and sector v is given by:

$$a_{KZ} Z + a_{KV} V = K_G(\Omega) \text{ where, } K_G' < 0 \tag{8}$$

In Equation (8) the reason behind $K_G' < 0$ is that when there is an improvement in the standard of environment, that is, when the maximum allowable pollution level is reduced, there is an increase in the use of green capital as the producers are compelled to adopt environment-friendly technology.

2.2. Working of the Model

The working of the model is simple. From Equation (1) we can solve for r. Using the value of r in Equation (2) we can get w. From Equation (4) we can express R in terms of P_V. As R can be expressed in terms of P_V, by using this relation, from Equation (3) we can get the value of P_V, using which again in Equation (4) one can get the value of R. From Equation (5) we can express V in terms of Z, by using this

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relationship in Equation (8), one can get the value of Z and again by using the value of Z in Equation (5) we can get the value of V. Thus, both Z and V becomes known. Now we are left with two equations, that is, Equation (6) and Equation (7), and two unknowns – X and Y. So, we can solve for the values of X and Y from these two equations.

3. COMPARATIVE STATISTICS

Here we would like to examine the impact of a strict environmental policy in the form of improvement in the environmental standard (by imposing reduction in maximum allowable pollution) and also in the form of an increase in the tax rate on output of the polluting sector. Both the measures can be interpreted as a drive towards an improvement in environmental quality of the economy.

First, we would like to examine the impact of a strict environmental policy, that is, a reduction in the maximum allowable level of emission in all the economy. A strict environmental policy implies a reduction in Ω. When we examine the change in Ω, then the system or the model becomes decomposable as the input-output co-efficients can be determined independent of the output system. From Equation (5) we can see that V can be expressed in terms of Z. So Equation (8) can be expressed in terms of Z only. In Equation (8), as Ω falls because of a tough policy, we see that K_G rises. To maintain the equilibrium, it implies that Z should also increase. As $\hat{Z} = \hat{V}$, it also implies that V should rise.[8] This is shown by the following two equations that express change in Z and V with respect to change in Ω:

$$\frac{\hat{Z}}{\hat{\Omega}} = \frac{\varepsilon}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \tag{9}$$

and:

$$\frac{\hat{V}}{\hat{\Omega}} = \frac{\varepsilon}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \tag{10}$$

Both the two equations above show an inverse relationship between Ω and output of sector Z and sector V because ε is negative (less than zero) in sign. So as Ω falls, the output levels of both sectors v and sector z increase, it implies that the availability of effective labour decreases in rest of the two sectors, that is, in sector X and sector Y. This creates a *"Rybczynski effect"* for which output of the capital intensive sector or sector X rises and that of the labour intensive sector or sector Y falls. Mathematical expressions of these results are shown below (see Appendix for detailed derivations):

$$\frac{\hat{Y}}{\hat{\Omega}} = \left\{ -\frac{\left(\lambda_{KZ} + \lambda_{KV}\right)\lambda_{KX}}{\left(\lambda_{LX}\lambda_{KX} - \lambda_{KY} + \lambda_{LY}\lambda_{KX}\right)} \frac{\varepsilon}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \right\} \tag{11}$$

and:

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$$\frac{\hat{X}}{\hat{\Omega}} = \lambda_{KY}\left\{\frac{\left(\lambda_{KZ}+\lambda_{KV}\right)}{\left(\lambda_{LX}\lambda_{KX}-\lambda_{KY}+\lambda_{LY}\lambda_{KX}\right)}\frac{\varepsilon}{\left(\lambda_{KZ}+\lambda_{KV}\right)}\right\} \tag{12}$$

Again as ε is negative in nature, the above two equations express a direct relation between Y and Ω and an inverse relation between X and Ω, respectively.

These findings can be expressed with the help of following proposition:

Proposition 1: A strict environmental policy in the form of a reduction in the maximum allowable pollution increases the supply of green capital and also increases the production of wastes and output of waste recycling sector. It increases output of the non- polluting sector and reduces output of the polluting sector, given that the non-polluting sector is more capital-intensive than the polluting sector.

So far we have discussed the effect of change in environmental standard. Now, we would like to see the effect of change in tax rate (α) on the output of all the sectors as well as on the input prices.[9]

From Equation (13)[10] we find that the price of the waste-generating intermediate sector (sector v) and price of the price of the polluting sector (sector y) is given as:

$$\frac{\hat{P}_V}{\hat{P}_Y'} = \frac{\theta_{KZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)} \tag{13}$$

The above expression is positive, so, the relation between $\hat{P}_V$ and $\hat{P}_Y'$ is direct, that is, as $\hat{P}_Y'$ falls, $\hat{P}_V$ falls. The economic interpretation is simple. An increase in the tax rate on the output of the polluting sector reduces effective price of the product of the polluting sector, $P_Y{}'$, as r is already determined from Equation (1), a fall in, $P_Y{}'$ causes a fall in w, as we find from Equation (2). For given $P_{V,}$ a fall in w causes a rise in R from Equation (4). However, P_V is not given as sector v is the non-traded sector. This is evident from Equation (3) where we find, for given P_Z, a rise in R implies a fall in P_V. So we conclude a fall in $P_Y{}'$ causes a fall in P_V. As R increases, it implies that a_{KZ} and a_{KV} also falls, as a result of which Z increases and consequently V also increases, (as $\hat{Z}=\hat{V}$) it is shown by the following equation:

$$\frac{\hat{Z}}{\hat{P}_Y'} = \left\{-\frac{\left(\lambda_{KZ}A_2+\lambda_{KV}A_1\right)}{\left(\lambda_{KZ}+\lambda_{KV}\right)}\right\} = \frac{\hat{V}}{\hat{P}_Y'} \tag{14}$$

As w falls (for given r), w/r falls or we can say that r/w increases. It also results in a fall in a_{KX} and a_{KY} for given X and Y. So, there is excess supply of capital. From Equation (7) we see that a fall in w results in an increase in a_{LY} and a_{LV}. It results in a reduction in the availability of labour for sector x and sector y as $\{L-(a_{LZ}+a_{LV}a_{VZ})Z\}$ falls. This is known as *"Rybczynski-type effect."* This will result in an increase in the output of sector x and a fall in that of sector y, given that x is the capital-intensive sector than sector y. We thus have:

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$$\frac{\hat{X}}{\hat{P}_Y'} = \frac{A_5\lambda_{KY} - \lambda_{LY}A_6}{\lambda_{LX}\lambda_{KY} - \lambda_{KX}\lambda_{LY}} \tag{15}$$

and:

$$\frac{\hat{Y}}{\hat{P}_Y'} = \frac{\lambda_{LX}A_6 - \lambda_{KX}A_5}{\lambda_{LX}\lambda_{KY} - \lambda_{KX}\lambda_{LY}} \tag{16}$$

These results are presented by the following proposition:

Proposition 2: An increase in the tax rate on the output of the polluting sector increases the output of waste-generating intermediate sector as well as the output of waste recycling sector, it also increases the output of non-polluting capital-intensive sector but decreases the output of the labour-intensive polluting sector.

4. CONCLUDING REMARKS

In this paper we build up a model, using the H-O-S general equilibrium structure, assuming the presence of four sectors in the economy. Out of these four, two sectors are "non- polluting" and other two are "polluting". One sector from each category use green capital, that is, use advanced sophisticated, pollution free technology. A "non-polluting" sector takes the help of green technology to recycle wastes and a polluting sector does so to generate wastes for the purpose of recycling. In such a set up we have shown that the regulating authority possess the dual instrument to deal with pollution, that is, they may impose a pollution tax on the price of the product of the polluting industry and also they can reduce the maximum allowable level of emission which would compel industries to go for green technology. In this paper, we have shown the effects of both a reduction in the maximum allowable level of pollution as well as an increase in the tax rate on the output of the polluting sector.

In both the cases we have come across same results. In both the cases, we have seen that, either due to an increase in tax rate or because of a reduction in the maximum allowable emission level, the output levels of waste generating intermediate good sector and waste recycling sector have increased. We have also shown expansion of the non-polluting capital-intensive sector and contraction of the of the labour-intensive polluting sector. So, output levels of three of the four sectors go up out of which two are "non-polluting" in nature and that of the remaining sector goes down. One thing to be noticed here is that sectors which use green technology have expanded.

These results are significantly different to other findings in the field of "tax versus standard" studies. Most of the studies in this sphere have recommended either increase in pollution tax as superior to the reduction in the maximum emission level or vice-versa, depending upon their respective areas, under focus, which the impact of these two means are compared upon. But, our study reveals that both the measures would provide us the same result under some reasonable conditions.

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ENDNOTES

1. The term "globalization" is used in a broad sense in a developing nation where "greater integration of the world economy through heightened trade and investment flows and greater mobility of factors" are expected.
2. The investigating works of Mansfield (1961, 1968) may be mentioned.
3. See Pappu, Saxena and Asolekar (2006) for details.
4. "Dirty goods are those goods that create pollution during the production process.
5. See Chichilnisky (1994), Chaudhuri and Gupta (2004) for details.
6. Moreover, sector V produces an waste augmented intermediate product and the entire output of sector V have been demanded by sector Z.
7. Apart from sector V, all other sectors produce final commodities in this model.
8. See Appendix at the end of this chapter for detailed mathematical derivations.
9. Here we have shown the impact of a change in tax rate α in terms of change in the price of the polluting sector (sector Y) after tax being imposed, that is, in terms of $\hat{P}_Y^{'}$. As α rises, $P_Y^{'}$ falls. So, α and $P_Y^{'}$ have an opposite relation between them. This can be proved very easily. We know that $P_Y - \alpha = P_Y^{'}$ (see equation 3.2). Differentiating this expression with respect to $P_Y^{'}$, we get, $-\frac{da}{P_Y^{'}} = \frac{dP_Y^{'}}{P_Y^{'}}$, Or, $-\frac{a}{P_Y^{'}}\frac{da}{a} = \hat{P}_Y^{'}$, Or, $-\frac{a}{P_Y - a} = \hat{P}_Y^{'}$, Or, $-\gamma\hat{a} = \hat{P}_Y^{'}$ and $\gamma = \frac{a}{P_Y - a}$, So the nature or sign (positive or negative) of any relationship which is expressed in terms of $_{KY}$ will become

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exactly of the opposite nature or sign (positive or negative) when expressed in terms of P_Y-α. For example, if the impact of $\hat{P}_Y^{'}$ on $\hat{Z}$ is negative, it will become positive when expressed in terms of $\hat{\alpha}$. This inverse relationship between $\hat{P}_Y^{'}$ and $\hat{\alpha}$ and its verbal explanation will be applicable on all those mathematical expression that shows a change in any variable with respect to a change in $\hat{P}_Y^{'}\left(\hat{P}_Y^{'}\right)$.

[10] Equation (13) and Equation (4.1) (in the Appendix) are same, only for the sake of the simplicity, it is numbered differently, first, here and later in the Appendix.

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APPENDIX A

Mathematical Expressions of the Basic Model

$$\bar{w}\, a_{LX} + r\, a_{KX} = 1 \tag{1}$$

$$w\, a_{LY} + r\, a_{KY} = P_Y - \alpha = P_Y' \tag{2}$$

$$\bar{w}\, a_{LZ} + R\, a_{KZ} + P_V a_{VZ} = P_Z \tag{3}$$

$$W a_{LV} + R a_{KV} = P_V \tag{4}$$

$$a_{VZ} Z = V \tag{5}$$

$$a_{KX} X + a_{KY} Y = K \tag{6}$$

$$a_{LX} X + a_{LY} Y + a_{LZ} Z + a_{LV} V = L \tag{7}$$

$$a_{KZ} Z + a_{KV} V = K_G(\Omega),\ K_G' < 0 \tag{8}$$

APPENDIX B

Detailed Derivations of Different Expressions

Derivations of equations considering change in the environmental standard, that is, a change in the maximum allowable level of emission (Ω).

Differentiating Equation (1) we get:

$$a_{LX}\, d\bar{w} + \bar{w}\, d\, a_{LX} + a_{KX} dr + r d\, a_{KX} = 0$$

as $\bar{w}\, d\, a_{LX} + r d\, a_{KX} = 0$ (By Envelop Theorem) and $d\,\bar{w} = 0$, we get,

$$\hat{r}\ \theta_{KX} = 0 \text{ or, } \hat{r} = 0 \tag{1.1}$$

Differentiating Equation (2) we can get:

$$a_{LY}\, dw + w d\, a_{LY} + a_{KY} dr + r d\, a_{KY} = d\, P_Y'$$

Again by using Envelop Theorem ($w d\, a_{LY} + r d\, a_{KY} = 0$) from the above equation we get:

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$$\hat{w}\theta_{LY} = \hat{P}_Y' \text{ or } \hat{w} = \frac{\hat{P}_Y'}{\theta_{LY}} \tag{2.1}$$

Differentiating Equation (3) and using Envelop theorem we get:

$$\hat{R}\theta_{KZ} + \hat{P}_V\theta_{VZ} = 0 \text{ or } \hat{R} = -\hat{P}_V \frac{\theta_{VZ}}{\theta_{KZ}} \tag{3.1}$$

From Equation (4) we get:

$$\text{wd } a_{LV} + a_{LV}\text{dw} + \text{Rd } a_{KV} + a_{KV}\text{dR} = 0$$

By applying Envelop Theorem in the above expression we can get:

$$\hat{w}\theta_{LV} + \hat{R}\theta_{KV} = \hat{P}_V$$

Using the value of $\hat{R}$ from Equation (3.1) in the above expression we get:

$$\hat{w}\theta_{LV} - \hat{P}_V \frac{\theta_{VZ}}{\theta_{KZ}}\theta_{KV} = \hat{P}_V$$

Again, using the value of $\hat{w}$ from Equation (2.1) in the above expression we get:

$$\frac{\hat{P}_Y'}{\theta_{LY}} = \hat{P}_V\left(1 + \frac{\theta_{VZ}\theta_{KV}}{\theta_{KZ}}\right) \text{or } \frac{\hat{P}_V}{\hat{P}_Y'} = \frac{\theta_{KZ}}{\theta_{LY}(\theta_{KZ} + \theta_{VZ}\theta_{KV})} \rangle 0 \tag{4.1}$$

Using Equation (4.1) in Equation (3.1) we can get another expression of $\hat{R}$, expressed as:

$$\hat{R} = -\hat{P}_Y' \frac{\theta_{VZ}}{\theta_{LY}(\theta_{KZ} + \theta_{VZ}\theta_{KV})} \tag{4.2}$$

From Equation (5) we see that as a_{VZ} is fixed, we can say:

$$\hat{Z} = \hat{V} \tag{5.1}$$

From (6) we find that:

$$a_{KY}\,\text{dX} + \text{X d } a_{KY} + a_{KY}\text{dY} + \text{Y d } a_{KY} = 0$$

$$\text{or X } \frac{a_{KX}}{k}\frac{dX}{X} + \frac{Xa_{KX}}{k}\frac{da_{KX}}{a_{KX}} + \frac{Ya_{KY}}{k}\frac{dY}{Y} + \frac{Ya_{KY}}{k}\frac{da_{KY}}{a_{KY}} = 0$$

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or $\lambda_{KX}\hat{X} + \lambda_{KX}\hat{a}_{KX} + \lambda_{KY}\hat{Y} + \lambda_{KY}\hat{a}_{KY} = 0$

or $\lambda_{KX}\hat{X} + \lambda_{KX}\hat{a}_{KX} = -(\lambda_{KY}\hat{Y} + \lambda_{KY}\hat{a}_{KY})$

From Equation (1) and Equation (2) we get: $\hat{a}_{KX}$ and $\hat{a}_{KY}$ are fixed,

so, $\lambda_{KX}\hat{X} + \lambda_{KY}\hat{Y} = 0$ or $\hat{X} = -\frac{\lambda_{KY}}{\lambda_{KX}}\hat{Y}$ (6.1)

From Equation (7) we get:

$$a_{LX}\,\mathrm{dX} + \mathrm{Xd}\,a_{LX} + a_{LY}\mathrm{dY} + \mathrm{Yd}a_{LY} + a_{LZ}\mathrm{dZ} + \mathrm{Zd}a_{LZ} + a_{LV}\mathrm{dV} + \mathrm{Vd}a_{LV} = 0 \quad (7.1)$$

As $\hat{a}_{LX}$, $\hat{a}_{KY}$ and $\hat{a}_{LZ}$ are fixed from Equations (1), (2) and (3) respectively and by using elasticity of substitution from Equation (4), we can express $\hat{a}_{LV}$ as a function of $\hat{P}_Y'$. It is proved in equation (4.B.3), (proven later). But here we are dealing with change in maximum allowable emission level or Ω and therefore the effect of pollution tax rate, α, is held constant. So, $\hat{P}_Y'$ which shows the price after tax (P_Y – α) can be considered as zero. So, we can say $\hat{a}_{LV} = 0$. By using $\hat{a}_{LX}$, $\hat{a}_{KY}$, $\hat{a}_{LZ}$ and $\hat{a}_{LV} = 0$ in Equation (7.1) we get:

$$\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} + \lambda_{LZ}\hat{Z} + \lambda_{LV}\hat{V} = 0$$

Using the result of Equation (5.1), in the above expression we can get:

$$\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} + \lambda_{LZ} = 0 \text{ or } \lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} = \left(\lambda_{LZ} + \lambda_{LV}\right)\hat{Z}$$

Using the value of X from Equation (6.1) in the above expression we get:

$$\lambda_{LX}\left(-\frac{\lambda_{KY}}{\lambda_{KX}}\hat{Y}\right) + \lambda_{LY}\hat{Y} = -\left(\lambda_{LZ} + \lambda_{LV}\right)\hat{Z}$$

or,

$$\hat{Y} = -\frac{\left(\lambda_{LZ} + \lambda_{KV}\right)\lambda_{KX}}{\left(\lambda_{LX}\lambda_{KX} - \lambda_{KY} + \lambda_{LY}\lambda_{KX}\right)}\hat{Z} \quad (7.2)$$

From Equation (8) we get:

$$a_{KZ}\,\mathrm{dZ} + \mathrm{Zd}\,a_{KZ} + a_{KV}\mathrm{dV} + \mathrm{Vd}\,a_{KV} = K_G' \text{ or } \lambda_{KZ}\hat{Z} + \lambda_{KZ}\hat{a}_{KZ} + \lambda_{KV}\hat{V} + \lambda_{KV}\hat{a}_{KV} = \varepsilon\hat{\Omega}$$

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as $\hat{Z} = \hat{V}$ (from equation 5.1), the above equation can be written as $\hat{Z}(\lambda_{KZ} + \lambda_{KV}) + \lambda_{KZ} = 0$.

Here also, like the previous case, we can get the value of from Equation (3) and the value of from Equation (4) in terms of . The fact that and can be expressed in terms of is proved in Equation (3.B) and in equation (4.B.2) respectively (proven later). Repeating the reasoning of the last case used after Equation (7.1), we can say that the values of and are zero (0) in this case as we are dealing with change in Ω and not in α . So, from the above equation we can get:

$$\hat{Z} = \frac{\varepsilon\,\hat{\Omega}}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \tag{8.1}$$

Again, by using the result obtained in Equation (5.1), we get:

$$\hat{V} = \frac{\varepsilon\,\hat{\Omega}}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \tag{8.2}$$

Using Equation (8.1) in Equation (7.2) we get:

$$\hat{Y} = \left\{ -\frac{\left(\lambda_{KZ} + \lambda_{KV}\right)\lambda_{KX}}{\left(\lambda_{LX}\lambda_{KX} - \lambda_{KY} + \lambda_{LY}\lambda_{KX}\right)} \frac{\varepsilon\,\hat{\Omega}}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \right\} \tag{7.3}$$

We use the above expression in the Equation (6.1) and get:

$$\hat{X} = -\frac{\lambda_{KY}}{\lambda_{KX}}\hat{Y}$$

$$\text{or, } \hat{X} = -\frac{\lambda_{KY}}{\lambda_{KX}} \left\{ -\frac{\left(\lambda_{KZ} + \lambda_{KV}\right)\lambda_{KX}}{\left(\lambda_{LX}\lambda_{KX} - \lambda_{KY} + \lambda_{LY}\lambda_{KX}\right)} \frac{\varepsilon\,\hat{\Omega}}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \right\}$$

$$\text{or, } \hat{X} = \frac{\lambda_{KY}}{\lambda_{KX}} \left\{ \frac{\left(\lambda_{KZ} + \lambda_{KV}\right)\lambda_{KX}}{\left(\lambda_{LX}\lambda_{KX} - \lambda_{KY} + \lambda_{LY}\lambda_{KX}\right)} \frac{\varepsilon\,\hat{\Omega}}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \right\}$$

$$\text{or, } \hat{X} = \lambda_{KY} \left\{ \frac{\left(\lambda_{KZ} + \lambda_{KV}\right)}{\left(\lambda_{LX}\lambda_{KX} - \lambda_{KY} + \lambda_{LY}\lambda_{KX}\right)} \frac{\varepsilon\,\hat{\Omega}}{\left(\lambda_{KZ} + \lambda_{KV}\right)} \right\} \tag{6.2}$$

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APPENDIX C

Detailed Derivations of Different Expressions

Derivations of equations considering change in the environmental pollution tax rate, that is, a change in α.

From Equation (2) we get:

$$wa_{LY} + ra_{KY} = P_Y'$$

$$wda_{LY} + rda_{KY} = 0$$

or,

$$\theta_{LY}\hat{a}_{LY} + \theta_{KY}\hat{a}_{KY} = 0 \text{ or } \hat{a}_{LY} = -\frac{\theta_{KY}}{\theta_{LY}}\hat{a}_{KY} \text{ (2.B)}$$

again,

$$\sigma_Y' = \frac{\hat{a}_{KY} - \hat{a}_{LY}}{\hat{w} - \hat{r}} \text{ or } \sigma_Y'\hat{w} = \frac{\hat{a}_{KY}}{\theta_{LY}} \text{ (as } \hat{r} = 0)$$

Using the value of $\hat{w}$ from Equation (2.1) in the above expression we get:

$$\hat{a}_{KY} = \sigma_Y'\hat{P}_Y'$$

Now from Equation (2.B) we get the value of $\hat{a}_{LY}$ as:

$$\hat{a}_{LY} = -\frac{\theta_{KY}}{\theta_{LY}}\sigma_Y'\hat{P}_Y' - \text{(2.B.1)}$$

From Equation (3) we get:

$$Rd\, a_{KZ} + P_V d\, a_{VZ} = 0$$

or,

$$\theta_{KZ}\hat{a}_{KZ} + \theta_{VZ}\hat{a}_{VZ} = 0 \text{ or } \sigma_Z = \frac{\hat{a}_{VZ} - \hat{a}_{KZ}}{\hat{R} - \hat{P}_V}$$

as $\hat{a}_{VZ} = 0$, we can say, $\sigma_Z = \frac{-\hat{a}_{KZ}}{\hat{R} - \hat{P}_V}$

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or, $\sigma_Z\left(\hat{R}-\hat{P}_V\right)=-\hat{a}_{KZ}$

or, $\hat{a}_{KZ}=\sigma_Z\left(\hat{P}_V-\hat{R}\right)$

or, $\hat{a}_{KZ}=\sigma_Z\left\{\frac{\hat{P}_Y'\theta_{KZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}+\frac{\hat{P}_Y'\theta_{VZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}\right\}$

or, $\hat{a}_{KZ}=\hat{P}_Y'\sigma_Z\left\{\frac{\theta_{KZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}+\frac{\theta_{VZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}\right\}$

or, $\hat{a}_{KZ}=\hat{P}_Y'\,\mathrm{A}_1$ (3.B)

where, $\mathrm{A}_1=\sigma_Z\left\{\frac{\theta_{KZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}+\frac{\theta_{VZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}\right\}$, $\mathrm{A}_1>0$.

Again from Equation (4) we get:

wd $a_{LV}+\mathrm{Rd}\,a_{KV}=0$ or $\sigma_V=\frac{\hat{a}_{KV}-\hat{a}_{LV}}{\hat{w}-\hat{R}}=$ (4.B)

Again, wd $a_{LV}+\mathrm{Rd}\,a_{KV}=0$ also implies:

$\theta_{LV}\hat{a}_{LV}+\theta_{KV}\hat{a}_{KV}=0$ or $\hat{a}_{LV}=-\frac{\theta_{KV}}{\theta_{LV}}\hat{a}_{KV}$ (4.B.1)

Using the above relation in the Equation (4.B) we get:

$\hat{a}_{KV}=\theta_{LV}\sigma_V(\hat{w}-\hat{R})$

or, $\hat{a}_{KV}=\theta_{LV}\sigma_V\left\{\frac{\hat{P}_Y'}{\theta_{LY}}+\frac{\hat{P}_Y'\theta_{VZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}\right\}$

or, $\hat{a}_{KV}=\theta_{LV}\sigma_V\hat{P}_Y'\left\{\frac{1}{\theta_{LY}}+\frac{\theta_{VZ}}{\theta_{LY}\left(\theta_{KZ}+\theta_{VZ}\theta_{KV}\right)}\right\}$

or, $\hat{a}_{KV}=\mathrm{A}_2\,\hat{P}_Y'$ (4.B.2)

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where, $A_2 = \theta_{LV}\sigma_V \left\{ \frac{1}{\theta_{LY}} + \frac{\theta_{VZ}}{\theta_{LY}\left(\theta_{KZ} + \theta_{VZ}\theta_{KV}\right)} \right\} > 0.$

Using equation (4.B.2) in equation (4.B.1) we get:

$$\hat{a}_{LV} = -\frac{\theta_{KV}}{\theta_{LV}}\hat{a}_{KV}$$

or, $\hat{a}_{LV} = -\frac{\theta_{KV}}{\theta_{LV}} A_2 \hat{P}_Y'$

or, $\hat{a}_{LV} = A_3 \hat{P}_Y'$ (4.B.3)

where, $A_3 = -\frac{\theta_{KV}}{\theta_{LV}} A_2 < 0$

Again Equation (8) gives us:

$Zda_{KZ} + a_{KZ}\,dZ + Vda_{KV} + a_{KV}\,dV = 0$

or, $\lambda_{KZ}\hat{Z} + \lambda_{KZ}\hat{a}_{KV} + \lambda_{KV}\hat{V} + \lambda_{KV}\hat{a}_{KV} = 0$

Using $\hat{Z} = \hat{V} =$ and the values of $\hat{a}_{KZ}$ and $\hat{a}_{KV}$ from Equations (3.B) and (4.B.2) respectively in the above expression, we get:

$$\hat{Z} = \left\{ -\frac{(\lambda_{KZ}A_2 + \lambda_{KV}A_1)}{(\lambda_{KZ} + \lambda_{KV})} \hat{P}_Y' \right\}$$

or, $\hat{Z} = A_4 \hat{P}_Y'$ (8.B)

where, $A_4 = \{ -\frac{(\lambda_{KZ}A_2 + \lambda_{KV}A_1)}{(\lambda_{KZ} + \lambda_{KV})} \} < 0$. (As, $A_1 > 0$ and $A_2 > 0$).

By differentiating Equation (7) we get:

$a_{LX}dX + Xda_{LX} + a_{LY}dY + Yda_{LY} + a_{LZ}dZ + Zda_{LZ} + a_{LV}dV + Vda_{LV} = 0$

or, $\lambda_{LX}\hat{X} + \lambda_{LX}\hat{a}_{LX} + \lambda_{LX}\hat{Y} + \lambda_{LY}\hat{a}_{LY} + \lambda_{LZ}\hat{Z} + \lambda_{LZ}\hat{a}_{LZ} + \lambda_{LV}\hat{V} + \lambda_{LV}\hat{a}_{LV} = 0$

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or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} + \lambda_{LY}\hat{a}_{LY} + \lambda_{LZ}\hat{Z} + \lambda_{LZ}\hat{a}_{LZ} + \lambda_{LV}\hat{V} + \lambda_{LV}\hat{a}_{LV} = 0$ (as $\hat{a}_{LX} = 0$)

or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} + \lambda_{LY}\hat{a}_{LY} + \hat{Z}(\lambda_{LZ} + \lambda_{LV}) + \lambda_{LV}\hat{a}_{LV} = 0$ (as $\hat{Z} = \hat{V}$)

or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} + \hat{Z}(\lambda_{LZ} + \lambda_{LV}) + \lambda_{LY}\hat{a}_{LY} + \lambda_{LV}\hat{a}_{LV} = 0$

or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} + \mathrm{A}_4\hat{P}_Y'(\lambda_{LZ} + \lambda_{LV}) + \lambda_{LY} - \frac{\theta_{KY}}{\theta_{LY}}\sigma_Y\,'\hat{P}_Y' + \lambda_{LV}\ \mathrm{A}_3\hat{P}_Y' = 0$

{by using the values of $\hat{Z}$, $\hat{a}_{LY}$, $\hat{a}_{LV}$ from Equations (8B), (2.B.1), and (4.B.3) respectively}

or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} = -\mathrm{A}_4\hat{P}_Y'(\lambda_{LZ} + \lambda_{LV}) + \lambda_{LY}\frac{\theta_{KY}}{\theta_{LY}}\sigma_Y\,'\hat{P}_Y' - \lambda_{LV}\ \mathrm{A}_3\hat{P}_Y'$

or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} = \hat{P}_Y'\{-\mathrm{A}_4(\lambda_{LZ} + \lambda_{LV}) + \lambda_{LY}\frac{\theta_{KY}}{\theta_{LY}}\sigma_Y\,'- \lambda_{LV}\ \mathrm{A}_3\}$

or, $\lambda_{LX}\hat{X} + \lambda_{LY}\hat{Y} = \hat{P}_Y'\,\mathrm{A}_5$ (7.B)

where, $\mathrm{A}_5 = \{-\mathrm{A}_4(\lambda_{LZ}+\lambda_{LV}) + \lambda_{LY}\frac{\theta_{KY}}{\theta_{LY}}\sigma_Y\,'- \lambda_{LV}\,\mathrm{A}_3\} > 0$ (as $\mathrm{A}_4 < 0$ and $\mathrm{A}_3 < 0$)

Again, by differentiating Equation (6) we get:

$a_{KX}\mathrm{dX} + \mathrm{X}\,\mathrm{d}a_{KX} + a_{KY}\mathrm{dY} + \mathrm{Y}\,\mathrm{d}a_{KY} = 0$

or, $\lambda_{KX}\hat{X} + \lambda_{KX}\hat{a}_{KX} + \lambda_{KY}\hat{Y} + \lambda_{KY}\hat{a}_{KY} = 0$

or, $\lambda_{KX}\hat{X} + \lambda_{KY}\hat{Y} + \lambda_{KY}\hat{a}_{KY} = 0$ (as $\hat{a}_{KX} = 0$)

or, $\lambda_{KX}\hat{X} + \lambda_{KY}\hat{Y} = -\lambda_{KY}\hat{a}_{KY}$

or, $\lambda_{KX}\hat{X} + \lambda_{KY}\hat{Y} = \mathrm{A}_6\hat{P}_Y'$ (6.B)

Equations (6.B) and (7.B) can be written in the matrix form as:

$$\begin{bmatrix} \lambda_{LX} & \lambda_{LY} \\ \lambda_{KX} & \lambda_{KY} \end{bmatrix}\begin{bmatrix} \hat{X} \\ \hat{Y} \end{bmatrix} = \begin{bmatrix} \hat{P}_Y' & A_5 \\ \hat{P}_Y' & A_6 \end{bmatrix}$$

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$$\Delta = \lambda_{LX}\lambda_{KY} - \lambda_{KX}\lambda_{LY}$$

$|\Delta| < 0$ as X is the capital intensive sector and Y is the labour intensive sector.

By using Cramer's rule we get the value of $\hat{X}$ and $\hat{Y}$ in terms of $\hat{P}_Y'$ as:

$$\hat{X} = \frac{\Delta_1}{\Delta} = \frac{A_5\lambda_{KY} - \lambda_{LY}A_6}{\Delta}\hat{P}_Y' \text{ and } \hat{Y} = \frac{\Delta_2}{\Delta} = \frac{\lambda_{LX}A_6 - \lambda_{KX}A_5}{\Delta}\hat{P}_Y' \text{ (6.B.1)}$$

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Chapter 71
Access to Safe Drinking Water: A Low Income Sustainable Water Purification System

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ABSTRACT

The focus of this chapter is to demonstrate that providing safe drinking water to communities in Majority World countries, specifically Kenya, Africa, is easily accomplished. Any water system, in order to be successfully constructed in impoverished Majority World communities, must be simple and inexpensive and the benefiting community must have a vested interest and ownership for the system to be effective. Establishing a vested interest by water recipients requires that the people providing the water purification technology understand the culture and worldview of the water system recipients. This approach is supported by literature review but more so by empirical evidence gathered by both authors.

INTRODUCTION

The World Health Organization (WHO) reports that diarrhea is a waterborne disease that kills around 760,000 children each year and is the second leading cause of death in children under five years old. There are nearly 1.7 billion cases of diarrhea each year. Diarrhea is both preventable and treatable (World Health Organization [WHO], 2015). WHO lists access to safe drinking water as the first key measure to prevent diarrhea.

Safe water supplies, hygienic sanitation and good water management are fundamental to global health. The global disease burden could be reduced by approximately 2.7% by increasing access to safe drinking water, improving sanitation and hygiene, and improving water management to reduce risks of waterborne infectious disease, especially diarrheal disease (WHO, 2015). Efforts to improve water, sanitation and

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hygiene interact with each other to boost overall health. Access to sanitation techniques such as simple latrines in communities that lack water treatment systems prevents drinking water contamination from human waste and reduces infection. High-tech public health measures may not necessarily be the best practice while frequent hand-washing with soap and safe storage of drinking water are low-cost, high-impact practices. Investment to improve drinking water, sanitation, hygiene and water resource management systems makes strong economic sense. The Stockholm International Water Institute reported in 2004 that there is a potential for a three to thirty-four United States Dollar (USD) benefit to be realized for every one USD invested in reaching the United Nations Development Program Millennium Development Goals for safe drinking water (Sanctuary, Tropp & Berntell, 2004). In addition to the value of saved human lives, other benefits include higher economic productivity, more education, and increased healthcare savings.

Historically speaking, the developed, western countries have viewed Africa as an impoverished continent that required an immense amount of help to alleviate the suffering of its people. To that end governments and faith based and non-government organizations (NGO) have poured an immense amount of economic aid into Africa looking to correct problems that prevent those countries from becoming economically stable and self-sufficient. According to Development Initiatives, $5.9 trillion US dollars are being spent each year in more than half of all developing countries (Development Initiatives, 2013). While recognizing that these expenditures are intended to be of major benefit to Majority World countries, most of the programs contain elements of paternalism which creates dependency and a sense of entitlement.

There are five types of paternalism: resource, where the solution to poverty is grounded in financial and material resource donation; spiritual, where the benefactor believes the materially poor can be taught much about spiritual concerns; knowledge, where the assumption is that the poor do not have good ideas about how to do things; labor, when the work is done for those who can do for themselves; managerial, where a time and efficiency model is the most expedient (Corbett & Fikkert, 2009). Corbett and Fikkert (2009) contend that paternalism must be avoided at all costs.

The colonialism of Africa, which started in the mid1800s and continued till the 1970s, changed the face of the economic, political and social fabric of the colonized countries forever (Settles, 1996). Oliver and Atmore reported that economic development and education were left up to the private sector (as cited in Settles, 1996, p. 9) but the colonizing countries controlled the foreign trade tax which was designed to benefit the colonizing country, not the colony (as cited in Settles, 1996, p. 9). This situation persisted after the end of colonialism and the effects are still felt today. The infrastructure of transportation and human services in Kenya, most notably in sanitation and water supply, is extremely underdeveloped by western standards. This infrastructure underdevelopment is due to the withdrawal of colonizing country control in the 1960s and an African worldview that interrupts the western process of development. This African worldview will be discussed in following sections.

The objective of this chapter is to present a specific example of an extremely effective way of making safe drinking water available to millions of people in the Majority World. Simple, cost effective, and empowering preventative solutions, such as the system discussed here, can lead to safe, reliable water supplies for all. These solutions need not involve intervention by the major economic and political powers. Providing safe water will require a decentralized process that involves participation and sustainability (Marshall, 2011).

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BACKGROUND

Diarrhea is a symptom of infection caused by a host of bacterial, viral and parasitic organisms, most of which can be spread by contaminated water. It is most common when there is a shortage of clean water for drinking, cooking and cleaning. Basic hygiene is important in the prevention of waterborne sickness. Water contaminated with human feces from municipal sewage, septic tanks, pit latrines or a lack of sanitation facilities is a major concern. Animal feces, which can enter the water system from a number of sources, also contain microorganisms that can cause diarrhea. Diarrhea can be spread from person to person where poor personal hygiene exists. Food is another major cause of diarrhea when it is prepared or stored in unhygienic conditions. Water can contaminate food during irrigation, and fish and seafood harvested from polluted water may also contribute to the disorder.

Africa is estimated to be the world's second largest and second most populous continent with more than 1.1 billion people living in about 30 million square kilometers of land (World Atlas, 2015). Kenya's population in 2013 was 41.8 million (Kenya National Bureau of Statistics [KNBS], 2015). According to the WHO/UNICEF Joint Monitoring Programme (2014) report, of those millions, 38% of them did not have access to safe drinking water and 70% are restricted to shared, open defecation or other unimproved sanitation facilities. Compare those numbers to the United States where 99% of the population in 2014 had safe drinking water available to them (World Bank, 2015). How sanitation and disease are dealt with is influenced by the African worldview, as explained below.

The African Worldview

Munza (2008) explains the African worldview in the following way.

A worldview is usually not something that is deliberately taught, it is simply a way of living. Our African worldview is absorbed. At nights we would have competitions in story telling that also taught traditional African values and worldview. When I was growing up within the Luba tribe my father was a chief, and he carefully instructed me in the traditions of my culture. Although he repeatedly told me that he was sending me to the white man's school, he wanted me never to forget the misumba. (The word misumba means literally the hunting or fishing camps that one occupies temporarily.) He wanted me to learn what I needed in order to make it in the world. 'Misumba ibidi hatanda, wasatwe keuyukene.' is a proverb which means, 'There are two camps in the world, but the third is unknown.' (p. 7)

Munza relates that the mother's womb is the first camp and the physical existence of the current world is the second camp. The third, unknown camp is the spiritual realm that follows death and cannot be known but is one's real home. The belief is that this existence is cyclical in nature and one may have to go to the other camps occasionally, but one may stay at home. The cyclical nature is born from generations observing the world around them. Munza (2008) states "How did we get this worldview? My father pointed out that the grass dies or is burned and then comes up again when the rains start. The sun disappears every evening and then reappears the next morning. Nature is cyclical, and so are our lives." (p. 8). Simply stated, the traditional faith on which the African worldview is based is an agrarian form of reincarnation which carries with it all the attendant customs, taboos, and rituals. The implications of this worldview are profound and it affects all aspects of life. Development is severely limited by the perception that this world is a *musumba,* which is the singular form of misumba. This perception is a

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major obstacle to development because to the African it makes no sense to build good houses and roads in a place one will be occupying only temporarily. The concept of development is almost absent. There is also the idea that one is to leave things to others at the time of death just as it was found. This includes style of life, housing, food, power, land or boundaries, and traditions (Munza, 2008).

In the African worldview, spiritual beings are the source of all diseases and therefore, the diseases cannot be satisfactorily treated with medicine and there is little sense of ability for change. Everything happens because one is bewitched or because the spirits predestined it. This affects both development as well as disease management. Traditional African practices toward healing derive major importance from beliefs that existed long before modern medicine was developed. The healers were considered charlatans and biomedicine antagonists who exploited an ignorant population. Each African country supports varying healing practices based on social and cultural traditions and heritages (Kubukeli, 1999).

Closely related to this is the use of a fetish to succeed or the belief that an individual does not have to work at being skillful. There are fetishes for success in school and business, for love in marriage, for security or protection against any action of one's enemies (MacGaffey, 1994).

According to MacGaffey (1994):

The material fetish as an object established an intense relation with, and exerted power over, the desires, actions, health, and self-identity of individuals whose personhood was conceived as inseparable from their bodies: the human body (as the material locus of action and desire) was subjected to the influence of amulets and the like that, although cut off from the body, functioned as its controlling organs at certain moments for example, for healing. (p. 1).

There are several additional traditional beliefs that delay development in Africa. Ancestral heritage is sacred and includes land, power, and traditions. Land boundaries must not be changed. Rights of other tribes or people are irrelevant. It is an unforgivable sin to compromise. Colonialism, as practiced by the European countries during the 19th and 20th centuries, changed boundaries and transferred people groups. Munza (2008) states "When you get meat, share it with your family, or you will not have someone to share with you when you don't have meat" (p. 15). Sharing is a required practice. It involves much more than sharing food or goods or taking care of family. This traditional form of sharing has been expanded to mean power or benefits if one has any social or political position (Munza, 2008)

The deeply entrenched cultural practice of nepotism is revealed in Kenya's political history. Kenya moved to a multiparty political system in 1992 after almost 30 years of independence from Great Britain. Many expected to see the end of political tribalism that was a hallmark for both the Kenyatta and Moi eras. Both former presidents favored their own tribes economically and are reputed to have stolen millions of shillings from the country. Unfortunately, election riots in 2007 showed that Kenyan politics are still divided along tribal lines and may stay that way for generations (Barsby, 2013).

Worldview Conflict

As westerners begin to interact with those individuals still holding tight to the traditional African culture and worldview, there are two things that may begin to happen to the westerner. First, appreciation may grow for how western culture differs from African culture and how thought processes are very different. Or secondly, one can choose at this point to not embrace the differences. For decades the western

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culture has tried to convert the African people and their culture into a form that resembles the west. This effort has resulted in programs that carry a large burden of paternalism and a sense of entitlement and dependency.

In order to achieve authentic development, Africans and their development partners need to understand that paradigms and strategies the partners suggest, demand, insist on, and force on the people will not work. An indigenous African agenda for development must be the basic principle behind programs (Ohiorhenuan, 2010). A notable deterrent to development are the three levels of culture Hall and Helman identified: behaviors visible to the outsider, behaviors known by the group but not relayed to outsiders, and rules that are known and obeyed by all (as cited in Esegbona-Adeigbe, 2011, p. 492). Hall further argues that the third, or primary level, is less understandable to the outsider, and more resistant to change because of its stability (as cited in Esegbona-Adeigbe, 2011, p. 492). These are the conditions that exist in the African culture of the 21st century.

The chapter authors believe that there needs to be a fundamental shift away from the *misumba* concept of temporary residency. The change cannot be forced on Africa but instead must come from within the African culture. But how can that be accomplished if, as Hall (1984) states "…no matter how hard man tries it is impossible for him to divest himself of his own culture…"? What must be done to move out of the quagmire of paternalism and attitude of entitlement into a state of unshakable independence? This problem is awaiting a solution.

Western culture derives rules for living from a totally different source than traditional African thought (Munza, 2008). Public service has become a way of life for some Americans and giving seems to have become a part of the national character. For such public service-minded persons the typical worldview includes being good stewards of the environment and the concept that humanity is to treat everyone as a neighbor. But compassionate instincts and generous spirits aren't enough because a disturbing truth is that all too much charity has become toxic, with devastating effects on the very people it's meant to help (Lupton, 2011). This manifests itself in a larger issue regarding the approach the developed (western) countries of the world have historically taken to help developing countries like those on the African continent. While recognizing the good intent of these efforts, often times these efforts do not achieve the expressed goals of the organization financing the effort, and the effort then fosters an atmosphere of paternalism, which may cause dependency. Lupton (2011) states "When we do for those in need what they have the capacity to do for themselves, we disempower them" (p. 3). Lupton (2011) then explains further that "Giving to those in need what they could be gaining from their own initiative may well be the kindest way to destroy people" (p. 4).

THE PROBLEM WITH SANITATION

There are approximately 2.5 million slum dwellers in Kenya's capitol city of Nairobi representing 60% of the Nairobi population. Kibera houses almost 1 million of these making it the largest slum in Africa and one of the largest in the world (The Kibera Law Centre, 2015). Until recently Kibera had no independent water supply so the people living there had to collect water from the Nairobi dam. The dam water is not clean and causes typhoid, cholera, and diarrhea. A study published by the United Nations Development Programme (UNDP, 2011) reports that there were 159 small-scale water providers within Nairobi city. This indicates that water is becoming more available within the city but that same report questions the

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quality of the water by noting that testing water quality is only done at the initial licensing stage without follow-up testing. The report later examines some serious implications about the water quality that is distributed (UNDP, 2011).

Sanitation is almost non-existent by western standards. One pit latrine (a hole in the ground) is shared by up to 50 to 500 people (Capital Broadcasting, 2015). Once the latrines are full, young boys are employed to empty them by taking the contents to the river. All greywater, water that has been used for other than flushing toilets, and much untreated sewage flows throughout the area in open ditches. Because clusters of pit latrines (four per cluster for 50 shacks) are widely scattered, human waste is often put in a plastic bag and tossed out the door of the shack. This practice is called air latrines and contributes greatly to the vastness of the sanitation problem.

The memory of the atrociousness of Kibera's sights, sounds, and smells may stay with a visitor for a very long time and may also cause a fundamental change in the visitor's attitude toward poverty. If the visitors are westerners they may begin to develop strategies to correct situations perceived as broken. But, maybe, just maybe, Africa is not broken. The LEAMIS training manual for their volunteers (LEAMIS International Ministries, n.d.) emphasizes that something is not necessarily wrong just because it is different. Perhaps each culture looks at the other as broken. Maybe both cultures need each other to correct the misconceptions about each other's world.

REALITY CHECKS: EXAMPLE OF A HELPING RELATIONSHIP THAT WORKS

A LEAMIS (a faith-based organization headquartered in the United States) team made arrangements with Bishop Paul Mbithi, founder and Senior Pastor of the New Life Restoration Ministries International (NLRM), to travel to Nairobi, Kenya in 2004 to establish a relationship that would hopefully have a long-lasting effect on the people of Kenya and the NLRM. Bishop Mbithi predicted that "Once the dust of Africa is on your sandals, you can never get rid of it!" (P. Mbithi, personal communication, June, 2004). The dust of Africa is the richness of the culture, the demand that one understand and live within that culture and the history of the people with all the diversity of family and tribal traditions. The efforts of western countries to lift the people of Africa out of material poverty over the decades can be labeled as a type of colonialism and paternalism and are not considered part of the dust. The LEAMIS team that met with Bishop Mbithi in 2004 was not fully cognizant of the differences between worldviews and the conditions they were introduced to in Nairobi were shocking. The NLRM headquarters is located on the edge of the Kibera slum that was described above.

LEAMIS and NLRM, as a result of the 2004 meeting, entered into an agreement that would help provide villages associated with the NLRM, in Kenya, with water filtration and chlorinating systems. The process for installing the systems that LEAMIS and NLRM established was not in consonance with the decades old approaches of church and non-government organizations that created an entitlement culture in Kenya as well as other countries in Africa. LEAMIS stopped telling people *what to do* and started showing them *how and why to do* for themselves and then allowed their students to make their own decisions. Empowering people is done through communicating what the issues are in a non-patronizing way, explaining why these conditions exist, gaining as much participant input as possible and not being critical of conditions. This approach not only provides valuable training, it builds trusting relationships.

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Figure 1. A typical street on the edge of the Kibera slum in Nairobi, Kenya in 2014.

LEAMIS and NLRM acknowledged the conditions and environment that foster poverty in Kenya, and then developed viable solutions for those problems. These solutions, that could be effective with changes in attitude and lifestyle practices, are based on the idea that personal involvement offers the best way to determine if our charitable investments are being put to good use (Lupton, 2011). However, material poverty cannot be eliminated by a single organization. What was done was not to presuppose solutions but let NLRM determine what some of those solutions might be. One of those solutions was to create a means for villages to gain access to safe drinking water. Establishing safe water supplies is an ongoing development process for both the helped and the helpers. This led also to workshops being created that allowed skills by which the local community constructed clean water filtration and chlorination systems and established cottage industries. LEAMIS encouraged evaluation of the existing conditions to determine which skills were most needed to improve the use of resources. Experiences with waterborne diseases such as typhoid and diarrhea, especially in infants and young children, were also investigated. The most useful result and workshop that came from this collaborative effort was the water filtration and chlorination system discussed further in this chapter. LEAMIS and NLRM have also incorporated the SODIS water purification process in their workshops, which adds another method for providing safe drinking water to the communities.

It is important to note that both authors have helped communities construct and operate these systems in rural African villages. The original Chlorine Production Unit (CPU) has been replaced by a newer, smaller and more energy efficient model. However, both CPUs perform the same function—generating chlorine to make filtered water safe to drink. The following account illustrates the importance of providing clean, safe water to communities around the world.

Kissi is a small town about one hour from Nairobi whose water source is a small pool of water located downhill from the two pit latrines that served this community of about fifty people. As the LEAMIS team prepared for the workshop session, a pastor from another town arrived on foot and proceeded to drink out of this small pool, because it was available. Tests of this water and another source about one

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half of a mile away confirmed that they were both contaminated and unsafe to drink. The man's use of this water is a very good example of the situation in Majority World countries wherein people will drink water they may know is unsafe because there is no safe water available. Even though the man most likely knew the water was unsafe and he was already infected with typhoid, he still drank the water. Such is the situation in Majority World countries.

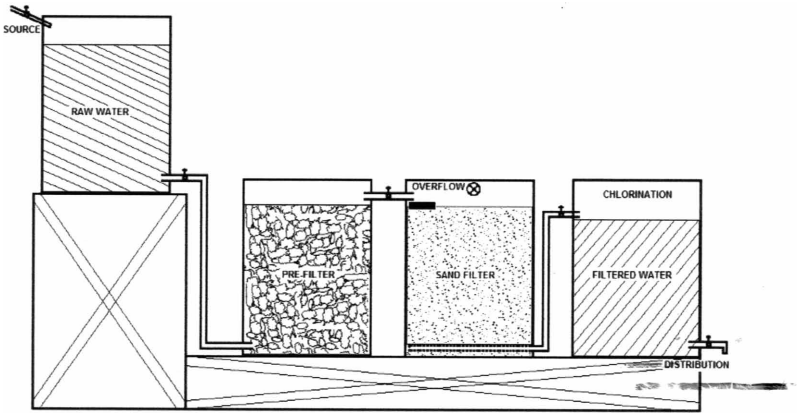
A PRIMARY SOLUTION: WATER FILTRATION AND CHLORINATION

The water filtration system developed in response to the requests of LEAMIS and NLRM is a three stage system based on the process common wetlands utilize to filter and clean water naturally. The first stage filters particulates with a rock or gravel component that is made of first large rocks then smaller rocks that capture smaller and smaller unwanted materials. The next stage is sand which creates a microbial biofilter that uses the biological flocculation process which allows living organisms such as bacteria, zooplankton, diatoms and algae to eliminate pathogens in the water (Tarsi, 2008). The sand filter is a microcosm of wetlands that occur in nature. Wetlands are extremely efficient in filtering water and can actually purify contaminated water and render it safe to drink. The third stage includes using chlorine to treat the water to remove pathogens not removed by the filtration and to kill parasites.

All of the containers in an ideal system are the same size to allow for uniformity of water distribution through the system. The recommended size of the containers is between 30 and 50 gallons. The first container is used to house the raw water. The second, Pre-filter, is filled with clean, 1-1.5 inch diameter pebbles or gravel. Raw water is piped in at the bottom of the pre-filter by hydrostatic pressure and allowed to percolate up to the top where it is piped onto the top of the second stage sand filter. The purpose of the pre-filter is to remove as much organic material as possible. Over time, this filter may clog and the gravel will need to be thoroughly cleaned or replaced.

The Sand Filter is filled with clean sand the texture of fine beach sand or sand that is used for mortar. There is a deflection rock on top of the sand to prevent the sand being stirred. About two weeks after initial use a microbial layer will form. This is why this filter is effective. This layer is made up of liv-

Figure 2. Elements of a filtration/chlorination system. Figure created by chapter author Robert Willems, 2014.



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ing organisms that naturally occur. Over time this layer will become denser and actually slow the water percolation. At that point a few inches the top layer of sand needs to be removed and new sand added. There is a perforated pipe in the bottom of this filter that will discharge filtered water into the third stage collection container where the water will be chlorinated.

Chlorination currently occurs by one of two methods. The first method is by bubbling chlorine gas through the filtered water. The chlorination unit uses ordinary table salt or unrefined rock salt. Water is added to the device and it is connected to a standard 12 volt car battery. The salt is broken down into sodium and chlorine which are given off as gasses. The byproducts that are captured by the unit are highly concentrated Clorox-type bleach on one side and a strong sodium hydroxide solution on the other. The chlorine gas is injected into the filtered water while the sodium is vented to the atmosphere or captured for other use. The former, when diluted, is ideal for use as an effective antibacterial cleaning agent and the latter is ideal to deodorize pit latrines, effectively removing their odor. The time required to bubble chlorine gas through the filtered water to raise the concentration to a level that will kill bacteria is approximately one minute for fifty gallons of water. According to the WHO (2003) the chlorinated water must contain a chlorine concentration level between 0.2 and 1.0 parts per million (ppm) to be considered safe for consumption. If the chlorine concentration drops under that, the water must be re-chlorinated and retested. The concentration level may be determined by using an ordinary swimming pool test kit. A very effective and dependable chlorine generating unit has been designed and patented by New Life International, www.waterfortheworld.com, where the units are available.

The second method of chlorination is to manufacture liquid chlorine by passing salted water through a Chlorine Producing Unit (CPU) and treating the filtered water with the chlorine. One of the most recent units installed in villages in Kenya is the Khlor Gen System (Hayes Pure Water, 2014). The Khlor consists of a chlorine producing unit powered by a motorcycle sized 12 volt dc battery and a solar panel to keep the battery charged. The complete system currently costs $365 US and is expected to last five

Figure 3. Original four barrel water filtration system installed in New Life Restoration Ministries church and orphanage in Nairobi, Kenya

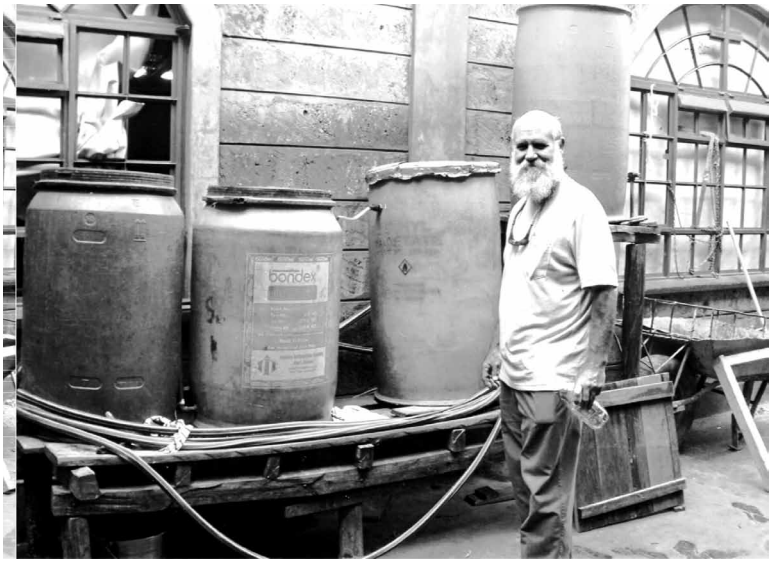

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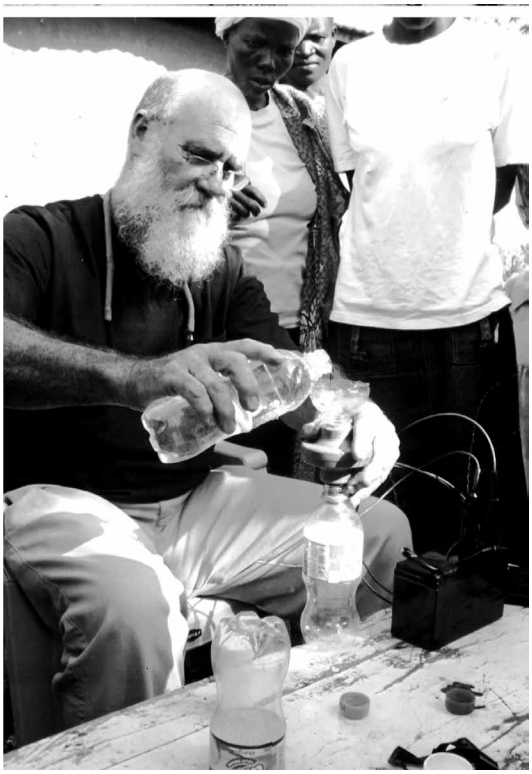
Figure 4. Chapter author Steve MacDonald demonstrating the newest Khlor Gen System to villagers in Kenya in 2014 during the LEAMIS Water Purification Workshop



years under normal usage. The inventor of the Khlor reports that more than 4000 units have been installed worldwide (Hayes Pure Water, 2014). The system is easily transported in airline checked baggage and is simple enough to use that very little training is required. With exception of the chlorination unit all other materials for the systems can and should be purchased locally to assist the local economy and prevent creating a situation of paternalism or sense of entitlement.

The workshop that was developed to train members of the community in the operation of the filtration system is followed up with construction of a system by residents of the village. This ensures that those trained in the operation of the system will have ownership of the system and the community is empowered with the knowledge necessary to teach the concepts to others. Periodic maintenance and troubleshooting of the system is also included in the workshop. The entire process from workshop to completed filtration system can be accomplished in as little as two days. However, the experience of both authors has been that the process takes three to four days.

The reader is strongly encouraged, at this point, to visit the LEAMIS website at www.leamis.org to watch "2010 KENYA Trip" (found under the "Watch Our Videos" tab) which portrays the passion felt for bringing this technology and these systems to groups such as New Life Restoration Ministries. To date every system that has been installed in Kenya has completely eradicated waterborne disease (P. Mbithi, personal communication, March 3, 2014). The reader is also encouraged to visit Vimeo on-line video library and watch http://vimeo.com/76944942 to learn more about New Life Restoration Ministries and see how they have upgraded the original system installed in 2004.

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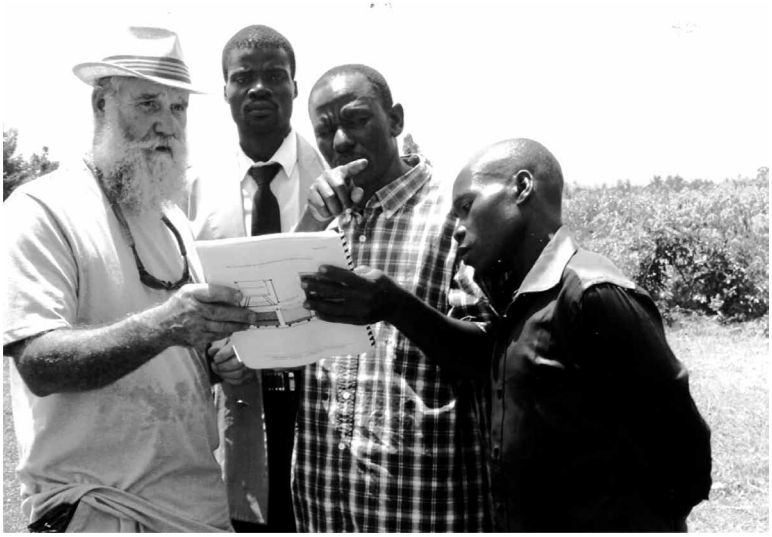
Figure 5. A group of NLRM members consult with one of the authors during the construction of a water purification system



SODIS: A Value Added Process

Solar Water Disinfection (SODIS) is a simple, environmentally sustainable, low-cost solution for treating drinking water at the individual level for people consuming microbiologically contaminated raw water. SODIS uses solar energy to destroy pathogenic microorganisms causing waterborne diseases and therewith it improves the quality of drinking water. Pathogenic microorganisms are vulnerable to two effects of the sunlight: radiation in the spectrum of Ultraviolet A (UV-A) light with a wavelength between 320 and 400 nanometers and heat. Eawag (2015) lists 42 scientific publications that discuss the SODIS method of water purification. The mortality of the microorganisms found in untreated water increases when they are exposed to both higher temperature and UV-A light at the same time. SODIS is ideal to disinfect small quantities of water of low turbidity, which is a measurement of the clarity of water. Contaminated water is filled into transparent plastic bottles and exposed to full sunlight for a minimum of six hours. During the exposure to the sun the pathogens are destroyed. If turbidity is greater than 50%, the plastic bottles need to be exposed to direct sunlight for two consecutive days in order to produce water safe for consumption. Filtering the water through clean cloth will reduce the turbidity which will increase the available water that can be successfully treated. The treatment efficiency can be improved if the plastic bottles are exposed to sunlight on reflecting surfaces such as aluminum or corrugated iron sheets.

SODIS is well suited for small households or individuals because of the simplicity of the process and that it uses plastic bottles that are usually very plentiful. There are two forms of plastic, polyethylene terephthalate (PET) and Polyvinyl chloride (PVC). PVC can be harmful through chemicals that leach into the water as the bottles age and are exposed to sunlight. The PET plastic bottle is much less volatile as it degrades in sunlight and is therefore much safer from a health standpoint.

Turbidity and availability of usable bottles are issues. If the raw water is too turbid the water cannot be treated. A simple test has been devised to confirm that the turbidity is low enough that the water can be treated. The test is to determine if the word “SODIS”, printed on a sheet of white paper, can be read

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looking through the water in the bottle. If the turbidity is low enough to classify the water as treatable, "SODIS" can be read. Availability of bottles can be a minor issue because of the recycle potential of PET which gives it a marketable value and bottles may be scavenged from debris piles. Eawag, The Swiss Federal Institute of Environmental Science and Technology, in cooperation with the Department of Water and Sanitation in Developing Countries (SANDEC), have perfected this inexpensive yet dependable water disinfecting technique.

One additional benefit of conducting both filtration/chlorination and SODIS workshops simultaneously is that in the event a CPU should cease functioning for any reason, the SODIS treatment of the filtered water will provide users with safe drinking water.

RECOMMENDATIONS

Reliable and safe water supplies must be developed if there is to be a reduction in the global disease burden. Individuals and NGOs interested in helping communities develop a safe water supply should carefully consider exactly how to help those communities without creating a situation where paternalism and entitlement become the norm. A suggestion is to study cultural competence information before attempting an encounter to assist Majority Word peoples. According to Ansuya (2012) Leininger's Culture Care Theory is one such useful basis for understanding the importance of culture in an individual's health and other behaviors. Leininger's work was written for nursing originally, but could be easily broadened to assist anyone seeking to implement health improvements in Majority World locations. Some of the essential elements of cultural competence include: valuing diversity, preforming cultural self-assessment, being conscious of dynamics of cross-cultural interactions, having cultural knowledge of the service area and developing adaptations of service delivery reflective of that cultural knowledge (Ansuya, 2012).

FUTURE RESEARCH DIRECTIONS

Several efficient, simple and cost effective water filtration and chlorination systems have been developed in the last decade. Consultations with leading authorities in the proper implementation of those systems will help ensure successful development of healthier communities. Further research directions could be focused on variations of the water systems that would work better in different communities. Also relationship building methods that assist in successful delivery, installation and on-going operation of water purification systems can be further developed.

CONCLUSION

Having access to clean, safe drinking water is a large scale problem for a majority of the world's population. Contaminated water is responsible for too many deaths each year, especially young children. Finding clean, pure and potable water is a life-sustaining necessity worldwide. Many people have to travel miles just to find water which much of the time is polluted and leaves the population victim to waterborne disorders such as typhoid and diarrhea.

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LEAMIS was instrumental in the development of an extremely effective, simple, cost effective, and empowering preventative solution that lead to safe, reliable water supplies for all. This has been accomplished without the intervention of major economic and political entities and the countless monies spent trying to save the continent. This very successful program relies on a decentralized process that insists on the participation of those benefiting from the water treatment systems. More than thirty systems based on the original system installed in Kibera have been installed in NLRM communities in Kenya since 2004. "The water purification systems LEAMIS has so far managed to install at various church locations here in Kenya have been quite revolutionary. Waterborne diseases have effectively been eradicated and children at our school in Kibera have been one of the greatest beneficiaries" (P. Mbithi, personal communication, March 3, 2014). When the installation of a system is accompanied with proper training and bolstered by a relationship such as the one enjoyed by NLRM and LEAMIS, the health and well-being of the community members are greatly increased.

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KEY TERMS AND DEFINITIONS

Dependency: The state of being when someone constantly relies on a person or organization for economic, political or emotional support. Those that are dependent often do not do for themselves what they can because some else will do it for them.

Flocculation: A chemical process occurring in biofilters that results in pathogens coming out of solution and attaching themselves to solids in the filter.

Majority World: Those countries that have traditionally been labeled underdeveloped or third world. The majority of the world's population resides in these countries.

Misumba: The hunting or fishing camps that an African temporarily occupies while living on the earth. The concept of a Misumba is one of the major components of the African worldview that hinders development.

Paternalism: A policy or practice of treating or governing people in a fatherly manner, especially by providing for their needs without giving them responsibilities.

Safe Drinking Water: Water that is either naturally potable or has been filtered and chemically treated to render it potable.

SODIS: A water purification process that capitalizes on the susceptibility of microorganisms to ultra violet light and heat.

Workshop: An informal training conference designed to transfer knowledge to attendees.

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Chapter 72
Increase of Transportation Efficiencies and Emission Reduction within a City

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ABSTRACT

On a worldwide scale population is increasing, necessitating efficiencies in transportation essential for a modern and healthy environment. Most cities have already reached their limitations on population and vehicle movement. Street layouts and cycling lanes, which were initially planned for a certain number of inhabitants, are now not able to cope with increasing demand. The same applies for fresh water supply and effluent treatment which have limitations also. With an increasing population in urban areas, restriction levels in these regions can be reached very quickly, creating a problem which needs to be addressed. A smarter city can only be developed when there is pre-planning on all of these issues, when there is an understanding of newly developed human behaviours, and when new inventions and technologies in urban areas can adapt to these changes.

INTRODUCTION

In order to develop a good eco-society, there are a number of elements that need to be in place before a city can be labelled as a "smart city". Refuse collection, recycling infrastructure and recycling amenities, low smog concentration, traffic flow of vehicles and people, substantial investment in renewables, and energy efficiencies will all have a major influence in achieving a smart city status.

Industrially developed cities are fighting against pollution by increased decarbonisation programmes. Supporting energy efficient systems with the help of renewable energy technologies, while at the same time carefully targeting the spending of those investments, is a key part of this strategy. This chapter will focus mainly on methods and technologies in the transportation sector which until now have been ignored but which play a major role in the pollution of cities. Transportation emissions are a major contributor to smog levels and therefore need to be addressed in any assessment of this problem.

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In order to have a modern eco-society, planners and engineers have to reassess their city in every area, evaluate required steps and take critical action against those problems identified. This chapter will highlight potential pitfalls and will demonstrate state of the art developments across the globe, enhancing a city's lifestyle and associated environmental management system accordingly.

BACKGROUND

Urban population is increasing at an alarming rate which, over time, will result in traffic flow problems, increased pollution density, crowded public transport, exhaustion of land availability for future property developments, and consequently a reduction of available social parks and woodlands. Reduced green zones in built-up areas result in a subsequent increase in CO_2 emissions, particles measured in parts per million (PPM), and noise levels.

According to the "Bevölkerungsfonds der Vereinten Nationen", the world population is predicted to reach 9.6 billion people by 2050, by which time more than two thirds of this population (approximately 6.4 billion inhabitants) will be residing within urban areas and cities (Malte Laub, 2015). This shocking prediction highlights the urgent need for more efficiency in cities, smarter traffic planning and innovative living accommodation.

In India, 30 people currently move from a rural area to a city every minute. This growth trend is expected to continue for the next 20 years. Experts are predicting that there will be a development of approximately 500 new cities within India in the next two decades (Heckel, 2015). This movement of people from rural to urban will result in enormous lifestyle changes, with a much greater proportion of people's lifestyle requirements having to be met in a smaller living space.

- **Issues:** With the constant growth of cities on a global scale, ownership of properties is becoming more limited and requires more land area. This demand on properties will increase rent and limit affordability, which will trigger higher living expenses in these cities. A higher population density for a city which has not been designed initially for this explosion of people puts pressure on waste disposal, the resources of treatment plants, and parking spaces for vehicles, and also leads to a surge in noise and emissions. This has a huge impact on current layout designs, beginning with traffic flow problems, public transportation systems, postal delivery, nearby parks and forestry, fresh water supply, and available grocery stores.
- **Controversies:** Living accommodation can be very limited and expensive in a growing city which consequently requires more housing solutions. This can apply when looking for new property developments while reducing social green field spaces like parks, amenities and small forests or nearby developments. Reducing social spaces will not please everyone, but doing nothing against a growing number of inhabitants won't solve the problem either.
- **Problems:** Some cities are not designed for rising population numbers and need to reinvent in order to adapt. In some cases not every city and urban area can deal with these until-now unknown problems and they will require professional help. Focus groups, advisors and other specialists are needed to deal with the above mentioned problems like waste treatment, water supply, the parking situation, limited public service transport, required rental properties, and other related pollution factors.

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- **Solutions:** Pre-planning in response to forecasts of increased population is essential for a stable city design. Every city should have a planning and design team focusing on a specific area with the help of a focus group. These groups need to analyse current system setups, address current and future issues, and evaluate possible options. The forecast data, which will include expected population numbers, is essential for a pre-planning procedure. Available land area and lead time to build properties must be considered when pre-planning, as it can take up to three years from filing a planning application to initial completion.

Transportation efficiencies and emission reduction are very important topics, which must and will be explored by many cities. Growing urban areas have come under pressure, as these problems have only recently been taken seriously.

Research Statement

The expression "smart city" is in very common usage nowadays to cover a very broad range of areas stretching from sustainable living, eco-friendly dwellings, smart integrated solutions via mobile phone applications, modern waste water treatment facilities using the off-gas for power and electricity production, and smartly controlled traffic flow guided junctions. All of this integrated technology has already changed behaviours and will certainly shape the coming years and even decades. Computer assisted guiding systems for disabled and elderly people, and robots serving food and accomplishing easy tasks like cutting lawns when required, are already a reality. This evolution is all part of becoming a more connected environment, helping in decision making processes, which will subsequently lead to higher efficiency. Televisions integrated into mirrors in bathrooms, informing people of breaking news, is not a future idea any more. This all is part of a smarter city structure, embedded in various fragments of this system.

This section however deals mainly with transportation related topics ranging from traffic flow design, energy saving innovations, new technology developments, and efficient system integration using public transport services. A comprehensive framework of innovative strategies has been introduced. Those technologies will highlight what deficiencies exist in the process of transforming a smart city to the next level. Best practice and examples from around the world which demonstrate the potential of each city have been researched.

Small Solutions Can Make a Huge Difference

There is not just one solution to reducing urban waste and pollution. Several small changes have the potential to have a major impact on these problems. There is enormous room for efficiency and improvements and, when all enhancement programmes are running concurrently, there could be a noticeable change. Below is a list of suggestions using different technologies and inventions, some of which are still on a pilot scheme basis.

Action Against CO_2 Reduction Requires Several Steps

Traffic systems and public transport need to be constantly re-evaluated for future action which may be required. The newest available technology has to be used, keeping traffic flow moving despite the fact

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that the population in urban areas is growing. "Smart traffic light systems", higher efficiency with parking spaces, more public transport incentives, and an increase in cycling lanes, car sharing, and usage of electric vehicles are all things that can make a city smarter. All these improvements will have the effect of decreasing carbon dioxide and other emissions due to higher effectiveness. This will also positively impact on the health and quality of life of people living in those areas mentioned.

Renewable Systems Will Play a Major Part of an Eco-City

Hot water solar panels that can produce free hot water in combination with photovoltaic panels can generate localised electricity as has been done widely in mainland Europe. This is one of the key elements that can contribute to reducing emissions in cities. Energy efficiency, architectural design of south facing buildings in the northern hemisphere and north facing buildings in the southern hemisphere, and draught and heat loss reductions supported by thermal coated triple-glazed windows will enhance sustainable living. These improvements will also reduce heat load and electricity bills, which can then lead to reduced emissions due to lower energy requirements from public, domestic and industrial premises. These combined with highly efficient electrical devices will conserve electricity consumption which is traditionally produced by nuclear power or peat, coal, oil and gas power plants. Therefore, electricity reduction is one of the best methods of saving by reducing the emissions and environmental pollution of energy production.

Smarter Building Design Integrated with Innovative Renewable Technology has been Enforced by Tougher Building Regulations

Most counties in Europe have a localised standard of building regulations. In order to get planning permission, buildings need to meet those standards, and technology and some type of renewable energy contribution need to be installed to comply with these standards. In order to compare different system types, energy performance of dwellings are measured in Maximum Permitted Energy Performance Coefficient (MPEPC). This performance certificate indicates the emissions produced and the quality of insulation in the house. For each m^2 of living space there is a certain heat and energy requirement. The better a house is insulated, the lower the heat demand; therefore, efficiency is increased. Nowadays, these certificate values are indicated in kWh/m^2 per annum. With this system the buyer and property developer know exactly what energy costs will be expected after purchase. In Germany, these certificates have to be renewed every 10 years in order to include new technologies and modernisation improvements which were carried out in the intervening years.

Energy performance certificates for houses used for letting and sales are mandatory in Germany since 2008. This energy and house performance certificate (Energieverbrauchsausweis) indicates the energy requirement as a value but also has, for the less technical person, a scale in letters ranging from A+ to H (dena, 2009). A house with an energy rating of "H" would be the worst performing house with literally no insulation and poor window glazing. A house with the "A+" accreditation would be classified as a passive house which does not require any import of heat and electricity. In another words, an A+ house produces its own required heat and more electricity that it consumes. Most passive houses have solar thermal panels for hot water production and photovoltaic panels for electricity production. If the annual electricity production is greater than their need, surplus electricity will be exported. Electricity could be used for geothermal heat pumps and, therefore, no fossil fuel is consumed. It could also be

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Figure 1. Photovoltaic panel mounted on roof top for electricity production
Source: Own picture.03.2015

used for wood pellet boilers, igniting the fire, powering the wood pellet auger and circulating the hot water for domestic heating purposes. Passive house designs are always costlier than normal dwellings, but eventual running costs are less over the life cycle of the building and it can be seen as an emission free house all year around (Figure 1).

Start and Stop Function in Trucks and Vehicles

Newer cars have a start/stop function which will stop the engine when the car is not moving, the gears are engaged and the clutch is not activated. This technology can reduce emissions in a traffic jam and will have the added bonus of saving fuel. All these systems work similarly and are ubiquitous on hybrids. When the car comes to a stop, the engine computer cuts spark and fuel. When the brake is dis-engaged, or the clutch engages, the engine fires back up. The engine starter has to be stronger than in normal engines to withstand the markedly increased on-off cycling. A more powerful battery is also required to satisfy the car's entire electrical needs with its more frequent engine off cycles. Otherwise, stop-start is about as easy a fuel-saving technology as driving downhill (Colwell, 2015).

This technology will help during traffic jams, reducing delay times at traffic lights and other situations where longer idling time is encountered before proceeding in driving off. Depending on the vehicle model, fuel type and engine size, the rule of thumb is that if the engine is switched off for more than 5 seconds a fuel saving will occur. This applied technology in cars is known as "blue motion technology", which has been developed for exactly these kind of situations. Most of the newer mid-range specification vehicles manufactured after 2009 will have this feature as standard.

Increased Road Tax Fees for Cars with High Emissions

It is generally becoming more common throughout Europe that road tax systems are based on emission levels only. The higher the emissions of a vehicle/truck, the higher the running costs and associated road tax. This will incentivise vehicle owners to invest in more modern engine technology which will lead

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subsequently to less road tax expenditure. Road tax is based on emissions of various fuel types like petrol, diesel, LPG, electricity, hydrogen, LNG and CNG due to various fuel densities and associated emission values. The higher the tax for a vehicle the more likely the owner will change it. Cars older than 10 years must also undergo an annual roadworthiness inspection which incentivises the vehicle owner to drive a newer automotive. This will help in reducing emissions and will likewise lead to less fuel consumption.

Travelling Ban for Amber and Red Emission Labels in City Centres

Particulate emission bands for vehicles in cities in Germany are classified in three categories: green, amber and red. Vehicles, therefore, have been classified into different emission bands, which must be denoted by a sticker displayed on the front windscreen. The vehicle registration office will issue those stickers according to the emissions of the vehicle. More than 50 cities in Germany have introduced areas where only low emission vehicles are permitted. Other locations are less restricted and allow amber coloured labels. A green labelled vehicle can drive through the city without any limitations, amber labelled vehicles are limited to certain areas and red labelled vehicles are prohibited from entering the city centre (ÖAMTC, 2014). This system has been in operation since January 2013 and will keep emissions lower in busy cities. Compliance is strictly controlled and any violation is prosecuted with a hefty fine.

Traffic Information for Vehicles and Public Service via Mobile App and Satellite Navigation

Commuters can be notified via mobile phone app, radio data systems or satellite navigation about current traffic status, enabling them to pre-plan required journeys and routes in a more efficient way. This has the potential to reduce traffic jams, making traffic flow more efficient, with the aim of reducing travelling time and emissions. Some companies are very efficient in this area, developing their own software and networks. One of the company developments is based in Zaragoza in Spain (Figure 2).

The Vehicle Traffic Monitoring Platform, part of the Libelium Smart Cities solution is a platform capable of sensing the flow of Bluetooth devices in a given street, roadway or passageway differentiating hands-free car kits from pedestrian phones. Sensor data is then transferred by a multi-hop ZigBee radio, via an internet gateway, to a server. The traffic measurements can then be analysed to address congestion of either vehicle or pedestrian traffic (Gascón, 2015).

Intelligent Streets Lights and Public Places Illumination

Most street lights in cities are switched on at sunset and switched off at sunrise. This technology is dated and not conducive to energy savings. There are several ways of developing smarter street lights whereby the first step should be changing the light bulb to a LED lighting unit. The second step should be that streets lights are switched on and off automatically, measuring lux rate, and when light is required should be dimmed to a programmed light emittance. This will prevent lighting up when not required or during daylight. In addition to this, light sources should be upgraded with a presence sensor, detecting moving objects, so that the light can be dimmed when full light output is not required (Leccese, 2014).

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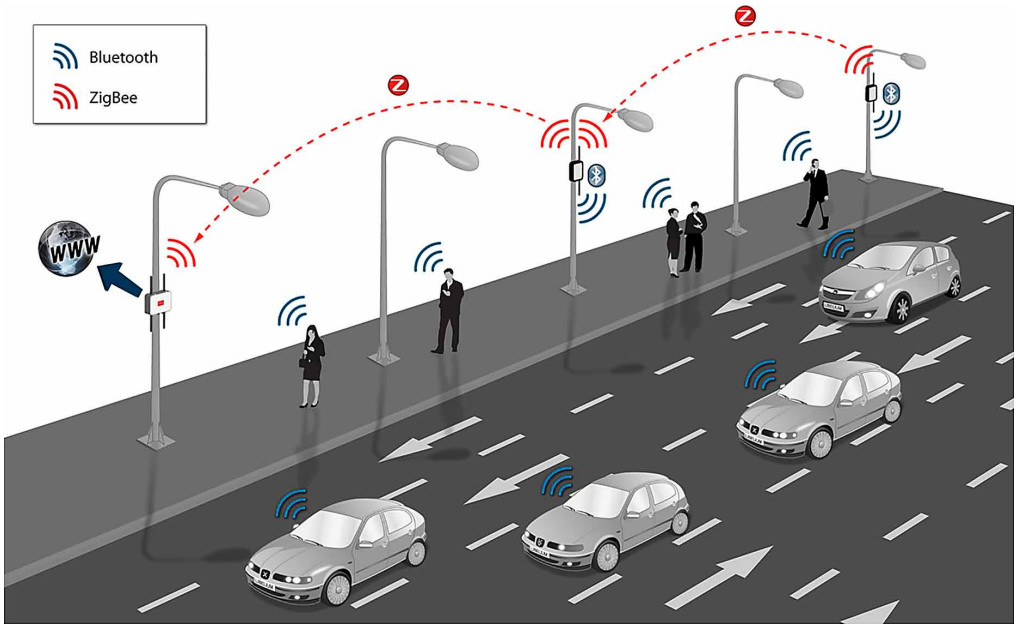
Figure 2. Vehicle traffic monitoring platform with Bluetooth Sensors over ZigBee, 15.05.2015



Smart Junction Crossings and Traffic Light Systems

The first traffic light was erected in Berlin in Germany in 1914. More than 100 years ago it was a unique innovation. Nowadays a city without traffic light systems is not imaginable or practicable. In some situations, waiting for a green light can take up to several cycles depending on the traffic situation and road layout. Sometimes despite having no other traffic in the vicinity a driver has to wait on a red light. This is a typical situation where a smart traffic light would be very beneficial.

Smart traffic lights work in conjunction with small sensors that have been integrated into the street, measuring the traffic flow, and can therefore calculate the travelling speed of oncoming vehicles. These systems can also predict the time of arrival at a particular junction and as a result have the ability to switch the traffic light to green if optimal conditions prevail. In addition, autonomous cameras are connected to this system, recognising emergency vehicles like ambulances, fire brigade vehicles, police vehicles, etc. and regulating the traffic lights for priority. This makes journeys for emergency staff safer and has the potential to decrease travel time in reaching the emergency situation, when seconds can make a difference between life and death. This technology will automatically reduce passing-through times at traffic junctions, reduce "stop and go" behaviours, increase throughput of vehicles and eventually reduce particle emissions, thereby reducing the emission levels within cities. All sets of traffic lights are connected with sensors and smart technology, enabling communication between the various sets of traffic junctions.

According to Carlos Gershenson, a researcher from Universidad Nacional Autónoma de México in Mexico, the estimated upgrading cost for a full functional junction is in the region of only 25,000 US dollars which is approx. 19,000 Euro. Politicians in Mexico City are in talks with a researcher group in upgrading major traffic junctions and therefore reducing costs due to mass production down to 2,000 to 4,000 US dollars (Gershenson, 2015). This will enable smaller councils to afford this smart technology, reducing emissions and noise levels in their area.

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Available Parking Space Display and Mobile App Functions

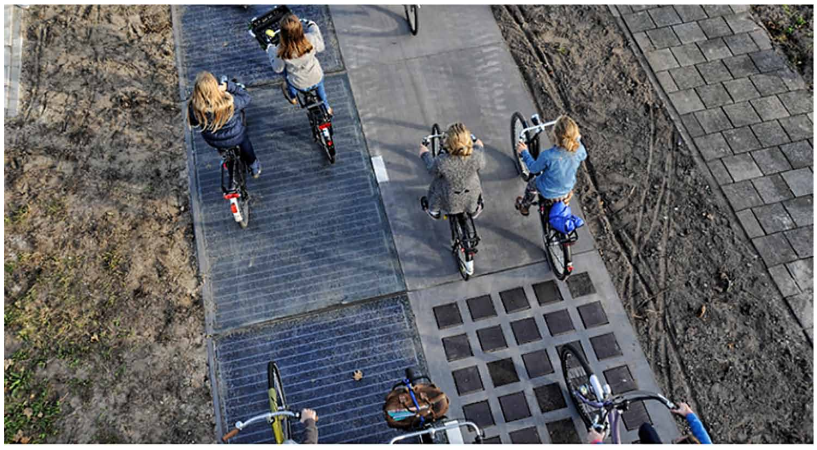
A mobile app should be designed for individual locations fed with live data, identifying empty parking spaces and locations, and notifying customers when a parking space becomes available. This will reduce time and effort for the vehicle driver looking for a free parking space, make parking space searches more efficient and reduce vehicle numbers on the road. Bigger car parks should have a display board outside their premises informing customers about the current number of car spaces available. The app could also inform electric vehicle (EV) owners about free parking spaces to charge up their vehicles. In the future these apps could also be used for charging point pre-bookings. This technology would secure an available parking space for an EV driver knowing the exact location and time of arrival in advance.

Photovoltaic (PV) Solar Panel Cycling Lane for Smarter Emission Free Electricity Production

The Dutch government has designed and installed the world's first photovoltaic solar panel cycling lane which was opened to the public in December 2014. This cycling lane has the potential to produce electricity during daylight while at the same time functioning as a cycling lane. The electricity production of this trial solar cycling lane has already excelled during the winter months, according to a recent announcement by the solar road spokesperson (Wit, 2015). The 70 metre test track has inserted solar panel crystalline cells into a cast concrete base instead of tarmacadam. This is protected by a tempered 10 mm safety glass. This surface is also proven to be slip resistant. The surface was tested with various protection coatings to compare their chemical properties but no complaints were submitted and reaction to this new innovation is very positive. Further investment and installations are expected by the end of 2015 with expansion to major towns in the Netherlands.

Horizontal PV on cycling lanes has the potential to produce emission free electricity, necessitating less need for oil rich tarmacadam and with no required uptake of available land space with conventional PV solar farms. This form of renewable energy production has been gaining acceptance by the Dutch community with no complaints filed so far (Figure 3).

Figure 3. Horizontal PV renewable energy
Source: http://www.solaroad.nl/en, 19.05.2015



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Freephone Traffic Engineering Hotline

Since 2009, the City of Cologne in Germany has a Freephone hotline connected to the traffic engineering office where commuters can make suggestions on any traffic improvements they feel would be advantageous for the city. On average, the engineering office receives approximately 900 calls per annum with some very valuable ideas coming from people who are dealing with these traffic problems on a daily basis. Since this traffic efficiency initiative has begun, commuting in the city of Cologne has improved noticeably (Verkehrsdienst, 2015). There was one particular traffic junction about which motorists complained regularly. At one particular time during heavy traffic in the morning, waiting time was more than 8 minutes. Trams and Metro have priority before cars, followed by cyclists and finally pedestrians. After the traffic light setup was assessed and adjusted in conjunction with other surrounding traffic lights, the waiting time was adjusted to an average of 110 seconds, which was archived with an impressive waiting reduction time of more than 400%. These improvements show clearly the need for an efficient system like this. Initially, this hotline was only introduced as a trial phase for 6 months but, after a successful take up by the citizens, the service is still running.

Tax Incentives for Low Emissions Cars

In the USA there are fast lanes in place enabling cars and car pooling commuters to drive in the fast lanes once the car has more than three or more occupants. This incentivises car sharing in driving to work, for example, which correspondingly reduces the number of cars on the road. The same principle is being applied in Germany for hybrid and electrically propelled cars. Any violation of these rules can be prosecuted, with hefty fines imposed.

High-Occupancy Vehicle Lane (HVO) on Motorways

High-occupancy vehicle lanes are also known as HVO lanes, transit lanes, 2+ lanes and diamond lanes, and are designed to increase the enthusiasm for sharing vehicles on the way to work, for example. These lanes are normally less busy, vehicles can drive faster and, because they carry less traffic, they create a more relaxed driving experience. They are designed for peak times and can only be used for carpooling with at least two occupants in the vehicle. Depending on country and state there are other vehicle exemptions imposed for school buses, emergency and law enforcement vehicles, motorcycles, and low emission vehicles. These lanes are created with the intention of reducing the numbers of cars on the road and increasing average occupancy numbers in cars while reducing congestion on the roads (Figures 4 and 5).

BENEFITS IN USING HVO LANES

- **Save Time:** It can avoid congestion and arrive at destination more quickly than those who don't carpool
- **More Reliable Commute:** Avoiding congestion means a quicker and more consistent commute time
- **Save Money:** It costs less to ride a bus or to share a ride than to drive alone every day. Regular carpooling could cut fuel costs by 50%

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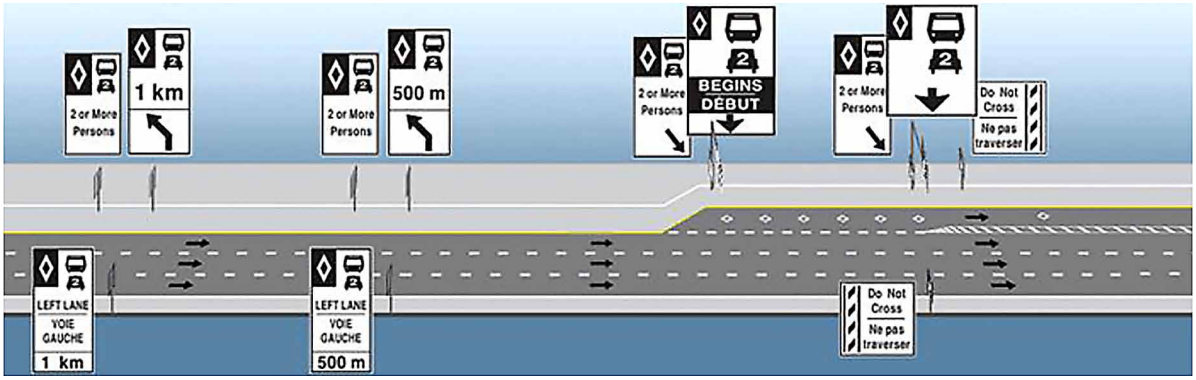
Figure 4. High-occupancy vehicle lanes
Source: (Christopher K. Leman, 1994)

Figure 5. High-occupancy vehicle lanes
Source: (Transportation, 2015)



- **Conserve Fuel:** less fuel waste sitting in traffic
- **Less Stress:** Letting someone else drive while relaxing on the drive to work

BENEFITS FOR CITIES

- **Manage Congestion:** An HOV lane can handle a lot of growth in demand. Once a general traffic lane reaches capacity, it becomes congested and moves fewer vehicles
- **Make Better Use of Infrastructure:** One highway lane can carry 1,500 to 2,200 vehicles each hour. A lane full of buses and carpools moves many more people than a standard traffic lane.
- **Transit Priority:** Buses and transit occupants have priority. A single transit bus can replace 57 single-occupant cars!
- **Provide Choices:** HOV lanes make carpooling and public transit more effective and reliable choices for commuters

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- **Support Mobility:** Taxis and airport limousines that use HOV lanes can return to duty faster after dropping off a fare or arrive sooner to pick up a fare
- **Support Electric Vehicles:** Electric vehicles with green plates can use HOV lanes until June 30, 2016
- **Re-Thinking HOV:** High Occupancy Vehicle Facilities and the Public Interest (Ontario, 2013)

According to an analysis by the U.S. Census Bureau in 2004, the share of people carpooling was 12.2 percent in 2000, which accounts for the second largest share: 77 percent of people drive alone; 4.7 percent use public transit (Hideo Konishi, 2010).

Road Tax Exemption for Electric Vehicles

The German government has also extended road tax exemptions for any electrically propelled vehicles, initially agreed for five years, which has recently been extended to 10 years until 2025. This will also help to get more electric vehicles (EVs) registered, with the aim in having 1,000,000 EVs on the road by 2020.

Other countries in Europe have similar incentives to stimulate the EV market. Due to very high investment costs for EVs, mainly due to the high purchase cost of the battery, it is evident that market growth cannot be achieved without some form of incentive. For that reason, many countries have schemes to stimulate the EV sales market. In the Netherlands for example they have a low private motor vehicle and motorcycle tax called "BPM" for EVs, which is divided into various categories related back to the CO_2 emission band. The highest tax for emission > 110 gram/km is set with 25% BPM and pure EVs are only charged a tax of 4% if < 50 gram/km (TACA, 2015). Therefore, not all EVs have a low tax band, but the lower the emissions the less tax charged, and consequently the greater the incentive for introducing environmentally friendly vehicles (ACEA, 2015).

Tax incentives can be introduced in different formats, like a tax rebate when purchasing an EV, the introduction of road tax exemption, tax reduction for companies reducing their liabilities/annual circulation tax, and top-up grants. Some countries also differentiate CO_2 bands, which are then linked to associated support levels, while some countries have no incentive scheme in place. This highlights the fact that certain countries have no interest in supporting EVs, while others are very inventive with a broad range of incentive schemes introduced.

Most EVs are classified as emission free or CO_2 neutral but this is not a comprehensive reflection of the situation. This does not apply to EVs if they are using regular sockets where the electricity is only supplied from the national grid to charge vehicles. Countries have various emission levels depending on how electricity is produced, i.e. coal, turf, oil, gas, waste, etc. In reality, only an emission free EV is CO_2 neutral when charged by photovoltaic, wind, hydro, geothermal, and biogas-produced electricity which produce literally no emissions. It could be argued that some fossil fuel energy was required to build those systems but this equally applies to traditional fossil fuelled power stations. Many companies in Austria and Germany are charging their EVs on site with electricity produced from their own installed photovoltaic roof panels, which represents a totally CO_2 emission free charge.

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Park and Ride Systems

Park and Ride (P&R) systems are a very effective way of reducing the numbers of vehicles in a city. This commuting system, whereby vehicle owners can park their vehicle at a car park outside the city free of charge, is very common in Germany. These car parks can accommodate a couple of hundred vehicles. The intention is that urban and rural commuters will travel to a P&R location, park their vehicle on that site and travel the rest of their journey by public transport to their intended destination. This system minimises the number of vehicles driving directly into the centre of the city, thereby reducing traffic flow, noise, pollution, and fuel emissions. This makes the centre of the city a more pleasant environment for tourists and shoppers and also for residents.

Gigaliner Trucks for Long Haul Logistics

Depending on the availability and cost, cargo can be transported by airplane, ship, truck and/or train. A combination of multiple shipping solutions is also possible but this depends very much on the timeframe for goods. If goods are transported via trucks, there might be a clever way of dealing with this delivery by road. Long haul goods which have to be shipped more than 250 miles can be carried in so called "super liner", "gigaliner" or "giant" trucks. These trucks are longer and heavier, and therefore specifically designed for long distances. The maximum total weight of these giant trucks, which are 25.25 metres long, and is 60,000 kg. Two of these trucks can replace three ordinary long distance trucks due to a higher storage capacity. This makes the running costs of fuel, insurance, the number of qualified drivers required, and maintenance cheaper and therefore more competitive. Currently, there is only one section of the German motorway approved by the government which has a special license for testing these trucks on the motorway.

These gigaliner trucks are longer than regular trucks by as much as 7.5 metres and therefore more dangerous for overtaking, as they create a longer obstacle for any overtaking vehicle. One hundred trucks have been granted special permission in Germany for a trial period beginning in 2012 and ending in 2016 (Figure 6).

The aim of these trucks is to transport goods from the collection point to a central collection location close to the destination. These huge trucks are prohibited from driving inside the city and only designed for long haul journeys. At this central point, or "Umschlagepunkt", which is naturally located outside bigger cities, delivery goods can be reloaded to smaller vans and delivery trucks. Delivery to nearby places can be arranged with electric vans with few emissions coupled with shorter journeys.

Within the frame of the Logistics Action Plan, the European Commission is analysing the impacts of a potential introduction across the EU of Longer and Heavier Vehicles (LHVs), i.e. vehicles measuring up to 25.25 m and weighting up to 60 tons. Such vehicles are expected to improve the efficiency of the road freight sector but their impacts on the environment, infrastructure and safety need to be analysed in more depth. The present study aims at providing an overview of the technical aspects associated with LHVs regarding energy efficiency, infrastructure (road wear and bridges) and safety issues. This is carried out at vehicle level based on a comparison with standard 40t heavy duty vehicles (HDVs). Some technologies that can potentially improve the performance and reduce the damage caused by LHVs are described and issues that require further and detailed research are also identified (Leduc, 2009)

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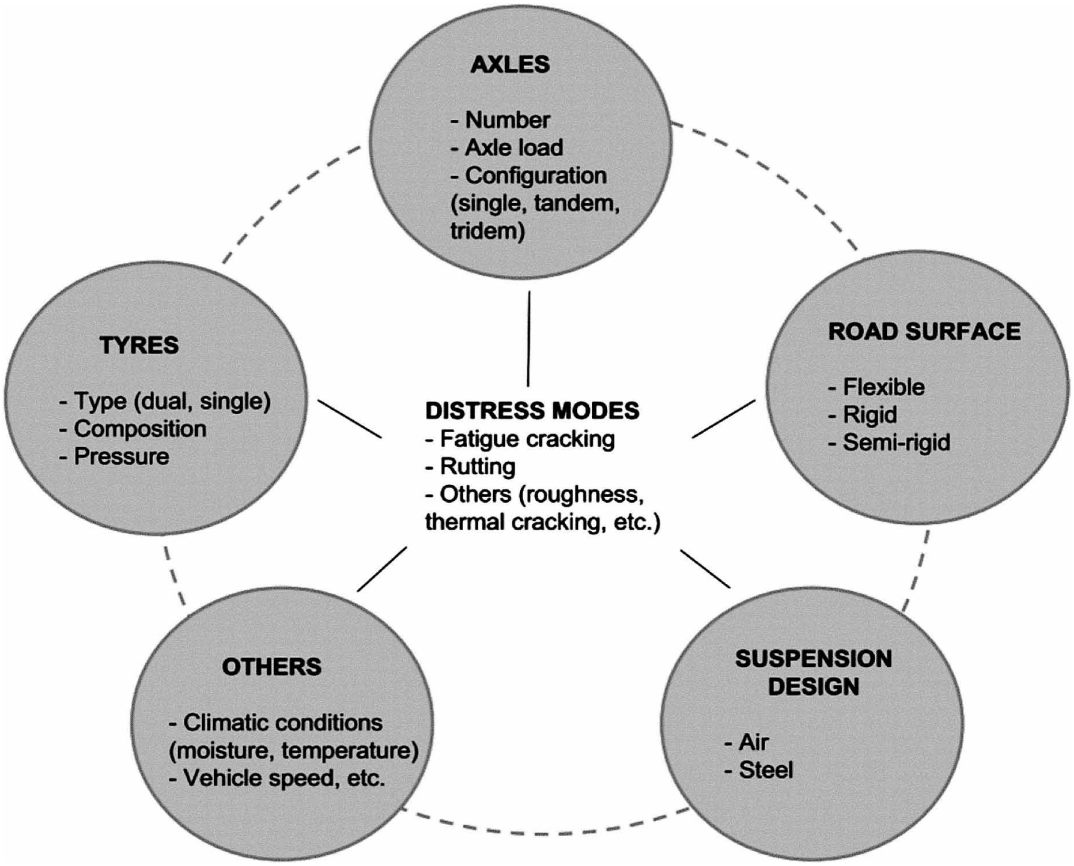
Figure 6. Gigaliner trucks
Source: (Leduc, 2009)



Tax Saver Commuting Ticket Scheme

Since 2000, Ireland has introduced a commuting tax saving scheme incentive for public transport, which can have a total tax saving for employees of up to 51%. This incentive reduces tax on the total gross income while travelling to work using a multi ticket valid for bus, train, Luas or ferry pass for one year from purchase.

Cycle to Work Scheme

The Irish government has also introduced a second incentive aimed at health conscious professionals and has found a unique advertising strategy for this incentive. The scheme is officially called "Burn Calories Instead of Emissions" which has proven popular over the last number of years. Any regular/electrified bicycle or Pedelec can be purchased up to a total value of €1,000 including safety equipment, with tax savings of up to 51% similar to the tax saver commuting ticket.

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Bicycle Rental from Multiple Points within a City

In various cities across Europe bicycle rental schemes are available. These schemes are very effective for tourist cyclists, enabling them to discover the city emission free. Cities usually have several bicycle hubs spread around the city centre, facilitating customers in collecting and dropping off bicycles whenever suits them. Any person can hire a bicycle for a day, three days or a full week depending on the user's requirements. In order to take a bicycle, the customer has to register at a hub, using a booking terminal while giving their credit card details as a deposit for security. This registration process normally takes less than 5 minutes and rental fees are in the region of €10 to €20 a day which is equivalent to $12 to $24. Those central hubs usually have more than 15 bicycles available and most cities offer a free app for mobile phones as well. These apps can show the nearest hub location for picking up or returning bicycles. This is a very attractive, environmentally friendly and healthy option for discovering a city with a great degree of flexibility. This has a big advantage in that cyclists can be flexible in their cycling trips with the option of not cycling back to their starting point if unable to do so.

Eco-Label Introduction in Pubs, Hotels and Restaurants

Pubs, bars and restaurants could introduce an eco-label showing customers their commitment to producing and sourcing sustainable food. Eastern located countries have already an embedded tradition of buying food and groceries from the local market. This reduces transportation emissions while avoiding unnecessary imports of food and also impacts positively on local employment. At the same time, it strengthens the local community and keeps money in the local economy. The idea is to reduce waste and packaging to a minimum, and this can then be displayed in the form of a certificate which will be issued annually.

All restaurant customers can see the benefits of using locally produced food for the same price and most customers would opt to frequent these particular restaurants. This in not only a marketing incentive, but also a sustainable way of sourcing local food with low packaging requirements, electricity coming from renewables, 80% of light bulbs fitted with energy Ratings of A, etc. (Commission, 2009). Achieving an eco-label is not easy and will take some time and effort but customers will certainly appreciate it. Spot checks and annual inspections are just one part of ensuring standards are met. There are several criteria that have to be achieved in getting this certification with a 34 point questionnaire. Depending on the size of the business, some smaller hotels need to fulfil 5 fewer points if they do not have a leisure centre/spa on their property.

Efficiency of Public Transport

Public transport also has to be affordable, efficient and convenient, making it easy for people to choose this form of commuting. Only an efficient and reliable transportation system can be attractive for customers, which means that expectations are set high. Affordability is also one of the major factors in decision making when choosing public transport. It goes without saying that reliability would be a number one priority. Affordability would be the second consideration in attracting customers followed by frequency of trains, buses, metros and so on. Comfort and modern layout would also be an optimum feature when choosing public transport systems. Modern technology like free Wi-Fi broadband on board will certainly attract business people on their way to work or on business trips.

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Incentivise Compressed Natural Gas and Biogas Powered Vehicles and Trucks

Compressed Natural Gas (CNG) powered vehicles have much fewer emissions when compared to petrol and diesel powered vehicles. The savings on emissions have been scientifically proven ranging from 12% up to 99% on carbon monoxide, carbon dioxide, soot, nitrogen oxide, hydrocarbon and sulphur. Biogas, when measured in kWh in comparison to fossil fuels, is also cheaper in almost all countries, is cleaner, and creates less engine noise and, in Germany, for example, road tax is lower due to lower emissions. Also quieter noise levels for early morning delivery vehicles is becoming increasingly popular in cities.

Low CO_2 Footprints for Packaging and Wrapping of Food/Goods

Low emissions with reduced oil rich packaging content for wrapping of goods is becoming important for many people. Therefore, companies using environmental eco wrapping need to focus on promoting the environmental benefits when advertising. Reducing emissions is even more important for multinational companies which need to show their efforts on their websites and inform people of how environmentally responsible they are (Figure 7).

Customers will naturally prefer a certain product if there is little or no price difference. This eco driven behaviour is good for the environment and certainly reflects an attitude change in Europe which has been noticed over the last number of years.

One of these multinational companies could be, for example, DHL. This company has a separate ordering section for environmentally connected customers who want to send a parcel emission free. This is good for the environment and is also good public relations. A CO_2 emission free parcel order has the advantage of a "feel good factor" for the consumer and helps the company in reducing their generated

Figure 7. Green logistics
Source: (Logistic cluster, 2015)

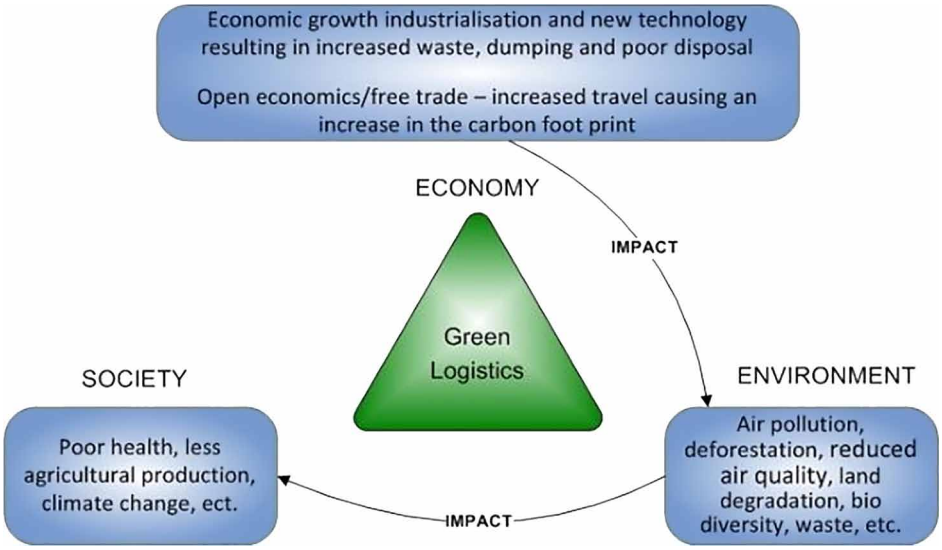

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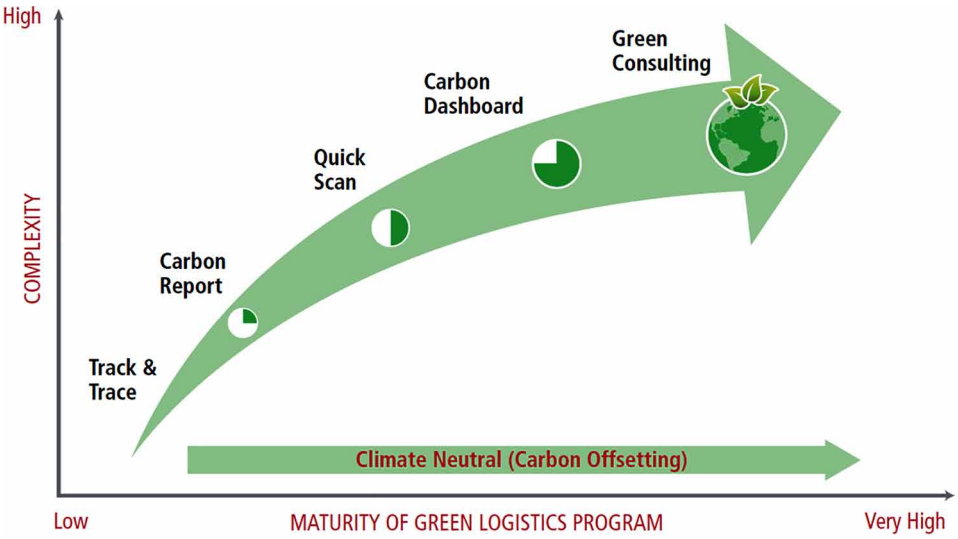
Figure 8. Maturity of Green Logistics Program
Source: (Department, 2014)



emissions. These "green logistic shippings" are a little bit costlier but in return the company is doing something to offset emissions like planting a tree, supporting a project in a third world country, etc. (Figure 8).

Automatic Waste Collection Notification

Waste bins should be fitted with weight sensors whilst transmitting a collection notification to the nearest waste provider when required. This technology would reduce unnecessary collection journeys picking up partially filled waste bins. This system has the potential to increase efficiency and subsequently reduce fuel consumption when applied to the waste collection fleet, including all waste, recycling, paper, and food waste collection bins. These intelligent systems are costlier than a regular waste bin but, with fewer collection intervals and greater fuel savings, this will have the advantage of recouping the higher investment cost very quickly. With the implementation of this technology, waste collection noise due to less frequent collections can reduce noise levels, which will also improve the quality of life for residents.

Soot Filters and Emission Limitations for Industrial Buildings in Germany

Air pollution in urban areas can cause health issues, and other associated problems. For that reason the German government has introduced a legislative law enforcement introducing tighter restrictions on particulate filters on vehicles and for industry. The automotive industry has developed particulate filters, first for petrol and later for diesel powered engines, and these have become much more effective in keeping these emissions trapped inside the particulate filter (Melkonyan D. A., 2012). The industry has also had to comply with legislation, which has improved the air quality in urban areas significantly. There are three major reasons for the improved air quality in industrialised areas. Firstly, the quality improvement was linked to very strict law enforcement. Secondly, the filter technology improved during

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research, with newer materials and better practical applications. Thirdly, an allowed "grace period" for industries concluded in the early 1980s, followed by lower emissions on a year by year basis (Figure 9) (Erste Verordnung zur Durchführung des BundesImmissionsschutzgesetzes - Verordnung über kleine und mittlere Feuerungsanlagen - 1.BImSchV, 2010).

Since the early 80s, soot filters installed at commercial premises have reduced smog levels significantly in Germany. The impact on coal and oil fired businesses for steel processing, aluminium smelting and major energy consumers was especially noticeable. This was due to cleaner air, fewer smog emissions and brighter days in cities, which also improved the health and quality of life of citizens.

District heating coming from power plants is also a very efficient way in using exhaust heat from incineration plants, for example. This heat has already been produced in burning waste which can then be used further in supplying heat via heat exchange to buildings. This heat is also known as by-product, which means that heat was produced during incineration which was subsequently consumed further via heat transfer. These are smart ways in using a by-product for something useful, making heating systems affordable.

Reduction of Emissions Coming from Vehicles are a Major Step Forward in Having a Cleaner City

Car manufacturers are also obliged to reduce their emissions, which has required more research on the engine efficiency of their cars over the last few decades. The European Economic Community as it was known at the time was initially formed by six industrial countries after the Second World War, namely Belgium, Germany, France, Italy, Luxembourg and the Netherlands, with more countries joining over

Figure 9. Steel industry in Qian City in North China
(Source: Spiegel online, 01.07.2015)

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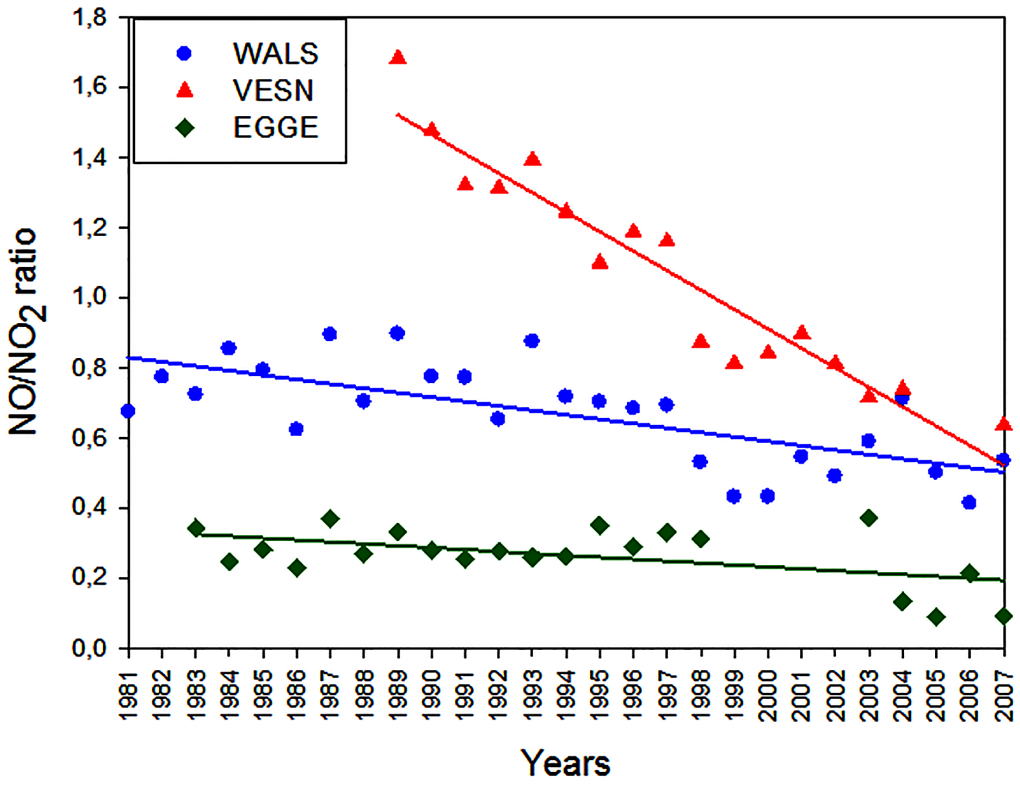
the years (Commission, Erst sechs, dann 28 - Europäische Nachbarschaftspolitik und Erweiterungsverhandlungen, 2015). At the moment there are 28 Member state partners in the EU (European Union). The EU members' medium term plan is that the proposed legislation will be agreed, with a universal regulation for all EU member states eventually in place. Since January 2015, heavy goods vehicles cannot be registered at the licencing office if they do not comply with the newest Euro particulate 6 norm. The same rule applies for vehicles below 2,610 kg in total weight but the deadline for those vehicles to comply was September 1st 2015 (Wolkenstein, 2014). The Euro 6 norm for diesel powered engines, known as the 715/2007/EC document, requires lower emissions of mg of NOx /km. Flexi-fuel vehicles with a bioethanol mix of 75% and more have different emission ratios as well as petrol powered vehicles (Industry, 2006). Emission ratios are measured in seven different categories, based on engine fuel requirements and vehicle type – for example, passenger cars, light duty vehicles, heavy duty vehicles, etc.

The impact of these stricter requirements is evident and can be seen in the chart below. Emission measurements from three different locations in the state of North Rhine Westphalia in Germany were taken over a time period of 26 years and accumulated accordingly. The three different colours and locations indicated in red (busy motorway), blue (industrial area) and green (local forest) suggest a very similar indication of emission reductions (Figure 10).

Emission levels within urban areas can fluctuate very much depending on time of day and day of week. The graph below illustrates that there is a noticeable NOx increase during mid-week which takes place between 5.00 and 8.00 a.m. This incline from low to peak can reach up to 250% from early morning

Figure 10. Yearly emissions emittance in Duisburg of NO/NO_2
Source: (Melkonyan D. H., 2015)



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emission levels. This emission chart represents the traffic frequency of vehicles on the road. The traffic participation is more distributed and, even on a Saturday and Sunday, traffic increased only slightly after 4.00 p.m. It can be concluded that weekend traffic behaviour is totally different to weekdays. Mid-week traffic is therefore mostly related to working commuters travelling to work in the morning and returning back home in the evening (Figures 11 and 12).

It needs to be highlighted that over the last 30 years high emission reductions have been possible even though vehicle registration numbers are increasing.

Green Logistics and Eco-Friendly Parcel Delivery

Major logistics companies have seen a huge opportunity in advertising their products with a green label. They are promoting their delivery of goods with a positive message, while at the same time the customer can trace back the produced emissions depending on the importance of the arrival time of ordered goods. DHL, for example, have a special section on their website informing customers on emission loading per delivery. If an express delivery within 24 hours has been selected, air freight is considered, which will increase emission factors by 3 to 10 times in comparison to trucks. The best and lowest emission delivery is by rail with a much lower emission ratio. So, in this case, the customer has the power in choosing emissions produced, depending solely on their delivery selection.

Figure 11. Hourly emissions of NOx in urban areas within one week
Source: (Melkonyan D. A., 2012)

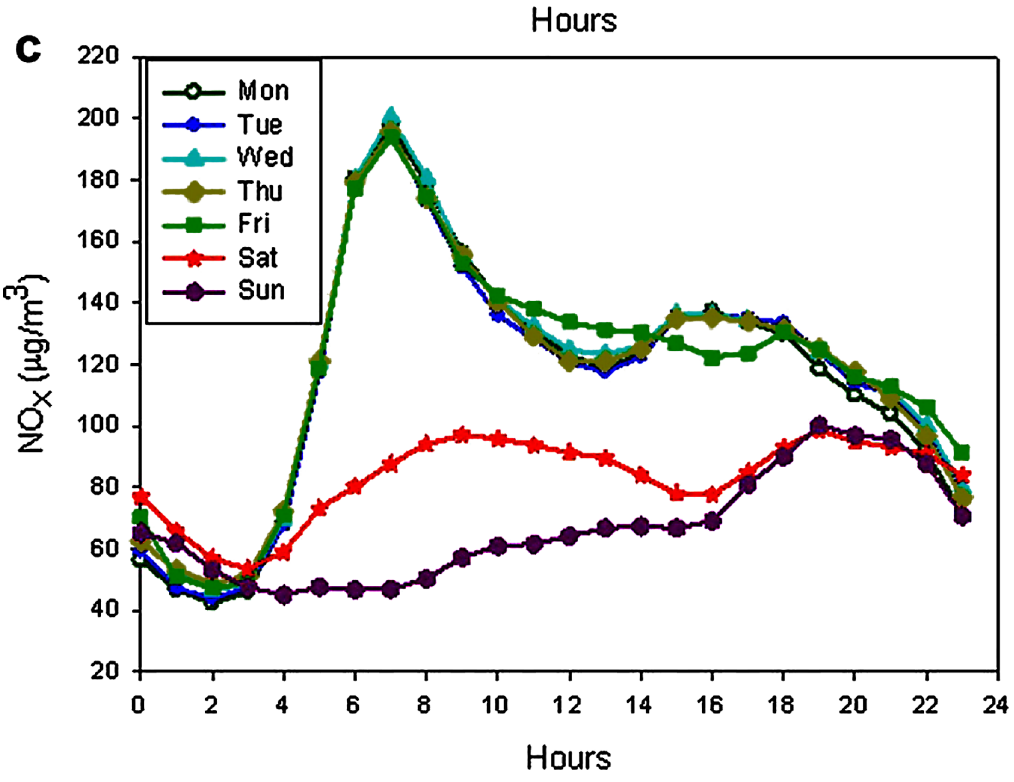

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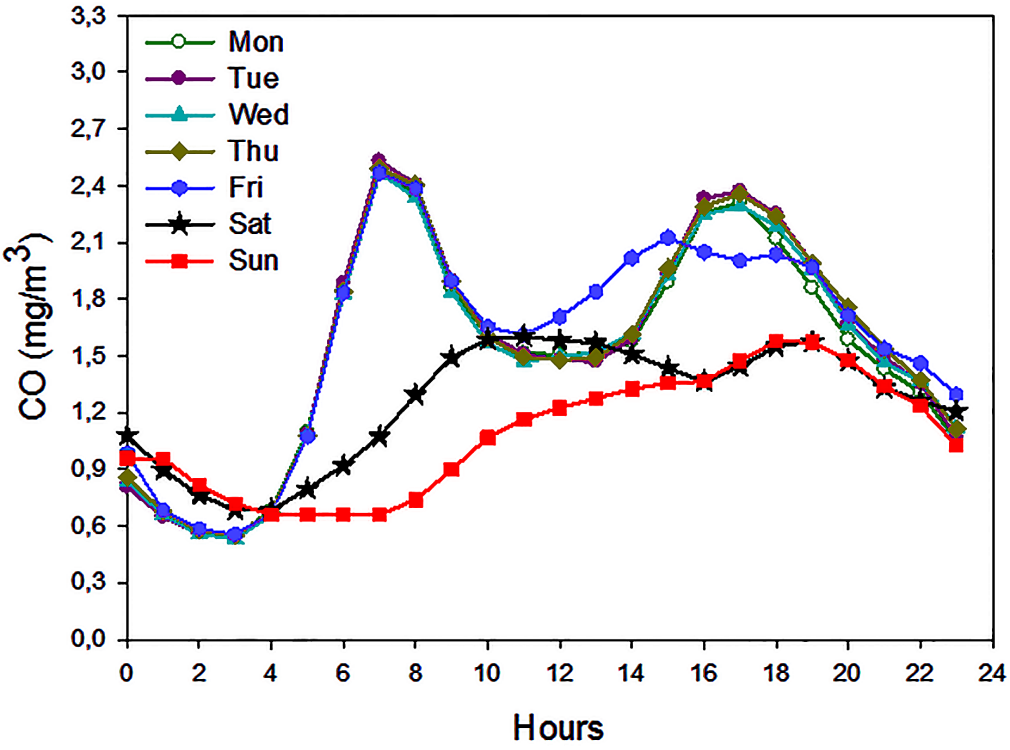
Figure 12. Hourly emissions of CO in urban areas within one week
Source: (Melkonyan D. A., 2012)



For even more environmentally oriented customers, DHL can offer an innovative CO_2 neutral product of delivery, due to the fact that they will reinvest money in projects offsetting those emissions produced. The delivery of these parcels are approx. 5% to 10% more expensive, but money will be reinvested in sustainable projects like wind turbine farms, tree planting, electric delivery vans, etc. Since its introduction, this idea looks as if it will have huge potential on a long term basis. If companies are using this type of service, they can also highlight their contribution in reducing emissions and therefore they can show this commitment to their own customers.

Green logistics are seen to be reducing emission impacts and action on the environment. The main activity in green logistics is coordination of activities within a supply chain in such a way that emissions are kept as low as possible. This all comes down to economics, which has an impact on low emission goods delivery, which can only be achieved in pre-planning routes in a very efficient way. In the past the haulage industry focused on having low running costs while making high profits. This business model has changed direction dramatically. Nowadays, customers are much more selective in picking delivery companies. The cost for air pollution, dumping waste and packaging costs, climate change contribution, soil degradation, noise, emissions and selective transportation methods now appears in the calculated cost.

Logistics need ICT - The use of the most modern information and communication technologies (ICT) plays a significant role in logistics: Information and communications technology became the trigger and guarantor for efficient solutions and processes. The internet of things and cyber physical systems are heralding another new era in logistics (Hompel, 2015).

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A Small City Powered with More Than 950 Environmentally Friendly Biogas Buses as a Leading Example

Malmö is a small city in the south-westerly part of Sweden with a population of close to 300,000. Due to its geographically advantageous location, Sweden has electricity production from hydro power. Because of this the electricity price in Sweden is very competitive. In spring 2015, Sweden had a surplus electricity production from hydro power, supplying their own and the European market as a whole with affordable electricity. This is one of the major reasons why Sweden is not producing electricity from biogas, opting instead for converting biogas as a fuel for their bus fleets. The first biogas production and upgrading process started in the early 90s. This decision was taken 20 years ago and made Sweden an expert in biogas conversion and usage in the transportation sector. Most other European countries are producing electricity from biogas which needs less treatment, is easier to handle, and involves no transportation and storage issues but, because Sweden already has ample production from hydro power, it is not financially worthwhile for them to convert biogas to electricity.

Skånetrafiken is the name of a district in Sweden which regulates the public transportation market, a semi-state organisation funded by the taxpayer in Skåne County, which is one of 25 counties in Sweden. This organisation does not have an active role in owning, maintaining or running these transport vehicles; its role is of a supervisory nature. At the moment there are 10 contractors operating approximately 950 buses of which 98% are biogas/natural gas and biodiesel buses, 5 electric buses and 20 ordinary diesel buses (Sörensson, 2015). The aim of this particular region is to have 100% environmentally friendly buses replacing natural gas and diesel buses with biogas and electric buses by 2020.

A new innovation has also been introduced – a hybrid bus which can carry more people using only one instead of two buses for popular routes and peak time compensation which is powered by biogas and electricity. This is a 24-meter hybrid CNG-electric bus, using regenerative braking power charging a battery which, when accelerated, produces electricity which can then be used to power the bus, which subsequently reflects positively on fuel consumption (Cody, 2009). This bus is able to carry up to 151 passengers and uses smart technology, saving electricity where available. The doors, for example, open only if passengers are pushing the door opening button and sophisticated software shows the bus driver's daily performance, fuel consumption ratios between recouping electricity by braking and biogas. The company is also able to trace back each individual driver's performance which can be easily measured and improved with training (Figure 13).

Delivery Restriction for Trucks within Malmö Which has a Huge Impact on Their Future Businesses

Malmö has even more ambitious plans for reducing traffic journeys from heavy goods vehicles by introducing a very strict enforcement for companies driving through the city. Several politicians and environmental groups are supportive of this idea. Currently they are working on how this can be implemented without impacting on business negatively. The premise of this proposal is that trucks will only be allowed to enter the city if their load storage capacity is greater than 90%. This would mean that several businesses would need to do a joined-up thinking in sharing one truck for different deliveries. This will reduce transportation movements which will also improve profitability due to there being fewer trucks in the fleet and more efficient delivery systems. Plans and proposals have been discussed and the system is currently under review.

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Figure 13. Van Hool ExquiCity 24 hybrid CNG-electric
Source: Own picture, 2015

Nowadays the Choice of an Environmentally Friendly Taxi is in the Customers' Power

Since 2010, Malmö central train station has a highly sophisticated taxi rank system in place. Customers can select their taxi of choice on a touch screen terminal, choosing the size – normal or multi-seater – and fuel type individually. On the display it will be shown if there are any taxies available and if not how long the estimated waiting time will be. Initially when this eco-friendly taxi initiative (Miljöbil) was introduced, it was more for promotional purposes and seen as experimental, but is now being readily accepted. It started off with a couple of eco powered taxies; which can be hybrid, gas, biodiesel, bioethanol or electric vehicles, but nowadays these taxies are the preferred choice for the majority of customers. This shows that consumer behaviour is changing, leading towards a more environmentally friendly focused future. Taxi fares for all choices are the same but the customer can clearly dictate their support for those requested services. Since the introduction of this system, customer choice has dictated that eco vehicles can, if offered for the same fare, be the preferred choice.

CO_2 Neutral Produced Electricity from Renewable Energy Sources

Electricity suppliers also have a large variety of environmentally supportive products that the consumer can select. In Germany, for example, there are more than 1,100 electricity providers competing with each other in offering the best possible deal for customers. Again, the consumer can select the production source of electricity coming from wind power generation, solar photovoltaic farms, hydro, geothermal, up to biogas produced electricity. Over the last decade, electricity production costs from renewable sources have gone down and are currently very competitive. In some cases, renewable energy production can be even more cost effective than nuclear and coal fired power plant production with the benefit of producing few or no emissions.

Some electricity providers can also indicate the location where electricity is produced. A mix of various renewable energy systems are also possible for those who do not care where the electricity comes from as long as it comes from a sustainably produced source. This enables ordinary customers who do not have the knowledge about this technology to select a good product from a climate friendly source.

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From this it is obvious that the customer has a large selection of choices and the power to make an active decision on emission production. According to an existing European law, all electricity providers need to show the CO_2 emissions produced per unit which is given in kWh. If electricity is produced from nuclear power this also has to be displayed as waste production measured in weight per produced kWh. Customers with a sustainable mindset can see on their monthly bill an indication of zero emissions produced. This positive message is a good motivator in supporting this type of industry for a similar price with the benefit of getting locally produced, clean, emission free electricity.

Energy Cities in Europe

Energy Cities, which is a trade mark, is operated by a European semi-state organisation based in Brussels. It has the aim of developing an existing or new city in a more sustainable, motivated environment. This presents the advantage of living in a more environmentally friendly area, with less pollution, more cycling lanes and electricity which is generated by a greater share of renewables. Water harvesting systems and waste water treatment plants are designed to use a limited amount of chemicals and work with natural plants like Norfolk water reed.

Since the unification of Europe more cities are representing themselves as eco cities offering a new way of sustainable living. "Energy Cities" was an initiative which was established more than 25 years ago, and has achieved great success, with astonishing participation rates. Since 2009 more than 6,000 city mayors have signed the "covenant of Mayors" and committed to go beyond the EU's CO_2 reduction target (Roumet, 2015). The principle behind this competition is to bring people together, sharing ideas, improving their living situations in the city, and learning from each other. There are several categories that any individual city can apply for, and nowadays more than 1,000 cities and local authorities from over 30 countries participate in this annual competition, highlighting their best show cases. Cities can be found on a "virtual" map, and it is possible to do searches for particular projects with associated contact details (Cities, 2015).

There is also promotional literature assisting cities and policy makers in preparing for these competitions. One particular document, "The big five", explains the five most important steps which are:

1. Include cities in energy policies and in international climate negotiations
2. Set new investment priorities to increase energy security
3. Use local resources to tap the full efficiency potential
4. Involve all actors to foster social innovation
5. Design future-proof cities with radical reduced energy needs

These guidelines are assisting cities – even with no previous knowledge of this innovation – to enter the competitions with the aim of fostering smarter living in their particular city.

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FUTURE RESEARCH DIRECTION

Taking into account all possible technologies and lifestyle choices that can make a difference, more research is this area is required. Future research should focus on the green economy and sustainability. Transportation of goods is also a very crucial factor when emission reduction is concerned. Every situation and circumstance is different; consequently, technology needs to be adapted to individual environments.

Discussion Section

This chapter predominantly deals with transportation systems and technologies. Every individual citizen can make a lifestyle choice even without actively doing something other than making positive selections. Decisions need to be made every day, but the crucial question is whether someone would sometimes like to go for a sustainable option for the same price as one that does not contribute positively to the environment.

Fuel and emissions pollution from transportation vehicles is unhealthy, noxious and not good for the environment. Therefore, every effort needs to be made in reducing those levels caused by traffic. Car-pooling, travelling by train instead of taking a short distance flight, cycling to the next bakery instead of taking the car, and electricity purchase from a local sustainable source are all choices we can make without huge sacrifices.

Older diesel engines are heavy polluters - Exhaust fumes from older diesel vehicles are the main source of fine particulate matter in cities. Some 1.7 million diesel cars in Austria are not equipped with particulate filters as standard, and older Lorries emit vast amounts of fine particulate matter. If the pollution levels in Vienna stayed below the WHO threshold for fine particulate matter (PM 2.5), people who are 30 years old today would live nine months longer. Living near busy roads causes a number of chronic diseases: One in three cases of coronary heart disease and one in four cases of chronic obstructive pulmonary disease in over 65-year-olds in Vienna can be attributed to traffic pollution (Gansterer, 2013).

CONCLUSION

All incentives need to be assessed carefully from a social, technical, political, and practical point of view with the objective of contributing towards a more environmentally friendly society as a whole. In order to complete these suggestions positively, a special project group should be in charge of coordination, implementation and project revision. It is also advisable to engage with communities during open days, theme days and workshops to include citizens in this project as much as possible. Support of those proposed improvements will only be visible if a high level of people engagement is present. These schemes should also have a deadline towards which all participants can work.

Education of young pupils and students in sustainable lifestyle choices is also vital. As mentioned in this section, there are feasible options without compromising lifestyle in any way. It is not a question of what we should do; what is more important is how we can do this without harming the environment.

Engineers and planners have the power to make changes in the city due to legislation and enforcement. There are so many showcases on a worldwide scale that some of these technologies can be introduced on a small trial basis and, when successfully completed, expanded on a national scale. A comprehensive

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framework for innovative strategies was emphasised to give the reader a more in-depth knowledge about various technology implementations across the world. Some improvements could be achieved within a couple of months while others need to be planned for a longer period.

This chapter as a whole has dealt with efficiency improvements in the transportation sector with the aim of reducing pollution from engine fuel emissions. It can be seen that, in order for this change to come about, behaviour and urban planning changes rather than financial input are required. Sometimes it is easier to achieve a solution if the solution required is financial rather than one requiring a radical change in behaviours and attitudes. However, in order to see progress in this area, urban planners and city councils will have to be open minded and proactive in relation to a different way of urban planning. It is probable that the expected increase in migration towards cities will force planners to consider alternative solutions for reducing urban waste and pollution.

The aim for this chapter was to cover all important areas of environmental reduction impacts, ranging from modern transportation systems, emission reduction of industries, residential heat and electricity production coming from renewables, tax incentives for eco vehicles, car sharing options and eco-label introductions for restaurants to smart building designs. These efficiency proposals cover a vast range but they have already been introduced by all participating cities successfully. It has been observed that, once transition has taken place gradually, moving away from petrochemical fuels towards more sustainable alternative solutions like hydrogen, electricity and biogas powered vehicles, subsequent consumer behaviour can have a positive impact in emission reductions. This has the effect of enriching air quality. With only limited fuel and energy resources available, every positive impact can help improve environmental quality and help conserve precious natural resources on this planet.

ACKNOWLEDGMENT

Conversion factors can be found in the book “Measure for measure: the story of imperial, metrics and other units” ISBN: 0-8018-7072-0, Maryland, The John Hopkins University Press, 2003.

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KEY TERMS AND DEFINITIONS

Eco-Society: A cultural driven society, focusing on environmental, efficient and health orientated civilisation.

Gigaliner: A haulage truck that is specially designed for long haul journeys with a total length of 25.25 metres and weighing up to 60 tons. These trucks are only allowed on specialised licensed motorway sections for a trial period until 2016.

Green Economy: Buildings and infrastructure are designed to be environmentally friendly and economically sustainable, made up from local sources and alternative biofuels.

Logistical Urban Central Hubs: Can be used for parcel delivery for distances of less than 5 miles, whereby the delivery vehicle will be electrically powered.

Semi-Central Urban Hubs: Logistics centres designed for short haul deliveries within a 20 mile20-mile radius of their customers.

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Smart City: Sophisticated, well designed and efficient living environment within a highly densely populated city.

Smart Traffic Light Systems: This is a new technology suitable for infrequent traffic, whereby traffic lights are controlled by sensors switching lights, depending on traffic flow.

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Chapter 73
Human Overpopulation and Water Pollution:
Reduction of Microbial Pollution by Vertical Flow Constructed Wetland

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ABSTRACT

The increased human population is threatening the natural water resources by reducing flows and deteriorating quality. High levels contamination of fecal microbes in Indian water resources is one of the worst impact on natural environment. The incomplete sewage treatment in existing STPs is the root cause it, along with disposal of untreated sewage. Fecal microbes even after the secondary treatment demands the further reduction, hence, an alternative method of vertical flow constructed wetland was adopted to examine the efficiency of the system. The study was aimed to primarily to suggest the suitability and comparative performance of wetland species, P. australis and C. indica. Study revealed the importance of fibrous rooting system of C. indica which helps to enhance aerobicity within the system and cause the reduced number of microbes. The additive enhancement of physical mechanism as well as competition among microflora within the wetland system and excretions from roots of C. indica plant might have been the reason of the significant highest removal of microbial indicators.

INTRODUCTION

The water demand supply gap is increasing continuously due to population explosion and alternate source of water are being explored to fill this gap. Reuse of treated effluents for non-potable purposes could significantly reduce this gap, as huge volume of wastewater is being generated and treated in urban metros and class II cities, but the incomplete treatment in STPs is polluting the existing water resources and thus

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high level of coliforms were found during monitoring of various rivers' water quality in India (Jamwal & Mittal, 2009; CPHEEO, 2013). Coliforms levels has been even reported in groundwater aquifers, considered generally safe which are being used directly for potable water in areas around Delhi (Mutiyar et al., 2013). In Rajasthan, where the study was performed, the general trend for treated wastewater disposal has been either for irrigation purposes or into recreational lakes as there are not many rivers around. Since, with both these reuse applications, public health is at risk due to presence of microbial contaminants, there is a need to find solution to mitigate this risk and the importance of studying microbial removal as tertiary treatment. Hence, this research was classified as "Applied research" that often comes from a practical need to know or find a possible solution to a real world problem with real world challenges.

The idea behind this research was to find an applicable solution for the reuse of treated wastewater within the existing semi-arid weather conditions to overcome the public health risk of abovementioned reuses. The wetlands have been reported to be efficient in terms of microbiological contaminants removal though no such study has been reported for investigating as well as comparing the survival of different plants, which were used for the study, in treated wastewater during tertiary treatment in semi-arid climatic conditions prevailing in Rajasthan with their performance vis-a-vis microbial reduction. Additionally, the cities are now expanding as a part of growing urbanization, the wastewater plants have now come within the city limits and high land demand for horizontal flow wetlands is becoming a constrain for application of wetlands in sewage treatment. To reduce the land requirement in wetlands, therefore the vertical flow constructed wetland system, which requires less land area, as a tertiary treatment step and to assess its suitability especially with a focus on microbiological contaminants was chosen for the study.

EXPERIMENTAL

Experimental Setup

Experimental setup was established at Civil Engineering Department, Malviya National Institute of Technology, Jaipur, India. The experiments were performed for 25 weeks during the months of November to April, followed by the acclimatization period of 12 weeks and then by physico-chemical analysis of 13 weeks. The historical average minimum and maximum temperatures during April are 21.8°C and 37.2°C, respectively, which is suitable for the plants growth - optimum temperature for growth of *Phragmites australis* is 30-35°C, for *Canna indica* is 12-32°C and for *Typha latifolia* is ~35°C. Four CW units were constructed using sintex tanks made up of polypropylene material, having dimensions 29 cm×25 cm×70 cm and has approx. 55 cm of packed bedding with an empty space of 2-5 cm at the top for aeration purpose. Initially, only three units, UN-ph, UN-cn and UN-ct, were constructed which were similar in terms of bed media configuration but different in terms of plantation (Figure 1a). After identifying that the unit planted with *Canna* (UN-cn) was more efficient than the other two units, the next objective was to further explore if the removal efficiency of this unit can be improved by improvising on the media. Hence, a layer of finer material (sand) was introduced in the system. In order to maintain the total height of the system as earlier in initial three units, after introduction of the sand layer the thickness of the coarse bottom gravels (16-20mm) was decreased from 29.2cm to 15cm (Figure 1b). It was considered necessary to keep the gravel layer for supporting the sand layer and also as a barrier between influent system and sand. The complete removal of gravels would have had operational challenges. Among the coarse (16-20mm) and finer (8-12mm) gravels layer, the coarse layer was reduced

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for a smooth gradation from finer to coarse material considering efficiency has been positively affected by the finer material. Figure 1 shows the transverse section of media distribution for all four CW units and Table 1 gives the detailed design configuration of the experimental set up for all the CW units. All plantations were allowed to acclimatize for about two to three months (13 weeks) before the experimental analysis starts. After the acclimatization stage, units were allowed to run for 38 weeks continuously with a constant flow rate of 6.8lt/day. The microbial analysis was performed for 25 weeks out of 38 weeks, while rest was performed for physico-chemical analysis.

Study Site and Flow Distribution

The secondary treated wastewater was sourced from the sewage treatment plant located in south Jaipur throughout the study period. The effluent from the field was brought to ensure actual effluent quality

Figure 1. Transverse cross section of two different types of constructed wetland units (a) Distribution of media for UN-ph, UN-cn and UN-ct (b) Distribution of media in UN-cn-sd

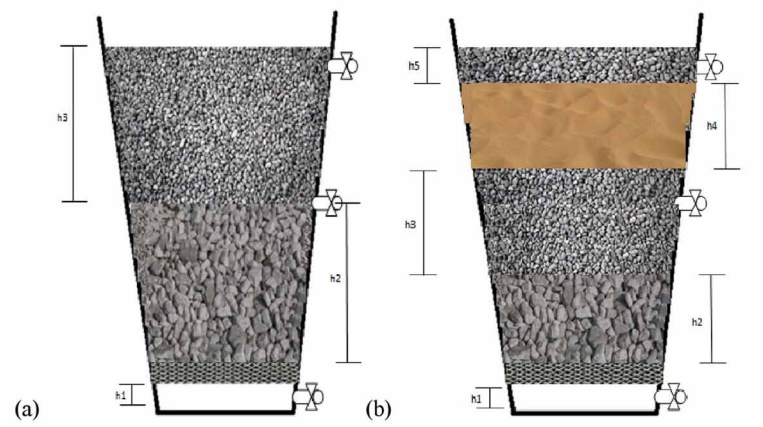

Table 1. Design configuration of experimental setup

Constructed Wetland Unit	Height and Type of Media				
	H1	**H2**	**H3**	**H4**	**H5**
UN-ph Planted with *Phragmites australis*	Inlet chamber	Media – Gravel Size - 16-20mm Height - 29.2cm	Media – Gravel Size - 8-12mm Height - 22.9cm	-	-
UN-cn Planted with *Canna indica*	Inlet chamber	Media – Gravel Size - 16-20mm Height - 29.2cm	Media – Gravel Size - 8-12mm Height - 22.9cm	-	-
UN-ct Control unit No plantation	Inlet chamber	Media – Gravel Size - 16-20mm Height - 29.2cm	Media – Gravel Size - 8-12mm Height - 22.9cm	-	-
UN-cn-sd Planted with *Canna indica* with sand layer	Inlet chamber	Media – Gravel Size - 16-20mm Height - 15cm	Media – Gravel Size - 8-12mm Height - 25cm	Media – Sand Size - 1-2mm Height - 15cm	Media – Gravel Size - 8-12mm Height - 1-2cm

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of STPs. So, to maintain the actual conditions for the study, the treated sewage was carried every third day to the study site, it was finally kept in a feeding tank of 100 liters capacity and used to feed all the connected CW units. Each treatment unit was separately connected to the feeding tank via peristaltic pump (Make: Enertech-ENPD victor 100; range: 0.3 - 450 ml per minute) and silicon piping of 2 mm inner diameter and 4 mm outer diameter.

A steel sieve was kept at 12 cm (H1) above from the bottom in each of the treatment unit, to separate the inlet chamber from treatment bed which also helps in uniform distribution of water throughout the treatment bed (Figure 1). The treated wastewater first flows into the inlet chamber via inlet valve, then rises upwards to the treatment bed to allow for continuous flow and is finally collected from outlet ports.

Sampling and Analysis

Sampling frequency was twice in a week wherein the time difference between the inlet and outlet sample according to the HRT of 2-3 days for every week. The influent samples were collected from inlet port located at the bottom and the effluent samples were collected from the outlet ports placed at the top of the units where the treated water flows out. Further, to confirm the role of finer material (sand) in the microbial removal in UN-cn-sd, the unit with sand was further analysed at middle point. Water samples of approximately 100ml were collected from influent and effluent to evaluate the performance of constructed wetland units. The sample collection was made using acid pre-washed PVC bottles and prepared by sterilization through autoclave before each sampling. For microbiological analysis, two species - *Total coliform* (being the most common indicator) and *Fecal streptococci* (more resistant to environmental stress and known as secondary indicator) were used. Such analysis of indicators organisms was performed using multiple-tube fermentation according to the method given in APHA (1998; 9221B and 9330B) within 2 hours of sampling.

The concentrations of microbial species were observed as MPN (most probable number) per 100 milliliters (MPN/100ml) according to the table 9221: IV in APHA 1998. Such MPN values were converted to log scale. The performance efficiency of the proposed system was calculated in terms of concentration removal observed for all parameters.

The log removal for microbial removal was calculated as: $\log_{10}(Ci) - \log_{10}(Co)$, where Ci and Co represent the influent pathogen concentration and effluent pathogen concentration, respectively.

Further, a statistical analysis was performed using two tailed t-test to determine the significance level at $p<0.05$ for different sets of experimental data.

RESULTS AND DISCUSSION

Removal of Microbial Indicators

Mean influent concentrations of *Total coliform* and *Fecal streptococci* were observed to be 5.49 and 4.87 log MPN/100ml, respectively. The mean effluent concentrations of these microbial species are presented in the Figures 2 and 3. Accordingly, the mean log removal from UN-ph was 1.01 and 1.01 log units, from UN-cn was 1.87, and 1.82 log units, and from UN-ct was 1.24 and 1.03 log units for *Total coliform* and *Fecal streptococci,* respectively. Interestingly, since the UN-cn-sd was designed as an improved system, showed the minimum mean outlet concentrations of indicator species (*Total coliform*

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Figure 2. Comparative insight of mean influent and effluent concentrations (logMPN/100ml) for the Total coliform from all four treatment units

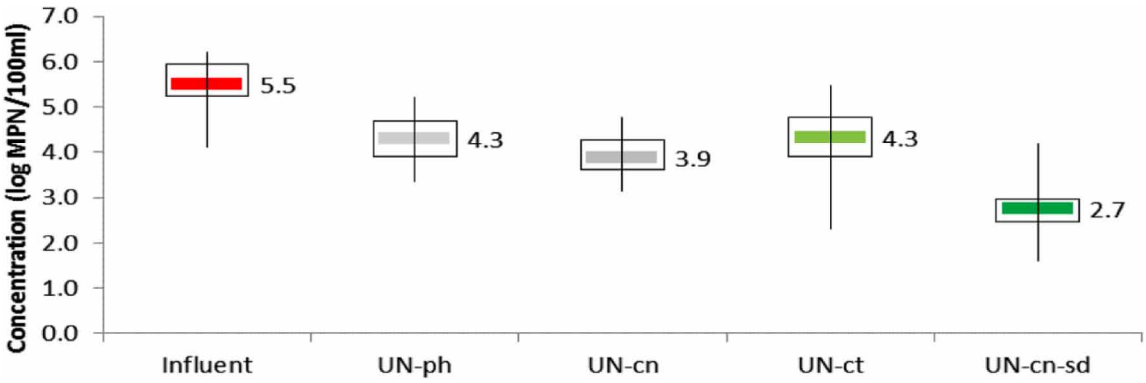
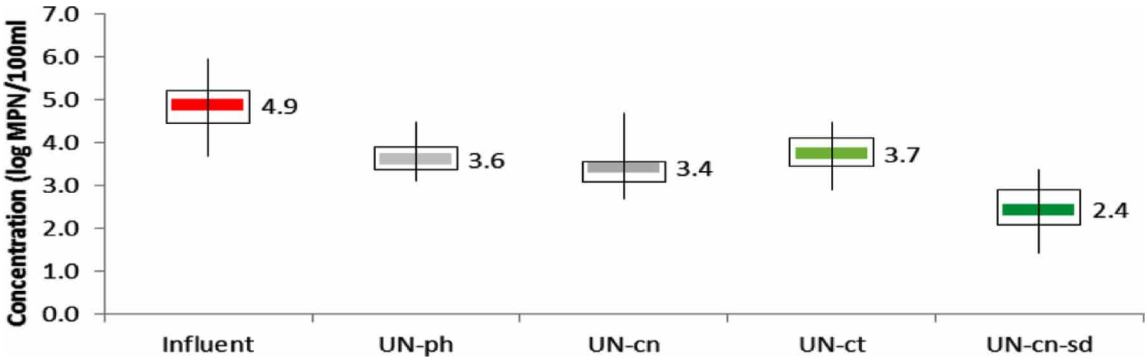


Figure 3. Comparative insight of mean influent and effluent concentrations (logMPN/100ml) for the Fecal streptococci from all four treatment units



and *Fecal streptococci*) were observed in the effluent from UN-cn-sd as depicted in Figure 2 and 3. The log removal from the UN-cn-sd unit is found to be highest with 3.01and 2.80 log units for *Total coliform* and *Fecal streptococci,* respectively. These results revealed that the maximum log removal of indicators from UN-cn-sd followed by UN-cn, UN-ct and UN-ph, in decreasing order.

The removal of *Total coliform* from the *Canna* planted units, UN-cn (1.87 log units) and UN-cn-sd (3.01 log units), were found to be comparatively higher than the removal of 1.52 log units observed in the study by Gersberg et al. (1989) wherein *Scirpus* was used in planted wetland for treating secondary treated effluent. Such observed removal efficiency of UN-cn and UN-cn-sd in the proposed study, were also found to be higher than 0.7-1.5 log unit observed during the study by Arias et al. (2003). However, the study suggested by Garcia et al. (2003) found higher removal of microbial indicators while using finer media in horizontal constructed wetland that agreements the use of Un-cn-sd. Such comparisons support the higher removal efficiency of microbial contaminants from unit UN-cn-sd containing finer material (sand) as compared to the other units with coarser media. Also, the mean removal of *Total coliform* from the unit UN-cn-sd (3.01 log units) lies in the range of 2.7-4.7 log units as observed in the

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study by Kadam et al. (2008), where domestic wastewater was treated through vertical flow constructed wetland. And, the removal of *Fecal streptococci* from the same unit UN-cn-sd (2.80 log units) was found to be higher than the range suggested by the author (1.7-2.5 log units).

Influent-Effluent Distribution During Treatment

Figure 4 and 5 are percentile curves, showing distributions of concentrations during the study period, clearly indicates that all the treatment units are significantly efficient in removal of the targeted indicator species from the secondary treated wastewater. The curves shown in Figure 4 clearly show that UN-cn is more efficient than UN-ph and UN-ct for removal of *Total coliform*, wherein the curves of UN-ph and UN-ct was close to each other. Interestingly, the curve for UN-cn-sd stood separately and shows that 90% of the observed effluent concentrations fall within the WHO recommended standard of 1000MPN/100ml (3logMPN/100ml). The mean *Total coliform* concentration in the effluent from UN-cn-sd was found to be 2.75logMPN/100ml whereas the 90th percentile concentration value was found to be 3.03logMPN/100ml. The almost same was observed for *Fecal streptococci,* where its 90% of the observed concentrations fall below the concentration of 2.90logMPN/100ml (Figure 5). These curves confirm the high removal efficiency of coliform as well as *Fecal streptococci* numbers from the secondary treated wastewater for the unit UN-cn-sd. However, the same pattern was observed for both of the indicators but the curves for *Fecal streptococci* were sturdier (less varying) than the curves observed for *Total coliform* which shows that *Fecal streptococci* is more resistant to the changing environmental conditions prevailing within the system.

Statistical Analysis

The results drawn above for both, *Total coliform* as well as *Fecal streptococci*, are also supported by the statistical analysis of the experimental results, where significant difference was found between removal from the units UN-ph and UN-cn but the difference between removal from UN-ph and UN-ct were found to be statistically non-significant. These results indicate that the presence of *Phragmites australis* have negligible impact whereas the presence of *Canna indica* is of significant importance for deciding the

Figure 4. Percentile curves for Total coliform concentration (logMPN/100ml) in influent and effluents from four constructed wetland units

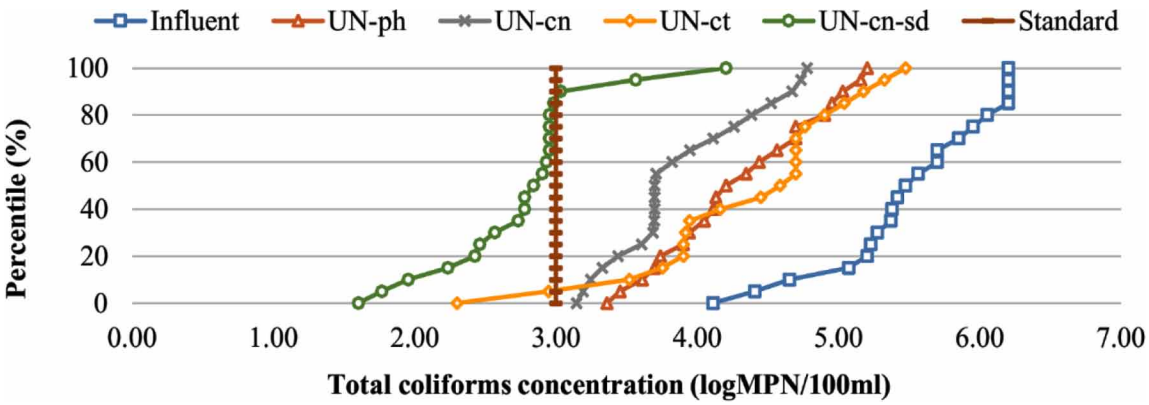

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Figure 5. Percentile curves for Fecal streptococci concentration (logMPN/100ml) in influent and effluents from four constructed wetland units

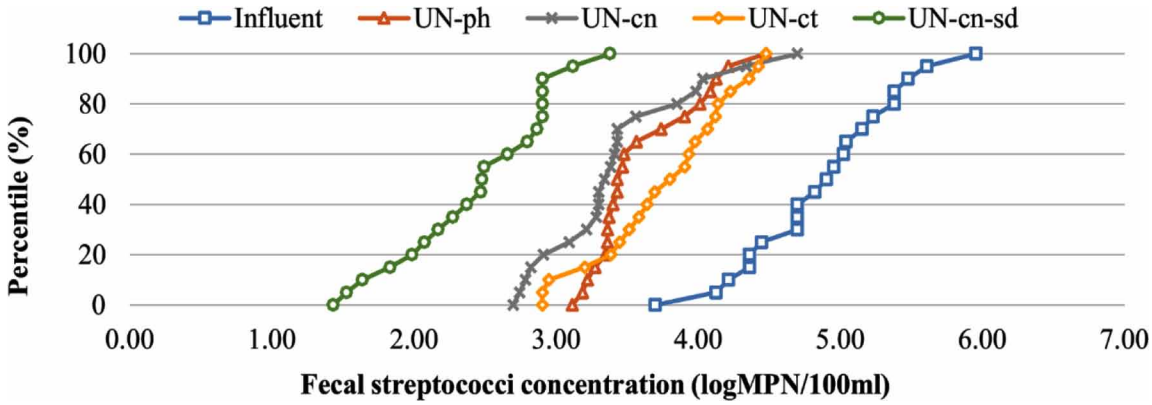

Table 2. Difference in performances of different units estimated by statistical analysis using t-test at significance level of p-value<0.05 between removal efficiencies of various microbial contaminants

Units Parameters	TC	FS
UN-ph vs UN-cn	S	S
UN-ph vs UN-ct	N	N
UN-ph vs UN-cn-sd	S	S
UN-cn vs UN-ct	S	S
UN-cn vs UN-cn-sd	S	S
UN-ct vs UN-cn-sd	S	S

*S = significant difference, N= non-significant di9fference

fate of indicator organisms. Furthermore, the significant difference was observed between the removal from UN-cn-sd as compared to UN-ph, UN-cn and UN-ct, finally confirms the result of highest efficiency from UN-cn-sd for these two indicator species, *Total coliform* and *Fecal streptococci* (Table 2).

Analysis of UN-cn-sd for Indicator Organisms: Middle Point Analysis

The Un-cn-sd unit was also studied via middle point along with sampling at inlet and outlet points to know the effect of finer material sand on microbial removal efficiency in different zones. The transverse cross-section of the wetland unit UN-cn-sd shows that below the middle point, a layer of smaller sized (8-12mm) gravels was placed above the larger sized (16-20mm) gravels, such that the smaller sized gravels accounts for only 30% of the total area from inlet to middle point. Whereas above the middle point smaller sized (8-12mm) gravels and finer material sand (1-2mm) occupy the total area. Figure 6 and 7 present the varied concentration of *Total coliform* and *Fecal streptococci* during the monitoring period at inlet, middle and outlet points of the wetland unit. The observed mean concentrations for *Total coliform* were 5.36, 4.89 and 2.72 log MPN/100ml, respectively, and for *Fecal streptococci* are 4.40, 4.13

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Figure 6. Concentration of Total coliform (log MPN/100ml) at inlet, middle and outlet points of UN-cn-sd during the monitoring period

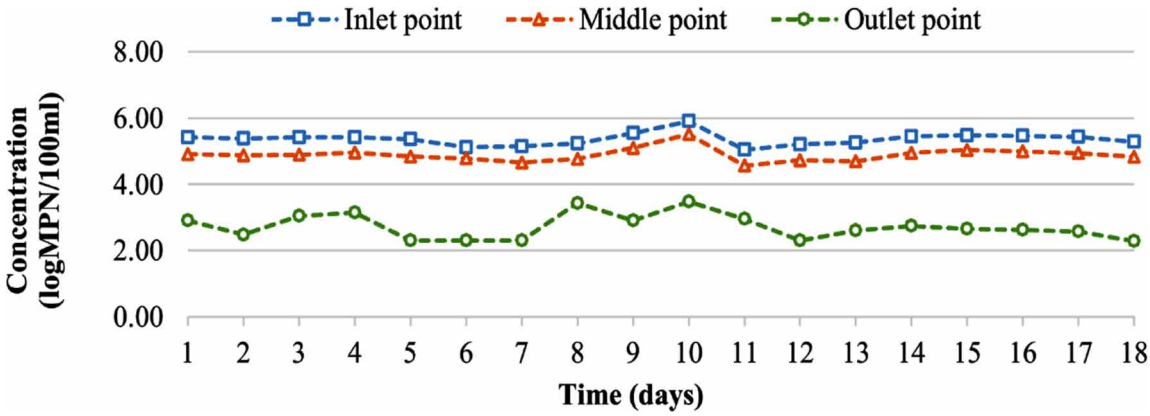
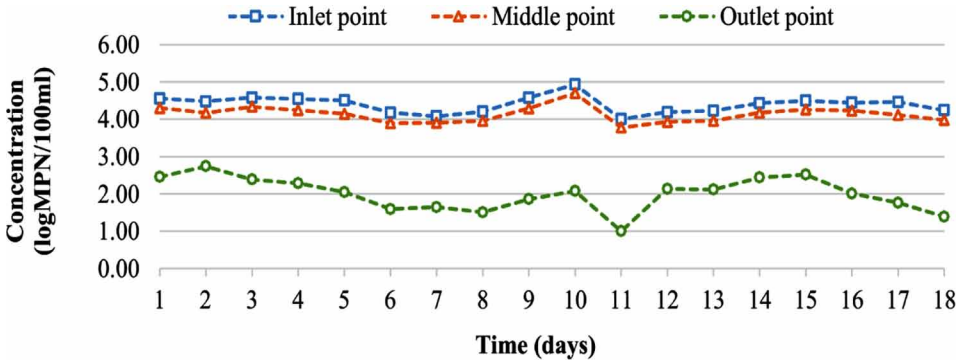


Figure 7. Concentration of Fecal streptococci (log MPN/100ml) at inlet, middle and outlet points of UN-cn-sd during the monitoring period



and 2.00 log MPN/100ml at inlet, middle and outlet points of the unit, respectively. Mean log removals for *Total coliform* were 0.48 and 2.64 and for *Fecal streptococci* were 0.27 and 2.40 from middle and end points, respectively. Significantly lower outlet concentrations were observed from the outlet point as compared to the middle point. Such concentration distributions reveal that the incorporation of finer material sand greatly improves the performance of the wetland unit.

Removal Mechanism of Microbial Species

The high performance of *Canna indica* planted unit UN-cn is related to its higher capacity of phytoremediation and to its fibrous rooting system which has capability of high root zone aeration, larger root surface area and high root numbers (Wenyin et al. 2007; Zhang et al. 2007; Bose et al. 2008). The increased root surface area helps to enhance the physical mechanisms such as:

- Aggregation,

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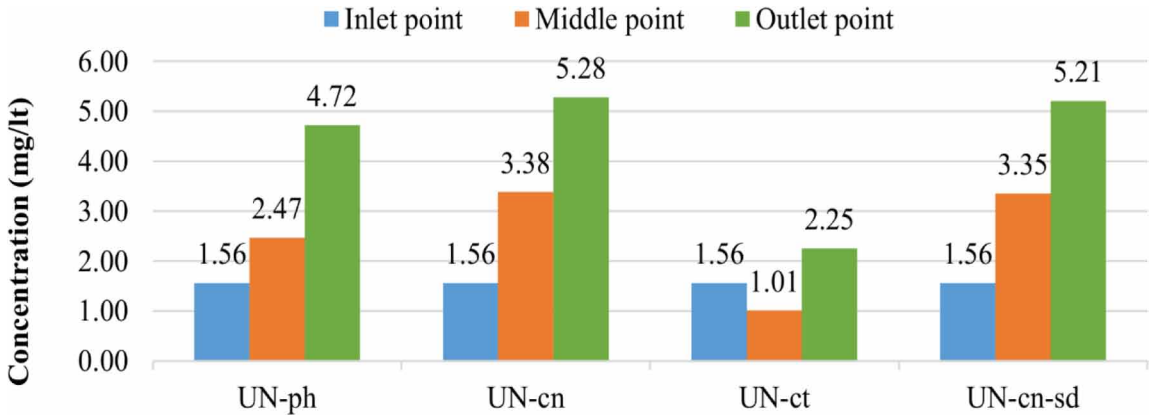
- Adsorption,
- Oxidation,
- Sedimentation,
- Filtration,
- Solar irradiation,
- Straining, and also increases the possibilities of natural death and predation for microbial removal (Gersberg et al. 1989; Williams et al. 1995; Quinonez-Diaz et al., 2001; Stott et al., 2001; Pundsack et al., 2001; Karim et al., 2004; Stevik et al., 2004; Auset et al., 2005).

The major removal of microbes could be occurred due to the release of antimicrobial extract, especially from the rhizomatic part of the plant *Canna indica* (Abdullah et al. 2012; Gaur et al. 2014). The increased surface area along with the enhanced physical mechanisms lead to increased active sites for biochemical reactions to happen and increased area for development of bio-film within the treatment bed. And, in this way, the performance efficiency of the treatment bed is essentially effected by the microbial community present within the bed since the removal of contaminants from wastewater are majorly mediated by microbial activities (Reddy, 1983).

The performance efficiency of wetland systems can also be correlated with the concentration of dissolved oxygen (DO) in the wetland environment; increased bacterial die-off due to increased dissolved oxygen has been already discussed earlier in reported studies (Pearson et al., 1987; Fernandez et al., 1992). The removal mechanism in oxygenic environment is dominated by surface destruction of microbes through oxidation leading to the reduction of oxygen sensitive bacteria (Gross et al., 2007). This effect was dominantly observed for indicator microbial species in the proposed study throughout the monitoring period. As per the results of the study shown in Figure 8, higher DO values were observed throughout the treatment bed of *Canna* planted unit, UN-cn as compared to the units UN-ph and UN-ct. This could be due to the high aeration capacity of *Canna indica* roots which create an unfavorable environment for the microbial population and thus leading to higher removal efficiency of microbial contaminants. The high removal efficiency due to high aeration in planted filters is also suggested by Decamp et al. (1999).

Figure 8. Mean dissolved oxygen (DO) concentrations in mg/l observed for four constructed wetland units at middle and outlet points



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The lowest DO values were observed at the middle and outlet points of the unplanted control unit UN-ct, which proves the significance of vegetation in creating an oxygenated environment suitable for higher removal of microbial species. The low DO values in UN-ct is in accordance with the design characteristic of up-flow constructed wetland which have aerobicity at the top followed by anoxic environment at the bottom (Ong et al., 2009; Ghosh and Gopal, 2010). So, the low removal of indicator species from UN-ct might be related to the low concentration of dissolved oxygen for their survival. A deviation from the above discussion was found when it was observed that the planted unit UN-ph, although having a higher DO concentration as compared to the control unit UN-ct, showed lower performance in terms of removal of indicator organisms. This is in agreement with the previously reported studies by Hench et al. (2003) and Vacca et al. (2005). This could be justified through the observation by Torrens et al. (2009), who stated that the presence of *Phragmites australis* could be of less significance in vertical flow wetland as compared to the horizontal flow. The probable reason given for the decreased removal from vegetated wetland as compared to the un-vegetated unit was the presence of enteric bacteria and other competing bacteria, as a part of the rhizosphere communities, around the exudates of *Phragmites australis* (Axelrood et al., 1996; Pierson and Pierson, 1996).

Improved Performance Efficiency of UN-cn-sd Over UN-cn

The higher removal efficiency of UN-cn-sd over UN-cn can be related to the additional benefits provided through the inclusion of sand layer and more gradation of the media layers in the constructed wetland unit. The inclusion of sand layer helps to maintain the moisture content required for rhizosphere and subsequently increases the contact time between water and treatment bed within the system. The incorporation of sand layer significantly enhances the advantages related to the higher root surface area of *Canna indica* discussed earlier, i.e. enhanced physical mechanisms (aggregation, adsorption, oxidation, sedimentation, filtration, solar irradiation, straining), increased possibilities of natural death and predation for microbial removal, increased active sites for biochemical reactions to happen and increased area for development of bio-film within the treatment bed. The whole system functions in order to provide good aeration and removal of enteric microorganism's sensitive to high concentration of oxygen. The bacterial removal is maximized by the physical mechanisms like retention (filtration/ adsorption) and natural death (Ellis &McCalla, 1976; Reddy et al., 1981; Crane & Moore, 1984). Thus, the systematic increment in the favorable conditions for the removal of microbial contaminants in UN-cn-sd, along with the basic properties of UN-cn, makes it possible to achieve the high removal efficiency of the whole treatment system. Figure 9 clearly indicates that the log removal from Un-cn-sd increased from UN-cn by an amount of 60%, 54% and 45% for *Total coliform, Fecal streptococci* and *Salmonella typhi*, respectively. The results obtained are also in good agreement with studies reported by Vacca et al., (2005) and Sleytr et al., (2007) and are favorable when compared with the study given by Torrens et al. (2007), where less than 2 log unit bacterial removal was observed. Such studies favor the incorporation of sand layer, as a good choice of finer material within the wetland treatment beds, in order to enhance the adherence of microbes; Sleytr et al., (2007) also reported high concentrations of microbes in sediments of sand layer.

As far as the final effluent concentration of *Total coliform* is of concern, UN-cn-sd was the only unit capable of bringing down the concentration within the prescribed WHO standard limit for safe disposal into water streams; WHO limit is 3 logMPN/100ml and UN-cn-sd achieved 2.75 logMPN/100ml. The results related to UN-cn-sd suggests that it is highly efficient for the removal of all three microbial species. The above evaluation of results favors the suitability of *Canna indica* being used with sand media

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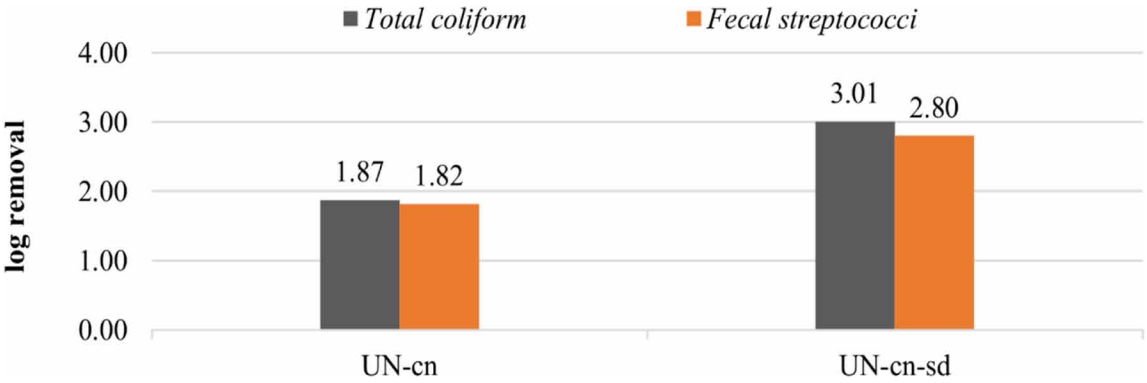
Figure 9. Comparative insight for improved efficiency of Canna indica planted units by incorporation of finer media sand



in vertical flow constructed wetland for post treatment of secondary treated wastewater in semi-arid climatic conditions prevailing in the region of Rajasthan, India. In such climatic conditions a compact and well-designed vertical up-flow constructed wetland unit, constituting fine material sand along with the coarse material gravel, with gradation, is able to reduce the public health risks associated with the disposal of secondary treated effluents.

CONCLUSION

The basic nature of sand and the root pattern of *Canna indica* might have helped during the study for reduction of microbial indicators. These two components increased the physical mechanisms and dissolved oxygen content and secretions of antibacterial substance within the system which may have created unfavorable environment to survive microbial species. So far, this study can be useful for the existing domain of the effluent treatment plants where chemical dosing is their tool to disinfect the secondary treated wastewater. And, the very simple and efficient approach to use of sand and gravel as media and *Canna indica* as a suitable plant species, can reduce their cost of establishment of treatment. This novel approach may be helpful for further studies to challenge the different treatment processes as a post treatment alternative.

NOTE

The views and opinions expressed in this article are those of the authors and do not necessarily reflect the official policy or position of any agency (MNIT & NMCG).

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Section 6
Critical Issues and Challenges

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Chapter 74
Nanotechnology for Filtration-Based Point-of-Use Water Treatment:
A Review of Current Understanding

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ABSTRACT

With significant infrastructure investments required for centralized water treatment, in home treatment technologies, known as point-of-use, have become a popular solution in the developing world. This review discusses current filtration-based point-of-use water treatment technologies in three major categories: ceramics, papers and textiles. Each of these categories has used silver for added antimicrobial effectiveness. Ceramics have had the most development and market infiltration, while filter papers are a new development. Textiles show promise for future research as a cheap, socially acceptable, and effective method. Also, a new method of silver incorporation in ceramics is explored.

INTRODUCTION

Approximately 1 billion people worldwide do not have access an "improved water supply", which is defined by the World Health Organization (WHO) as "a household connection or access to a public standpipe, a protected well or spring, or a source of rainwater collection"(Cosgrove & Rijsberman, 2000). This definition also requires that at least 20 liters per person per day are available within 1 km of a person's home. Because this definition does not refer to water quality, reliability of service, or even cost, it is estimated that an additional 2-3 billion people also have unsafe water supplies, at least for part of the

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time (Hutton & Haller, 2004). Studies have also shown that numbers reported by the Joint Monitoring Programme of the proportion of drinking water coming from improved sources are likely substantial overestimations when water quality data is included (Bain et al., 2012). Access as well as quality is key.

The dangers of consuming unsafe water are substantial, particularly for children. The WHO estimates that consuming unsafe water causes the deaths of over 4 million people per year, with more than 1.5 million of these deaths being children under the age of 5. This is about equal to having 10 jumbo jets crashing every day with 90% of the passengers being children (Dillingham & Guerrant, 2004). Not included in this figure are the added health burdens on children who experience cognitive impairment and growth stunting as a result of gastrointestinal infections caused by consumption of water with pathogenic organisms like Shigella, pathogenic strains of *Escherichia coli*, *Vibrio cholerae*, and *Cryptosporidium parvum (Dillingham & Guerrant, 2004)*. People living with AIDS are particularly susceptible to infections from waterborne pathogens because of their weakened immune systems (Dillingham et al., 2006). In many parts of sub-Saharan Africa, there is an unfortunate confluence of low-quality drinking water and high rates of HIV infection. Providing safe water to our global population has been identified as one of the Grand Challenges of Engineering by the National Academy of Engineering.

In most cities and suburban areas of the developed world, water is treated at centralized water-treatment plants and delivered directly to homes through distribution systems with chlorine residual. About 3-4 billion people receive this high level of service, which generally prevents gastrointestinal infections by waterborne pathogens. This service is usually not available in the developing world or even in some suburban and rural areas of the developed world. These regions cannot economically sustain centralized water treatment plants that meet the full demands of the population. A centralized water treatment facility is a very large investment not feasible for many communities. The treatment plants plus the distribution system is not practical in developing rural areas due to the financial and structural requirements for safe treatment and delivery of water. The WHO has suggested that one possible solution is to take a more decentralized approach to water treatment, wherein people treat their water in their households immediately before consumption. This idea, often referred to as point-of-use (POU) water treatment, has the potential to significantly improve the microbial quality of household water and reduce the risk of diarrheal disease and death, particularly among children (Thomas Clasen, Nadakatti, & Menon, 2006). Table 1 shows a summary of some point-of-use systems currently in use and their effectiveness against *Escherichia coli* (*E. coli*).

Ideally, local markets can ideally drive the proliferation of these technologies without reliance on government interventions and/or subsidies. Peter-Varbanets, et al. divides current point-of-use treatments being used into three general categories: heat and UV-based systems (boiling with fuel, solar radiation, SODIS, combined action of heat and solar UV, and UV lamps), chemical treatment methods (coagulation, flocculation and precipitation, adsorption, ion exchange and chemical disinfection), and physical removal processes (sedimentation or settling, filtration, including membranes, ceramic and fiber filters, and granular media filters, including sand filters and aeration).

Rural areas of developing countries have been unable to implement centralized drinking water treatment because it is expensive. This leads to using untreated natural water sources (rivers, lakes, groundwater or rain) (Peter-Varbanets, Zurbrugg, Swartz, & Pronk, 2009). Without centralized treatment and direct piping into the home, there are many steps before consumption including collection from the source, storage, contamination, and treatment (J. E. Mellor, Smith, Learmonth, Netshandama, & Dillingham, 2012). There are three types of conventional methods for treatment including physical, chemical, and biological (Praveena & Aris, 2015). Common practices for point of use water treatment not utilizing

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Table 1. A summary of E. coli removal efficiency in some POU technologies that use silver nanoparticles

Type of Material	Removal Efficiency (LRV)	Removal Efficiency (%)	Silver Concentration (mg/L)	References
Ceramic				
Ceramic materials (clay from Indonesia)	3		10	(Rayner et al., 2013)
Ceramic materials (clay from Tanzania)	2.8		10	(Praveena & Aris, 2015)
Ceramic materials (clay from Nicaragua)	2.5		11	(Praveena & Aris, 2015)
Ceramic materials (clay mixed with sawdust)		92	.02	(Kallman, Vinka A. Oyanedel-Craver, & and James A. Smith, 2011)
Ceramic filter (40%soil, 10%flour, 50%grog)		97.8-100	<.1	(V. A. Oyanedel-Craver & J. A. Smith, 2008)
Fiber				
Synthetic fiber		100	10	(S. Chen, Liu, & Zeng, 2005)
Natural fiber pure cellulose paper	8.7		.1	(T. A. Dankovich & Gray, 2011)

(Praveena & Aris, 2015)

filtration include boiling, chlorination, or solar disinfection. Membrane systems for use in the home have become increasingly popular, but still remain too expensive for the poorest of countries. Microbial pollution is the most threatening issue with water supplies, and fecal contamination of a water supply leads to water-borne diseases. Boiling of water is the most common form of treatment in developing countries, but is not as effective as hoped. A study in semi-urban India found 40.4% of stored drinking water of those who reported boiling their water were contaminated with fecal coliform (Thomas Clasen et al., 2008). In addition, 25.1% had more than 100 fecal coliforms (FC) per 100 mL, while the WHO standard is 0 FC/100mL) (Thomas Clasen et al., 2008). Boiling also creates a high-energy demand and poses the additional problem of deforestation when wood fires are used to boil the water. Assuming that households boiled 6 liters per day, the estimated monthly fuel cost for boiling water in semi-urban India was US $1.50 for households using liquid petroleum gas and US $3.21 for those using wood (Thomas Clasen et al., 2008). The cost is higher for those using wood as fuel because of the opportunity cost of lost time earning money that is instead spent gathering wood. Places like Bangladesh also lack access to the fuel necessary to boil water (A. Huq et al., 1996). Chlorine has been tested as an in-home option and has proven effective, but unpopular; household users complain about the taste and have reported a refusal to drink the water since the smell is similar to that of household bleach (Kirchhoff & McClelland, 1985). Solar disinfection has been proven as effective but requires sunlight and a large supply of plastic bottles while only treating a limited amount of water at one time (D. S. Lantagne, Quick, & Mintz, 2006). When there is limited water quantity, common solutions include groundwater wells and rainwater harvesting. However, groundwater wells are not always well planned and can become polluted, while temporal and spatial variations in rainfall can make rainwater harvesting unreliable in the absence of large-volume storage (Peter-Varbanets et al., 2009).

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BACKGROUND

High surface area to volume ratio leads to better bactericidal activity, making nanomaterials excellent adsorbents (Praveena & Aris, 2015). This chapter will focus on one particular nanomaterial, silver. Silver has been used for disinfection for millennia and in wound treatments since the 1960s (LeOuay & Stellacci, 2015). Silver has bactericidal activity in its oxidized state, Ag^+ (Karel, Koparal, & Kaynak, 2015). Silver nanoparticles are between 1 and 100 nm in size (T. A. Dankovich, 2012).

Growth studies of microbial cultures have been performed with both silver and copper nanoparticles. One study showed that silver and copper nanoparticles have great promise as antimicrobial agents against *E. coli, B. subtilis*, and *S. aureus (Ruparelia, Chatterjee, Duttagupta, & Mukherji, 2008). E. coli* is a common choice for testing the effectiveness of a technology since it is a gram-negative, rod-shaped bacterium, 1-2 μm long and 0.1-0.5 μm in diameter, and a common water microbe with strains that cause gastrointestinal infections (Brown, Chai, Wang, & Sobsey, 2012). Silver nanoparticles perform better as an antimicrobial agent against *E. coli* and *S. aureus* than copper. Copper nanoparticles form an oxide layer and demonstrate better antimicrobial activity towards *B. subtilis* than silver, possibly due to a greater affinity to the surface-active groups. Ruparelia et al. admits that the antimicrobial mechanism of the silver and copper nanoparticles is not yet fully established, and a combination of silver and copper nanoparticles may produce a more complete bactericidal effect against mixed bacterial populations that would be more common in actual use (Ruparelia et al., 2008).

Silver is usually in concentrations of approximately 0.1 mg/kg in aquatic systems at subnanomolar levels. Higher silver concentrations in aquatic environments often come from waste streams of commercial or industrial processes. Silver in nature can be monovalent (Ag(I)) or metallic (Ag(0)). Studies have shown that free or hydrated Ag(I) exhibits toxic effects on a variety of aquatic organisms ranging from zooplankton to rainbow trout (Herrin, Andren, & Armstrong, 2001). Several studies have demonstrated that silver ions are selectively toxic for prokaryotic microorganisms, with little effect on eukaryotic cells (Park & Jang, 2003). However, the exact reasons for the antimicrobial ability of the nanoparticles are still unknown. Among all antimicrobial nanomaterials, nanosilver is probably the most widely used (Li et al., 2008). Silver's antimicrobial property is related to the amount and the rate at which it is released. Metallic state silver is inert, but silver will react with moisture in the skin or fluid in a wound to become ionized. Ionized silver is highly reactive, binding to bacterial DNA and RNA by denaturing. The nanoparticles bind to the cell membrane, a vital point of protection, and accumulate to causing irreparable damage (Pradeep & Anshup, 2009). This inhibits a bacterial cell from replication. In binding to tissue proteins, the silver brings structural changes to the cell wall and nuclear membranes causing the cell to distort and die (Rai, Yadav, & Gade, 2009). It has also been found that if the antimicrobial and the bacterial cell (negative charge) have the same surface charge, there is repulsion and less contact (Pradeep & Anshup, 2009). Oxygen presence in a system with bulk silver provides complete destructive oxidation of microorganisms (Pradeep & Anshup, 2009).

Health concerns are the chief barrier to the implementation of new technologies that use silver nanoparticles. Silver release from a treatment material is affected by the water's pH, temperature and chemical composition. Just 60 milligrams can be toxic to humans, while 1.3 to 6.2 grams is lethal (D. S. Lantagne, 2001). The WHO sets a limit to ensure that these technologies do not cause harm, stating that up to .1 mg/L can be tolerated without risk. The United States Environmental Protection Agency sets a maximum silver concentration for drinking water at .1 mg/L (Quang et al., 2013). The retention rate of silver in humans is only 0-10 percent, and silver is mainly stored in the liver and skin. The WHO

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set a guideline of 10 grams of silver in a lifetime (D. S. Lantagne, 2001). Potential human risks of silver consumption at high levels include high blood pressure, kidney damage, gastrointestinal irritation, cancer and neurological damage, in addition to DNA damage (Praveena & Aris, 2015). The silver levels after treatment must be within a safe range for human consumption. Risks to environment and human health are a rising concern. The technologies discussed in the chapter release silver at levels below the drinking water standard, meaning they are safe and may cause a substantial improvement in water quality and human health, particularly in resource-limited settings. Some of the ceramic technologies are made with silver nitrate instead of silver nanoparticles and thus release silver ions instead of nanoparticles.. There is a strong understanding of the health effects of silver in ion form, but the effects of silver in the nano form are less understood.

CURRENT POINT-OF-USE WATER TREATMENT TECHNOLOGIES

Herein, we discuss current point-of-use water treatment practices that use silver nanoparticles in porous media. The three main categories of treatment type that will be addressed are ceramic, paper and textile. These technologies us e filtration, which benefit from removal of turbidity and are gravity fed, which saves on energy costs (Albert, Luoto, & Levine, 2010). In addition, we present new data on a novel "silver-nanopatch" fabrication technique as applied to ceramic filters.

Ceramic

Silver has been imbedded in clay and can be designed to control silver release kinetics (Karel et al., 2015). Silver imbedded clay can also be used with textiles by soaking a textile then oven drying (Kasuga et al., 2011). Although this method has not been used for water, it has been used for air purifiers, and the clay has been used in plates to treat drinking water (Kasuga et al., 2011). Fired clay makes a ceramic that can be used for ceramic filtration which has been shown to have high effectiveness against bacteria and protozoa (D. S. Lantagne et al., 2006). Potters for Peace is a US-based nongovernmental organization (NGO) that has been teaching communities to produce and manufacture ceramic pots that filter water (D. S. Lantagne, 2001). The pots are made from water, clay and a combustible material like sawdust and shaped like a pot. The kiln is typically fired at 900 ˚C for 8 hours, below the melting point of silver (Praveena & Aris, 2015; Ren & Smith, 2013). During firing, the clay forms a ceramic and the sawdust combusts, leaving behind porosity for water flow. Some filter factories then perform a pressure test by submerging the filter to the rim in water for 10 seconds and to see if any wet spots appear on the interior of the filter pot. A wet spot would suggest a macropore that in turn may limit filter performance for pathogen removal (Rayner, 2009). Filters are then soaked and subjected to a flow test. If the filters pass a flow rate test they are then painted or dipped in colloidal silver solution that provides antimicrobial effects (Rayner, 2009). Water containing a colloidal silver has been filtered through as a way to embed the silver in the filters, but has been proven less efficient (D. S. Lantagne, 2001). Also, painting on silver nitrate is less efficient due to high washout, and silver nanoparticles are recommended (Rayner et al., 2013). Mixing in silver nanoparticles prior to firing has shown higher retention of silver in the ceramic and potentially better long term use when compared to the paint on or dipped application method which release silver at high levels quickly during early use (Ren & Smith, 2013). This has not been tested for bacterial disinfection nor has it been field tested, but it could be a promising alternative. The ceramic sits

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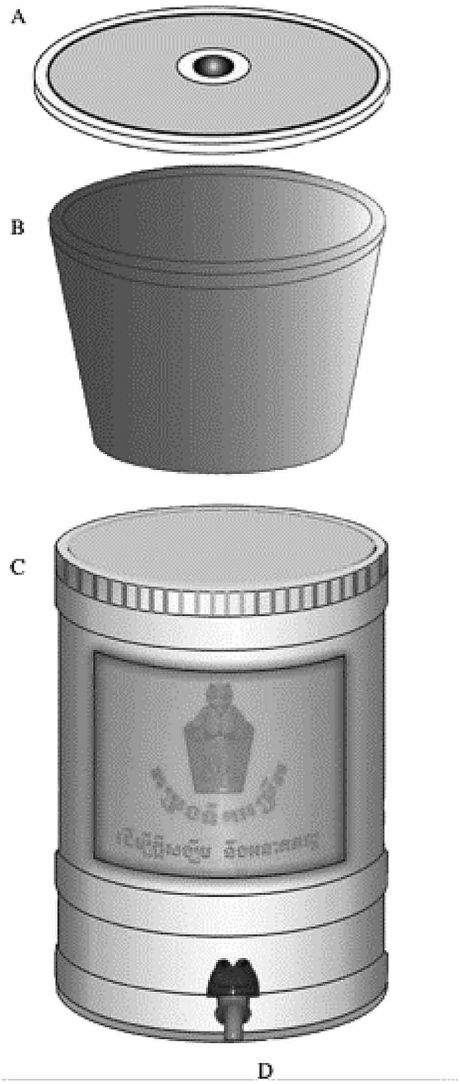
inside a 20-30 liter plastic bucket with a spigot. Figure 1 is a diagram of a completed ceramic water filter (Brown & Sobsey, 2010). These can be manufactured locally and pots are a common storage container for water already, so there is no break to the social norm (D. S. Lantagne et al., 2006). The filtering of water is gravity-fed and would save on energy cost. The clay-to-sawdust ratio by volume of 47% has proven best in optimizing flow rate without losing coliform removal (D. Lantagne et al., 2010). Also, the type of combustible used has been shown to make a difference even if the same size and amount is used, like sawdust versus coffee or rice husk (D. Lantagne et al., 2010).

Figure 1. Schematic of the ceramic water filter produced by Resource Development International—Cambodia (courtesy of Mickey Sampson). The complete filter unit consists of a lid (A), ceramic filter element (B) in a plastic container (C) that gathers treated water and dispenses through a tap at the base (D). *Brown & Sobsey, 2010.*



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The silver-impregnated ceramic water filters have shown to be both sustainable and socially acceptable as well as effective with physical filtration and chemical treatment both contributing to pathogen removal (Abebe et al., 2014). The ceramic filter without silver has been shown to successfully remove *E.* coli but the addition of silver improves the water quality of the effluent (Kallman et al., 2011). Porosimetry of the filters has shown that the pores of the ceramic are too big to remove bacteria by only size exclusion-- there are several other mechanisms like depth straining, particle bridging inertial impaction, interception, diffusion and electrostatic attraction that help with capturing bacteria (Matthies et al., 2015). The filter has also been shown to be a preferred option by a study of 400 households in Kenya. Households were given the option of three different technologies, PUR (chlorine-based), Waterguard (chlorine-based) and a ceramic water filter. The households had a two-month trial with each, and then were asked their preference again at the conclusion of the trial. The ceramic water filter was preferred both before and after (Albert et al., 2010).

The method of application of silver does not appear to be a factor affecting disinfection efficiency (D. Lantagne et al., 2010; V. Oyanedel-Craver & J. A. Smith, 2008). Instead the mass of colloidal silver that remains after the saturation period determines effectiveness. The bacterial removal may be helped by the ceramic pores being filled by silver instead of the bacteria in transport. Testing has shown between 97.8 and 100% removal of *E.* coli (V. Oyanedel-Craver & J. A. Smith, 2008). It is also important that the silver release remains below the regulatory limit for silver in drinking water, which is 0.1 mg/L. This level was not exceeded for any of the filters tested after passing water through the filter for about 200 min (V. Oyanedel-Craver & J. A. Smith, 2008). The shape of the filter, flat bottom versus round bottom, also has no effect (D. Lantagne et al., 2010).

Ceramic candles are often used in a gravity-fed, ceramic water filter system. The set up involves two 20 L plastic buckets stacked on top each other with the silver impregnated ceramic candles vertical allowing their effluent to flow to the bottom bucket and be dispensed out a spigot. Each candle can treat 20000 L depending on water quality (THOMAS Clasen, Parra, Boisson, & Collin, 2005). This technique has been associated with 70% lower diarrheal rates, and 92% of users report "feeling better" after using the filter (T. F. Clasen, Brown, Collin, Suntura, & Cairncross, 2004). Ceramic candles have shown that after 16 months, only 48.7% are still operating properly, and 54% of those produce coliform free water (T Clasen & Boisson, 2006). The main problem with this technology is breakage. The ceramic filters are popular with the end user, but with so many parts, any failure commonly leads to discontinued use because of difficulty to repair (T Clasen & Boisson, 2006). It has been found that the treatments are not always done correctly by the user (D. S. Lantagne & Clasen, 2012). This lowers the effectiveness of the technology and therefore does not provide recipients with the safe drinking water they should be receiving. Proper education on use and maintenance of the treatment system is vital (D. S. Lantagne, 2001). Proper maintenance of ceramic water filters can reduce early childhood diarrhea by an extra 45% (J. Mellor, Abebe, Ehdaie, Dillingham, & Smith, 2014). Often the new technology may be provided to a developing country, but with English directions. Keeping methods simple and similar to current practices could improve the utilization phase of treatment processes (D. S. Lantagne & Clasen, 2012).

The benefits of ceramic filtration include its proven effectiveness against bacteria and protozoa, its simplicity, its long-term use, and its low cost due to the ability to locally produce. One study of the ceramic filter reported a 90-99% removal of MS2, a viral pathogen (Brown & Sobsey, 2010), but conversely it has also been claimed that there is a minimal efficiency against viruses (Matthies et al., 2015). But with that, there is a risk of recontamination in the lower reservoir and need for education for optimal use (T. F. Clasen et al., 2004). Ceramic filters provide health improvements, cost-effectiveness

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and are environmentally friendly, making them sustainable and a better option than a centralized treatment system in the developing world (Ren, Colosi, & Smith, 2013). Unfortunately, ceramic filters have shown a 2% decrease in likelihood of use after each month of ownership with the most common reason being the filter breakage (Brown, Proum, & Sobsey, 2009), and 67% of the discontinued use is because of breakage (Sobsey, Stauber, Casanova, Brown, & Elliott, 2008).

As for human health effects, a study has shown that the use of silver-impregnated ceramic filters reduced diarrhea rates by 49% across age groups and sexes (Brown, Sobsey, & Loomis, 2008), and by 80% among HIV-positive users (Abebe et al., 2014). This is important since individuals who are immunocompromised can be particularly susceptible to gastrointestinal infections from waterborne pathogens (Abebe et al., 2014). There has also been epidemiological research on ceramic filter use and reduction of the hepatitis A virus (T. F. Clasen et al., 2004). Ceramic water filters have been found to reduce early childhood diarrhea by 41% over two years (J. Mellor et al., 2014), but the effectiveness is reduced after 3 years (J. Mellor et al., 2014).

Other ceramic technologies have been developed that do not use filtration. Silver-coated ceramic beads can be used in water, and has been tested by pouring through columns rather than a batch method (Han, Lee, Lee, Uzawa, & Park, 2005; Lin et al., 2013). Recently, a novel method of metallic silver formation in a porous ceramic was reported by Ehdaie et al. (2014). These researchers combined clay, sawdust, water, and silver nitrate, pressed the mixture into the form of a ceramic tablet, and fired the tablet in a kiln at 900 ˚C. During firing, the clay formed a ceramic, the sawdust combusts, and the ionic silver is reduced to metallic silver, forming metallic silver "nanopatches" with an average diameter of 2.71 nm as seen in Figure 2. The ceramic tablet can be added to a 5-15-L household water storage container and it passively releases ionic silver for the inactivation of *E. coli* and other gram-negative waterborne pathogenic bacteria. A 3-log reduction (99.9% removal) was shown for *E.* coli in a 10 L water source after 8 hours. This technology shows promise as a successful stand-alone technology for household water treatment for very low cost, or in combination with other filter or boiling treatments, where recontamination is a common issue (Ehdaie, Krause, & Smith, 2014). Similarly, colloidal silver has been coated on a ceramic brick for suspension in large drinking water storage tanks (Nover, McKenzie, Joshi, & Fleenor, 2013). This provides continuous, low-maintenance disinfection quickly (Nover et al., 2013), but the silver levels may become too high and require attention to residence time and size of the water container (Nover et al., 2013).

In a recent investigation in 2015, we conducted a study on incorporating this new method of silver application to ceramic filters. This study was done at the PureMadi Mukondeni Pottery Cooperative in Limpopo Province, South Africa. Currently, ceramic filters are being made by mixing sawdust, water and clay. The mixture is pressed into the shape of a filter and then fired. After that, a silver nanoparticle suspension is painted on the inside and the outside of the filters. With the help of local potters, filters were made using a new method. The new method of incorporating silver is mixing clay, sawdust and water with $AgNO_3$. During the firing process the Ag^+ reduces to Ag^0 forming small nanopatches, like in Figure 1. Filters were made with 0.3 g Ag (the same silver mass used in the paint on method) and 1.0 g Ag.

Filters were tested at the University of Venda, in Thoyondou, South Africa. Controls (filters fabricated by painting on silver nanoparticles), filters with 0.3 g of Ag, and filters with 1.0 g Ag were compared over 12 days for coliform bacteria removal efficiency. For testing, 4L of challenge water from a local stream was poured into the top reservoir of each filter. This was allowed to percolate and gather in the lower reservoir for 12 hours before collection. Samples were then tested for total coliform and *E. coli* removal using membrane filtration. To calculate results, the log of the effluent concentration (C) divided

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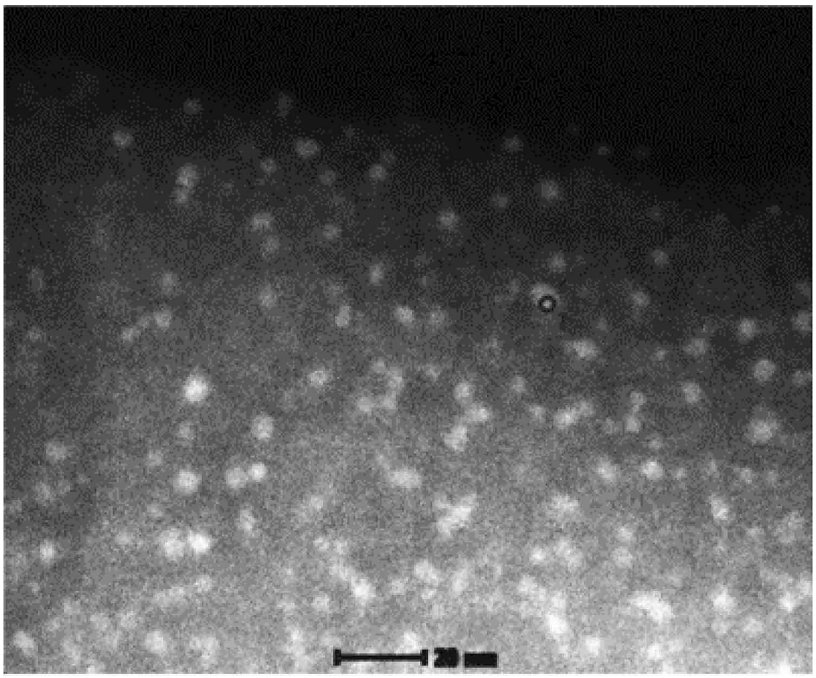
Figure 2. Transmission electron microscopy image of silver nanopatches in the center of a ceramic tablet using scanning electron microscopy mode. The scale bar represents 20 nm in length
(Ehdaie et al., 2014).



by influent concentration (C_0). Results are displayed in Figure 3. The error bars represent one standard deviation above and below the mean and show there is no statistical difference between using the paint on method and the new silver nitrate method of incorporating prior to firing.

The method is less expensive and easier to manufacture as the painting step is omitted and $AgNO_3$ is much less expensive than silver nanoparticles. Potentially, even more silver in the form of silver nitrate for be added to improve the performance of the filters without increasing filter cost. On the downside, filters that do not pass quality control tests (pressure or flow rate tests) will waste the silver that has been applied to them. Filters that are manufactured conventionally will not receive silver nanoparticle application until passing quality control tests. Further research needs to be done to expand this data set, but these results show promise for an improvement to the technology.

Paper

Paper is mostly made up of cellulose, the most abundant natural polymer. It is readily available, inexpensive, renewable, and biodegradable as well as having a great ability for metal ion sorption (Tang, Meng, Lu, & Zhu, 2009) (T. A. Dankovich, 2012). Paper is a cellulosic non-woven material like some fabrics (Ngo, Li, Simon, & Garnier, 2011). Silver nanoparticles have been formed on cellulose in bandages, clothing, food packaging, and much more. This proves a potential use of paper for water treatment (T. A. Dankovich, 2012). The most common way of synthesizing silver nanoparticles on cellulosic material is *in situ* chemical reduction of metal ions, with a reducing agent commonly being sodium borohydride

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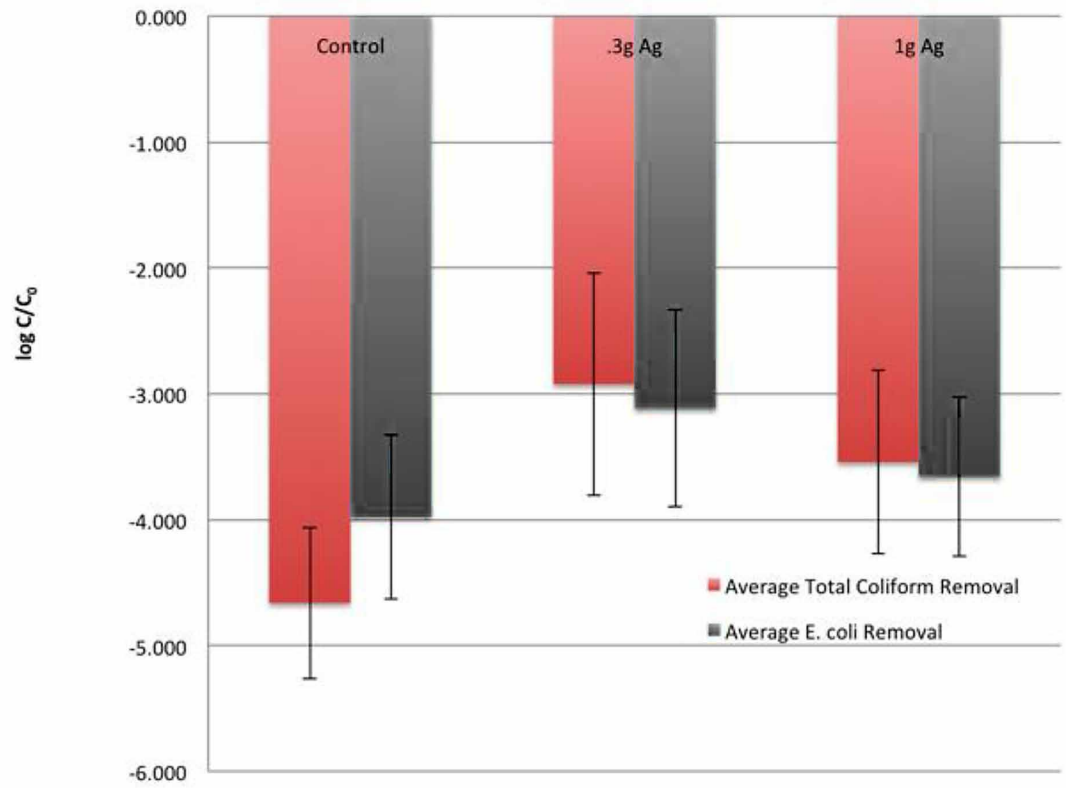
Figure 3. Plot of the average log removal of total coliform bacteria and E. coli by conventional filters manufactured by painting on 0.3 g of silver nanoparticles (Control) and filters fired after mixing with silver nitrate (0.3 and 1.0 g as Ag). During firing, the silver nitrate is reduced to produce silver nanopatches throughout the porous ceramic media.



(T. A. Dankovich, 2012; Tang et al., 2009; Zeng et al., 2007). Dankovich (2012) has described a method of creating silver nanoparticle (AgNP) paper by immersing blotting paper sheets (6.5 cm by 6.5 cm) in 20 mL of silver nitrate solutions at concentrations from 0 to 100 mM for 30 minutes. The sheets are then rinsed with ethanol to remove excess silver nitrate that was not absorbed into the blotter. To form nanoparticles, the paper is placed in aqueous $NaBH_4$ solutions (ranging from 1:1 to 10:1 molar ratio, $NaBH_4/AgNO_3$) for 15 min. Lastly, the paper is soaked in water for 60 min, and dried in an oven at 60° C for 2 to 3 hours (T. A. Dankovich & Gray, 2011).

A microware irradiation method for *in situ* preparation of silver nanoparticles in paper has also been developed. Using a microwave, or a conventional oven, a silver nanoparticle covered paper can be produced in a "green" way. Blotting papers are submerged in aqueous solutions of silver nitrate and glucose (T. Dankovich, Clinch, Weinronk, Dillingham, & Smith, 2014). The papers are then heated in either a microwave or a conventional oven before being soaked in water to remove excess reagents (T. Dankovich et al., 2014). Glucose functions as the reducing agent with higher concentrations leading to smaller, more uniform nanoparticles and a faster reaction time. The average size of the resulting nanoparticles can be measured with TEM images to be 5.5 nm (T. A. Dankovich, 2012). Figure 4 shows scanning

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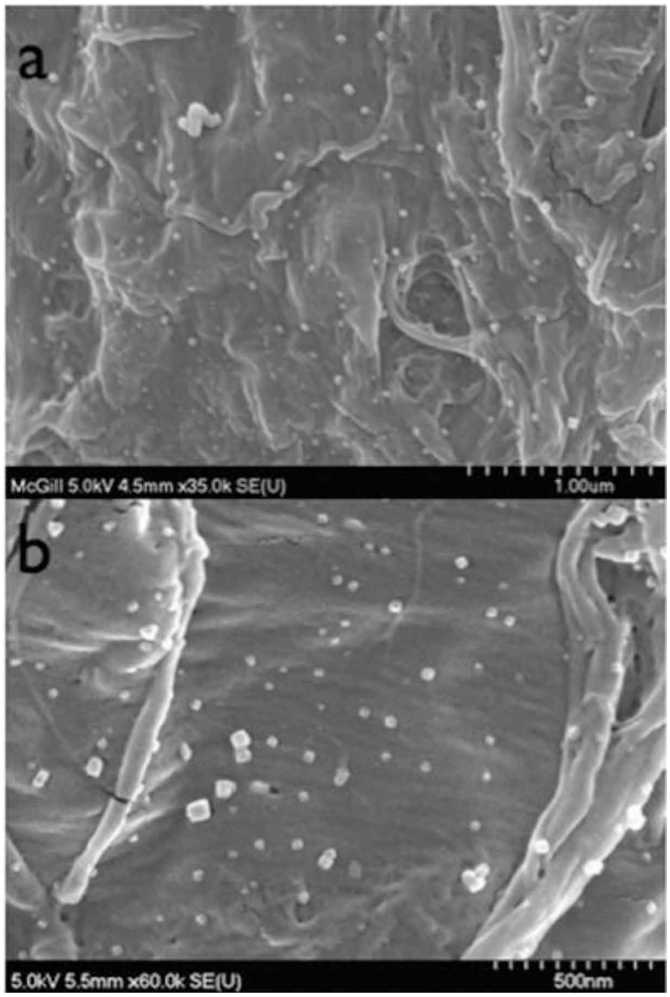
electron microscope (SEM) images of AgNP on paper (T. A. Dankovich, 2014). This way of producing the papers is more benign than the use of sodium borohydride as the reducing agent, while being just as effective (T. Dankovich et al., 2014).

Silver nanoparticles have the largest antibacterial effects with the smallest particle sizes, with average diameters under 10 nm being most effective. Results showed the AgNP paper was effective with *E. coli* bacteria suspensions poured through the sheets. After passage through the paper, effluent bacteria was isolated and used for plate counts, showing log 7.6 (±1.3) and log 3.4 (±0.9) reductions of viable *E. coli* and *E. faecalis* bacteria, respectively. Bacteria were reduced by log 0.95 (± 0.5), probably because some bacteria remained on the fiber surfaces in the blotting paper. Graphite furnace atomic absorption was used to measure the silver content in the effluent, which measured 0.0475 (±0.0177) ppm meeting the USEPA guideline for drinking water of less than 0.1 ppm (T. A. Dankovich & Gray, 2011).

Figure 4. SEM image of AgNP paper with 2.5 mg Ag g^{-1} paper, (a) 35 000× and (b) 60 000× magnification (T. A. Dankovich, 2014).



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Gottesman et al. (2010) describe a way of depositing silver nanoparticles onto paper by ultrasonication. The paper is held immersed in a solution of silver nitrate, ethanol, ethylene glycol and water which is then irradiated with a high intensity ultrasonic horn.. These papers have been shown to have minimal loss of silver from the coated surface, which is important for the longevity of the material. They were also shown to be effective against both gram-negative and gram-positive bacteria. This shows promise for water treatment and the avoidance of cross contamination (Gottesman et al., 2010).

Silver nanoparticles have been imbedded in paper by first immobilizing initiators on a paper's surface. Then a surface-initiated atom transfer radical polymerization technique has been developed to graft poly(tert-butyl acrylate) brushes to cellulose filters. Then the brushes are transferred into poly(acrylic acid) by hydrolyzation. Silver nitrate is then reduced to Ag^+ *in situ* by reducing agent sodium borohydride. These filters display good antibacterial ability against *E. coli* (Tang et al., 2009).

Textile

Silver nanoparticles are commonly used in clothing, especially socks, as an antimicrobial agent (Benn & Westerhoff, 2008). Antimicrobial silver is also popular for improving dressing for burn wounds. An ethanol/water medium with silver nitrate uses cation exchange between silver and sodium from sodium carboxymethyl cotton gauze (Parikh et al., 2005). The use of textiles for filtration is not a new idea. Different types of sari material have been used in Bangladesh as an inexpensive and easily available option for point-of-use water filtration (Colwell et al., 2003; A. Huq et al., 1996). Shesh, a traditional textile of North Africa, and more modern textiles like denim or shower curtains have also been tested for water filtration performance (Saidani-Scott, Tierney, & Sánchez-Silva, 2009). Textiles are very effective at removing turbidity when used for filtration (Tammisetti, 2010). The waterborne pathogen *Vibrio cholerae* often attaches to something larger like zooplankton, particularly copepods (Colwell et al., 2003; A. Huq et al., 1996). This makes for easier removal by fabric filtration. The larger particles are more likely to get filtered out via fabric filtration, while smaller organisms could pass straight through the holes in the fabric. Folding of the fabric is encouraged to increase efficiency so more levels of fabric are used for filtration (Colwell et al., 2003). The simple filtration technique of pouring water through a fabric folded at least four times has been shown to effectively remove zooplankton, most phytoplankton and particulates bigger than 20 micrometers (Colwell et al., 2003). Most importantly, follow up studies have shown that the method is accepted and sustainable by villagers in Bangladesh and also reduced the incidence of cholera by 48% (Anwar Huq et al., 2010). Gram-negative bacterium *E. coli* and Gram-positive bacterium *Staphylococcus aureus* are commonly used for antimicrobial activity with fabric testing and fungus *C. albicans* is also used frequently (Ilic et al., 2010; Ilic et al., 2009; Maneerung, Tokura, & Rujiravanit, 2007; Mecha & Pillay, 2014). Textiles show this promise because without alteration they remove larger suspensions and reduce turbidity.

Radetić (2013) offers a comprehensive overview of nanoparticle-embedded textiles. The quick push for silver nanoparticles in textiles led to a growing industry with lack of insight into the possible environmental effects. Cotton seems to be the original textile of choice, especially pre-dyed or printed. The natural fiber allows for silver application to be commonly done without any prep work. Cotton is also a common fiber that is easily available and widely used. Like paper, sodium borohydride and glucose are common reducing agents used for the formation of silver nanoparticles (Maneerung et al., 2007; Reda M. El-Shishtawy, 2011). Silk has also be used with the reduction of silver nitrate with reducing agents like hydrazine and glucose (Gulrajani, Gupta, Periyasamy, & Muthu, 2008). Wool is also a common fiber,

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but not as well explored for AgNP applications. It has been shown to have antimicrobial abilities, and its main benefit is said to be the bright brilliant colors it produces (Radetic, 2013). Silver nanoparticle wool composites have been made by the reduction of silver ions in solution by trisodium citrate in solution with merino wool fibers or fabrics (Kelly & Johnston, 2011). This process creates a bind between the silver metal nanoparticles and the amino acids of the keratin protein in the wool fibers with the reducing agent functioning as the linker (Kelly & Johnston, 2011). Cotton fabrics also do not need pre-treatment to be able to load silver nanoparticles efficiently, even though 3-aminopropyltriethoxysilane has been used for surface modification with improved results (Guo et al., 2013; Ilic et al., 2009; Liu, Lee, Norsten, & Chong, 2013), but, the ability of cotton textiles to retain moisture leads to an excellent environment for growing microorganisms (C.-Y. Chen & Chiang, 2008). Because of surface charges, inorganic particles and polymeric materials, like manmade textiles, demonstrate repelling between silver and the fiber at the interface; this requires a modification be made to the surface, but this commonly washes away with laundering leading to leaching (Dastjerdi, Montazer, & Shahsavan, 2009). Chelating monomers, like glycidyl methacrylate-iminodiacetic acid, can be used to graft onto cotton fibers to increase the amount of Ag^+ sorbed. The Ag^+ can then be reduced by UV radiation to form silver nanoparticles on the surface (C.-Y. Chen & Chiang, 2008). Polyester and polyamide offer two synthetic options, and polypropylene fibers (PP) are widely used in the manufacturing of medical and hygienic textile materials where a high level of antimicrobial activity is required (surgical masks, diapers, hygienic bands, etc.) (Radetic, 2013). Figure 5 show untreated PP fiber as well as a PP fiber loaded with silver nanoparticles. Activated carbon fibers have high adsorption capacities and can be impregnated with silver. Because of the high adsorption capacity and large surface area, bacteria will breed on the activated carbon filter (Yoon, Byeon, Park, & Hwang, 2008). Silver-deposited activated carbon filters have been shown to be effective for air filters, but also have a low life expectancy with greatly decreasing performance quickly when used for water filtration (LePape et al., 2002, 2004; Yoon et al., 2008). When designing a method to incorporate silver nanoparticles with textiles, it is key to control the chemistry of the solution including the pH, ionic strength, and surface complexation (Yin, Walker, Chen, & Yang, 2014). A crosslinkable polysiloxane layer can be used to permanently modify the surface of polyester with a polymeric layer on the surface that is resistant to light, heat, chemical and microbial attacks making it safer during washing (Dastjerdi et al., 2009; Dastjerdi, Montazer, & Shahsavan, 2010).

Another way of synthesizing silver nanoparticles in textiles involves using Tollen's reagent; silver nitrate is combined with NaOH to form Ag_2O powder. An ammonia solution is added and sonicated to produce an aqueous solution of Tollen's reagent, a complex ion, $[Ag(NH_3)_2]^+$. Cotton fabric is soaked in a boiling bath of Tollen's reagent solution then washed with deionized water and dried at room temperature forming silver nanoparticles (Montazer, Alimohammadi, Shamei, & Rahimi, 2012). Using electrostatic interactions, cellulose can be modified to be positively charged by using an epoxy substitution reaction on the abundant hydroxyl groups on cellulose to graft ammonium ions. This now positively charged cellulose fiber surface can be involved in adsorption of either negatively charged metal complex ions followed by reduction or with metal nanoparticles capped with negative citrate ions (Dong & Hinestroza, 2009).

In efforts to take a more "green approach", natural extracts from *Eucalyptus citriodora* and *Ficus bengalenis* are used in production of silver nanoparticles. Silver nanoparticles are produced on cotton fibers by an aqueous silver nitrate solution with fresh leaf extract. The leaf broth reduces Ag^+ to silver nanoparticles through the interactions of functional groups present in the leaf extracts (Ravindra, Mohan, Reddy, & Raju, 2010). This does not require any harsh chemicals or dangerous byproducts in the production process. *Curcuma longa* tuber powder and extract have also been used for their water-soluble

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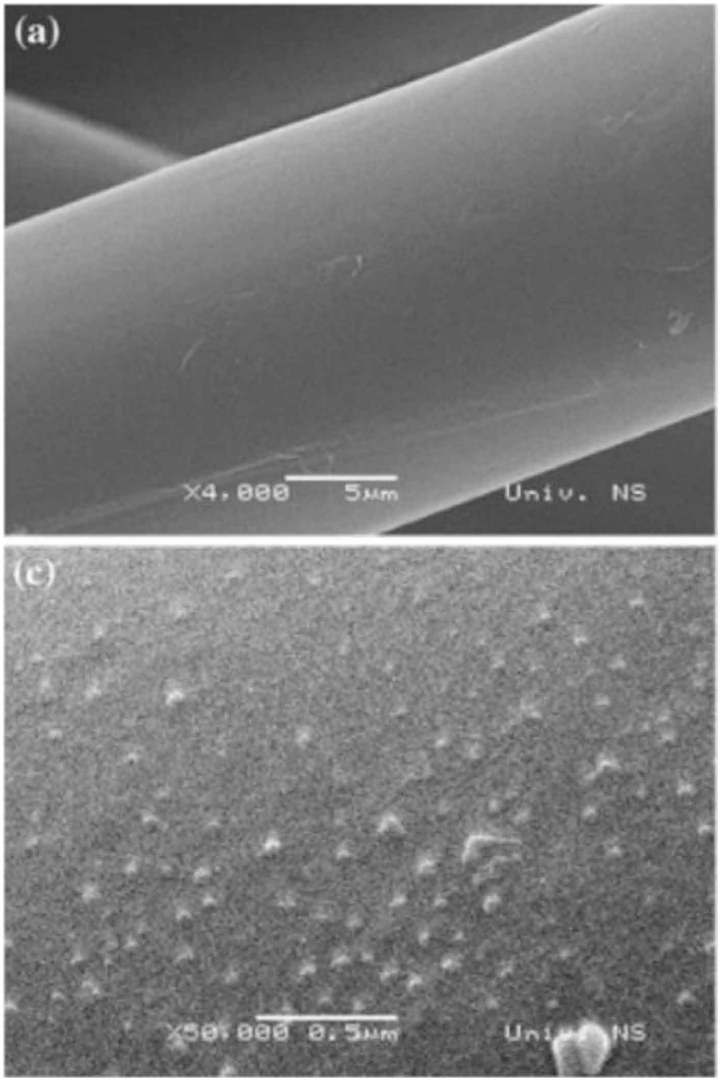
Figure 5. SEM image of untreated PP fiber and PP fiber loaded with AgNP (Radetic, 2013).



organics to reduce silver ions from aqueous silver nitrate to nano-sized silver particles on cotton cloth. The extract works better than the powder since there is more of the reducing agent to form the nanoparticles (Sathishkumar, Sneha, & Yun, 2010).

Low-temperature radio frequency plasma has been used to activate the surface of fibers for improved binding ability of colloidal silver nanoparticles onto polyester fabrics. The plasma treatment reduces the number of coatings necessary for the same level of antibacterial ability in half. These fabrics have been tested for antimicrobial ability as well as laundering ability and have proven to be an improved method. The antibacterial ability was tested against the common Gram-negative bacterium *E. coli* and Gram-positive bacterium *S. aureus* (Ilic et al., 2010).

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As with papers, the cellulose structure of fabric can be used to soak the fabric in silver nitrate solution followed by either physical (heat/UV) or chemical (sodium borohydride) reduction (Fernández et al., 2009). Microwaves are a way of delivering irradiation and heat after soaking with a reducing agent, like sodium citrate (Guo et al., 2013). Mecha and Pillay uses a modified version of the Dankovich method described in the previous section on woven fabric for microfiltration membranes (T. A. Dankovich, 2014). This is a point-of-use filter that is gravity fed and has coated membranes that are hydrophilic and have high water permeability ($p<0.05$). Filtration of turbid water (40–700 NTU) produced clear permeate (<1 NTU) and treatment of water spiked with bacteria (2500– 77,000 CFU/100 mL *E. coli*) showed the removal efficiency of coated membranes was 100% (Mecha & Pillay, 2014).

It has been reported that silver-nanoparticle-coated textile fabrics possess antibacterial activity against *S. aureus*. Silver nanocomposite fibers have been made containing silver nanoparticles incorporated inside the fabric but scanning electron microscopy has concluded that the silver nanoparticles incorporated in the sheath part of fabrics possessed significantly better antibacterial ability compared to the fabrics with silver nanoparticles in the core. The same results came from silver nanoparticles on polyester nonwovens (Rai et al., 2009). Aqueous silver nitrate has been electrospun with polymers to create a fiber that is then reduce with UV irradiation to create silver nanoparticle fibers (Lala et al., 2007). These fibers could then be woven into a textile for use in filtration. An interesting application method has also been developed for applying silver to TiO_2 thin film. An aqueous solution of 1 M silver nitrate ($AgNO_3$) is mixed with ethanol and a 0.6 mL aliquot of the solution is uniformly cast on the TiO_2 thin film. The film is then irradiated with UV light for 1 min, to deposit Ag nanoparticles in the porous film by photocatalytic reduction of Ag^+. The resulting $Ag-TiO_2$ film is thoroughly rinsed with DI water and dried by blowing air with an electric duster (Naoi et al., 2004). Schoen et al., presents an interesting textile technology that combines several mechanisms into one process. It is a "textile based multiscale device for the high speed electrical sterilization of water using silver nanowires, carbon nanotubes, and cotton" (Schoen et al., 2010). This gravity fed device can operate at 100,000 L/(h m^2) while inactivating >98% of bacteria with only seconds of total incubation time. An electrical mechanism rather than size exclusion, allows for the flow to be fast but effective with a very high surface area and large electric field with silver nanowire (Schoen et al., 2010).

CONCLUSION AND FUTURE RESEARCH DIRECTIONS

Increasing the market penetration of point-of-use (POU) technologies will require continued development of inexpensive, easy to use, socially acceptable technologies that do not change the taste of water. These design efforts must be complimented by education and training. Current filtration technologies possess many of the requisite design criteria. Each of the technologies introduced in the chapter have their own strengths and weaknesses. Ceramics filters are the most widely used technology and have the most market penetration to date, but the fragile nature of ceramics makes brakeage a concern. Fabric filters can successfully remove copepods, reducing cholera, but their effectiveness against other pathogens is unknown. Adding silver to fabrics and evaluating performance and social acceptance would be a significant advancement. Paper filters are the least developed technology but may be effective once the proper way of incorporating the technology into household point-of-use is determined. The new method of silver incorporation by the reduction of silver nitrate in papers and ceramics also shows promise as a way to avoid harsh chemicals and the potential health risks of silver nanoparticles.

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Moving forward, important work should also be done to understand the anti-bacterial activity of silver against all classes of bacteria (Pradeep & Anshup, 2009). New POU technologies, in addition to being effective, need to be culturally appropriate to encourage use and motivate the purchasing of the treatment system (D. S. Lantagne et al., 2006). An optimized POU technology should be easy to use, low maintenance, independent of energy and chemicals and have a low cost (Peter-Varbanets et al., 2009). Finding a technology that satisfies all these requirements is challenging. Other nanomaterials have proven effective against other waterborne pathogens and the potential for combination of silver with another metal could improve technologies (Ruparelia et al., 2008). Long term effectiveness is important, making the antifouling ability necessary (Praveena & Aris, 2015). Expanding production of, marketing and distributing any technology will also require research and knowledge of underlying economic factors (Sobsey et al., 2008). It has also been suggested that the introduction of multiple interventions to prevent the transmission of disease is the most effective way to improve the quality of all of the interventions (J. E. Mellor et al., 2012). Solving one point of exposure will not maximize effect. Multiple interventions to improve knowledge and treatments will have the most effect.

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Section 7
Emerging Trends

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Chapter 75
Novel Bioremediation Methods in Waste Management: Novel Bioremediation Methods

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ABSTRACT

Bioremediation technologies are one of the novel methods in the field of waste and environment management and are presently gaining immense credibility for being eco-compatible. Bioremediation using microbes has been well accepted as an environment friendly and economical treatment method for disposal of hazardous petroleum hydrocarbon contaminated waste (oily waste). Besides this, earthworms can be used to extract toxic heavy metals, including cadmium and lead, from solid waste from domestic refuse collection and waste from vegetable and flower markets. Other novel methods used recently for treatment of wastes are plasma incineration or plasma assisted gasification and pyrolysis technology. The technologies applied for conditioning include ultrasonic degradation, chemical degradation, enzyme addition, electro-coagulation and biological cell destruction. Genetic engineering is another method for improving bioremediation of heavy metals and organic pollutants. Transgenic plants and associated bacteria constitute a new generation of genetically modified organisms for bioremediation.

1. INTRODUCTION

It is believed now that wastes are no longer treated as waste and they can be used as a valuable resource. Biomass can interact and confront with water and soil pollutants in both active (live) as well as passive (dead) way, thereby offering numerous opportunities of exploring them for environmental clean-up. With rapid increase in urban populations particularly in the developing world, there is a growing problem of how to manage organic waste and to find alternatives to landfill disposal particularly for domestic food

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waste and that from vegetable markets. According to the research team, it is an unfortunate fact of life that much of this waste is currently dumped on the outskirts of many towns and cities and is causing serious pollution, disease risk and general ecological harm. It also represents a considerable wasted resource, whereas the organic matter might be exploited usefully in growing food crops (Glazer & Nikaido, 2007). Besides this, vast number of pollutants and waste materials containing heavy metals are also disposed into the environment per annum. Approximately 6 x 10^6 chemical compounds have been synthesized, with 1,000 new chemicals being synthesized annually. Almost 60,000 to 95,000 chemicals are in commercial use. According to Third World Network reports, more than one billion pounds (450 million kilograms) of toxins are released globally in air and water. The contaminants causing ecological problems leading to imbalance in nature is of global concern. Bioremediation is an option that offers the possibility to destroy or render harmless various contaminants using natural biological activity. As such, it uses relatively low-cost, low-technology techniques, which generally have a high public acceptance and can often be carried out on site (Vidali *et al.,* 2001). Compared to other methods, bioremediation is a more promising and less expensive way for cleaning up contaminated soil and water (Kamaludeen *et al.,* 2003). Bioremediation uses biological agents, mainly microorganisms, e.g. yeast, fungi or bacteria to clean up contaminated soil and water (Strong *et al.,* 2008). It results in the elimination, attenuation and/or transformation of polluting or contaminating substances by the use of biological processes.

1.1 Principles of Bioremediation

Bioremediation is defined as the process whereby organic wastes are biologically degraded under controlled conditions to an innocuous state, or to levels below concentration limits established by regulatory authorities (Mueller *et al.,* 1996). Most bioremediation systems are run under aerobic conditions, but running a system under anaerobic conditions may permit microbial organisms to degrade otherwise recalcitrant molecules. The microorganisms may be indigenous to a contaminated area or they may be isolated from elsewhere and brought to the contaminated site. Contaminant compounds are transformed by living organisms through reactions that take place as a part of their metabolic processes. Biodegradation of a compound is often a result of the actions of multiple organisms. When microorganisms are imported to a contaminated site to enhance degradation, the process is known as bio-augmentation. Since bioremediation mainly utilizes living organisms (plants) including microbes (bacteria and fungi) that degrade or detoxify substances hazardous to human health and environment. Microorganisms secrete extracellular enzymes that attack the pollutants and convert them into harmless products. Therefore bioremediation can be effective only where environmental conditions permit microbial growth and activity; its application often involves the manipulation of environmental parameters to allow microbial growth and degradation to proceed at a faster rate. For degradation it is necessary that bacteria and the contaminants should be in contact. This is not easily achieved, as neither the microbes nor contaminants are uniformly spread in the soil. Some bacteria are mobile and exhibit a chemotactic response, sensing the contaminant and moving towards it. Other microbes such as fungi grow in a filamentous form toward the contaminant. It is possible to enhance the mobilization of the contaminant utilizing some surfactants such as sodium dodecyl sulphate (SDS) (Hetherington et al., 2006). However, contaminants like chlorinated organic or high aromatic hydrocarbons are resistant to microbial attack and they are degraded either slowly or not at all. The main advantage of using bioremediation techniques is that they are more economical than the traditional methods of incineration and some pollutants can be treated on site thereby reducing exposure

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risks for clean-up personnel and potentially wider exposure as a result of transportation accidents. Since bioremediation is based on natural attenuation it is considered more acceptable than other technologies (Glazer & Nikaido, 2007).

Besides this, earthworms can also be used to extract toxic heavy metals, including cadmium and lead, from solid waste from domestic refuse collection and waste from vegetable and flower markets. Three species of earthworm, *Eudrilus eugeniae*, *Eisenia fetida* and *Perionyx excavates* can be used to assist in the composting of urban waste and to extract heavy metals, cadmium, copper, lead, manganese, zinc, prior to subsequent processing. The process of vermicomposting in this way allows such waste materials to be remediated and the compost can be used subsequently in growing human food without the risk of accumulating heavy metals in crops (Kamarudheen et al., 2014).

2. FACTORS AFFECTING BIOREMEDIATION

The factors affecting bioremediation process include existence of a microbial population capable of degrading the pollutants; availability of contaminants to the microbial population; environment factors (soil type, temperature, pH and the presence of oxygen or other electron acceptors and nutrients).

2.1 Microbial Populations for Bioremediation Processes

Microbes are diverse in their habitat, they will adapt and grow at subzero temperatures, as well as extreme heat, desert conditions, in water, with an excess of oxygen, and in anaerobic conditions, with the presence of hazardous compounds or on any waste stream. Their main requirements are an energy source and a carbon source. Because of the adaptability of microbes they can be used to degrade or remediate environmental hazards. Aerobic bacteria recognized for their degradative abilities are *Pseudomonas*, *Alcaligenes*, *Sphingomonas*, *Rhodococcus* and *Mycobacterium*. These microbes degrade pesticides and hydrocarbons, both alkanes and polyaromatic compounds as they use the contaminant as sole source of carbon and energy (Vidali, 2001; Prescott, 2002). Anaerobic bacteria are not as frequently used for degradation as aerobic bacteria but some of them are used for bioremediation of polychlorinated biphenyls (PCBs) in river sediments, dechlorination of the solvent trichloroethylene (TCE) and chloroform. Ligninolytic fungi such as the white rot fungus *Phanaerochaete chrysosporium* have the ability to degrade an extremely diverse range of persistent or toxic environmental pollutants. They utilize the substrates such as straw, saw dust, or corn cobs.

Methylotrophs grow by utilizing methane for carbon and energy. The initial enzyme in the pathway for aerobic degradation, methane monooxygenase, has a broad substrate range and is active against a wide range of compounds, including the chlorinated aliphatic trichloroethylene and 1,2-dichloroethane (Glazer & Nikaido, 2007).

2.2 Environmental Factors for Bioremediation Processes

The growth and activity of the microorganisms must be stimulated to increase their population for bioremediation. It is achieved through 'bio-stimulation' that involves the addition of nutrients and oxygen to help indigenous microorganisms. These nutrients are the basic building blocks of life and allow microbes to create the necessary enzymes to break down the contaminants. All of them will need nitrogen,

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phosphorous and carbon for their growth (Prescott, 2002). Microbial growth and activity is affected by pH, temperature and moisture. Although microorganisms have also been isolated in extreme conditions, most of them grow optimally over a narrow range, so that it is important to achieve optimal conditions. Hydrocarbons are readily degraded under aerobic conditions, whereas chlorinated compounds are degraded only in anaerobic ones. To increase the oxygen amount in the soil it is possible to till or spurge air. In some cases, hydrogen peroxide or magnesium peroxide can be introduced in the environment. Soil structure can be improved by adding gypsum and organic matter (Prescott, 2002). Nowadays, there are four main biological techniques used for treating soil and groundwater for stimulation of activity of indigenous microorganisms by the addition of nutrients, regulation of redox conditions, optimizing pH conditions; inoculation of the site by microorganisms with specific biotransforming abilities; application of immobilized enzymes; and use of plants (phytoremediation) to remove or transform pollutants (Vidali, 2001; Gupta, 2012). In the specific methods used for bioremediating contaminated soil and water, landfarming, composting, intrinsic bioremediation and slurry bioreactor are included.

3. BIOREMEDIATION STRATEGIES

3.1 *In-Situ* Bioremediation

Bioventing encourages the *in-situ* biodegradation of POLs (petroleum-oil-lubricants) by providing oxygen to microorganisms in the soil. The system supplies oxygen by injecting air directly into the residual contamination. Bioventing uses low airflow rates to provide only enough oxygen to keep up microbial activity. Optimal flow rates maximize biodegradation as vapors move slowly through biologically active soil while minimizing volatilization of contaminants. A basic bioventing system includes a well and a blower, which pumps air through the well and into the soil (Lee *et al.,* 2006). Biopile treatment is a full-scale technology in which excavated soils are mixed with soil amendments, placed on a treatment area, and bioremediated using forced aeration. The contaminants are reduced to carbon dioxide and water. The basic biopile system includes a treatment bed, an aeration system, an irrigation/nutrient system and a leachate collection system. Moisture, heat, nutrients, oxygen, and pH are controlled to enhance biodegradation. The irrigation/nutrient system is buried under the soil to pass air and nutrients either by vacuum or positive pressure. The treatment time is typically 3 to 6 months (Wu *et al*., 2009).

3.2 *Ex-Situ* Bioremediation

These techniques mainly involve the excavation or removal of contaminated soil from ground. Land farming is a simple technique in which contaminated soil is excavated and spread over a prepared bed and periodically tilled until pollutants are degraded. The goal is to stimulate indigenous bio-degradative microorganisms and facilitate their aerobic degradation of contaminants. In general, the practice is limited to the treatment of superficial 10–35cm of soil. Composting is a process by which organic wastes are degraded by microorganisms, typically at elevated temperatures in the range of 55° to 65°C. The increased temperatures result from heat produced by microorganisms during the degradation of the organic material in the waste. In windrow composting, firstly, contaminated soils are excavated and screened to remove large rocks and debris (Blanca *et al.,* 2007; 2008).The soil is transported to a composting pad with a temporary structure to provide containment and protection from weather extremes. Amendments (straw,

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alfalfa, manure, agricultural wastes and wood chips) are used for bulking agents and as a supplemental carbon source. Soil and amendments are layered into long piles, known as windrows. The windrow is thoroughly mixed by turning with a commercially available windrow turning machine. Moisture, pH, temperature and explosives concentration are monitored. At the completion of the composting period, the windrows are disassembled and the compost is taken to the final disposal area. Biopiles are a hybrid of land-farming and composting. These are typically used for treatment of surface contamination with petroleum hydrocarbons. They are a refined version of land farming that tends to control physical losses of the contaminants by leaching and volatilization. Biopiles provide a favorable environment for indigenous aerobic and anaerobic microorganisms. Here engineered cells are used for construction of aerated compost piles (Fahnestock *et al.,* 1998). Bioreactors/ slurry reactors/ aqueous reactors are used for *ex situ* treatment of contaminated soil and water. It involves the processing of contaminated solid material (soil, sediment, sludge) or water through an engineered containment system. Slurry bioreactor creates a three-phase (solid, liquid and gas) mixing condition to increase the bioremediation rate of soil bound and water-soluble pollutants as a water slurry of the contaminated soil and biomass (usually indigenous microorganisms) capable of degrading target contaminants. In general, the rate and extent of biodegradation are greater in a bioreactor system than *in situ* or in solid-phase systems because the contained environment is more manageable and hence more controllable and predictable.

The first patent for a biological remediation agent was registered in 1974, being a strain of *Pseudomonas putida* (Prescott *et al.,* 2002) that was able to degrade petroleum. In 1991, about 70 microbial genera were reported to degrade petroleum compounds and almost an equal number has been added to the list in the successive two decades. These organisms belong to at least 11 different prokaryotic divisions (Glazer *et al.,* 2007).

4. NOVEL BIOREMEDIATION METHODS

4.1 Plasma Incineration

A novel method developed and used recently for treatment of wastes is plasma incineration or plasma assisted gasification. It uses plasma that causes the volatilization of solid waste materials under anaerobic conditions. The plasma generates a huge amount of energy which otherwise cannot be produced by nuclear fission/fusion. Under such extreme conditions, waste materials get decomposed and oxidized partially to harmless innocuous products like carbon monoxide, hydrogen and water. During this process the organic matter of waste is converted into synthetic gas called S*ynGas* while inorganic fraction is converted into an inert vitrified glass and thus no ash is left to be land-filled. The major advantages of this technology are that it reduces the production of exhaust gas and thus lessens the air pollution; toxic materials produced are entrapped and encapsulated thereby making easier and safer to handle; and finally equipment is compact so it takes a minimum space for large disposal wastes (Amin et al., 2012).

4.2 Pyrolysis Technology

Another recently developed method for bioremediation is Pyrolysis technology (developed by Energystics Technologies, Ltd). This method involves the use of electromagnetic waves (EM). Direct and concentrated electromagnetic waves are allowed to fall on solid, liquid or gaseous waste. This technology directly

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couples electromagnetic energy with a target material to produce heat. When EM waves fall on the target, it absorbs energy producing temperature which is above the melting or vaporization temperature of target waste material. Such a high temperature causes the disassociation of strong molecular bonds in waste materials. This technology requires only a relatively small energy input because the technology does not utilize conductive medium. In order to demonstrate the effect of this technology on animal tissues, pyrolysis of beef carcass was done which resulted in complete dematerialization of the tissue leaving no residues or smoke. The major advantages of Pyrolysis technology are that it produces instantaneous but controllable heating and releases no harmful emissions (Shepera, 2004; Jones et al., 2004).

4.3 Conditioning

Conditioning is done to enhance the characteristics of bio-solids for their further processing. There are many conditioning technologies like ultrasonic degradation, chemical degradation, enzyme addition, electro-coagulation and biological cell destruction. These processes modify the inorganic and organic characteristics of waste which is critical to other processes (Hetherington et al., 2006).

4.3.1 Ultrasonic Degradation

This is the first step of the conditioning process. Solid wastes are subjected to acoustic waves to attain extremely high temperatures and pressures within biosolids. This result in the complete destruction of microbial cells due to shear stresses produced as a result of explosion of gas bubbles. This process is adjustable to high frequency and low frequency waves. The major advantages of this technique is that it causes an increase in rate of cell disruption, decrease in anaerobic digestion time, thereby reducing sludge quantity and increases the biogas production (Hetherington et al., 2006).

4.3.2 Chemical Cell Destruction

This process ensures disruption of the cell membrane of microorganisms in waste activated sludge process for the improved efficiency of anaerobic digestion and amount of biogas. The waste material is treated with caustic soda for about one hour. This causes the weakening of cell membrane of microorganisms and also decreases the viscosity of solution. For industrial scale treatment, MicrosludgeTM (Biocell) is used for this purpose. It uses industrial-scale high pressure homogenizer which causes a sudden and enormous pressure drop responsible for causing lysis of microbial cell in the sludge. This sludge is then liquefied, mixed with primary sludge followed by anaerobic digestion to produce biosolids and biogas (Hetherington et al., 2006).

4.3.3 Enzyme Conditioning

Enzyme conditioning is done with the help of microbes (both aerobic and anaerobic) that produces specialized enzymes (usually an enzyme mixture with specific nutrients like humic acids, amino acids) which degrade organic materials converting them into carbon dioxide and water. This method increases the dewaterability of biosolids and also reduces odours during digestion process (Hetherington et al., 2006).

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4.3.4 Electro-Coagulation

This is the recently developed method where electric current is used to increase the rate of anaerobic digestion of waste material. The electric current so produced dissolves an anode (sacrificial anode) and releases chemically reactive aluminum into the wastewater stream. The positively charged aluminum ions attract very fine negatively charged ions and particles towards them resulting in agglomeration. As a result, the agglomerated particles increase in size and settle down due to their increased weight (Hetherington et al., 2006; Amin et al., 2012).

4.3.5 Biological Cell Destruction

This process involves the use of a chemical agent that possesses strong oxidation properties. The agent weakens the cell wall of bacteria. These processed bacteria are then returned back to the activated sludge process where they decompose into carbon dioxide and water.

4.3.6 Thermophilic Fermentation

This method utilizes the microorganisms to increase the rate of digestion process at high temperatures. Thus sewage sludge and other waste residuals are converted into a fertilizer grade product. Another technology called ThermoMaster™ process has been developed in which auto-heated aerobic digestion is operated at a relatively short residence time (30 hours) to maximize the production of single-cell protein using an influent waste material as a substrate. The solids thus obtained are dried and pelletized (Hetherington et al., 2006; Amin et al., 2012).

4.4 Anaerobic Digestion

The first phase consists of volatile fatty acid digester where digestion takes place at around 35°C. In the next phase, the temperature is further increased in a thermophilic range of 50-56°C where further digestion takes place under anaerobic conditions. In the final phase, the heating is slowed down till temperature reaches around 35°C. Recent advancements in technology have led to the use of ozone treatment for anaerobic digestion. The biosolids are first subjected to anaerobic digestion and then are passed into a reaction tank where they are exposed to low levels of ozone. Studies have shown that only 0.06g of ozone per gram of dissolved solids is sufficient to destroy the biological activity of digested biosolids. The ozone treated waste material is then sent to thickening tank followed and back to digester in which both ozone treated and non-ozone treated waste materials are mixed. After this, waste material is either sent for dewatering or for ozone treatment (Vranitsky & Lahnsteiner, 2002).

4.5 Electro Dewatering of Waste Material

Conventional dewatering technologies, such as centrifuges, belt filter presses, and rotary vacuum filters, are not effective methods for treating sewage sludge with high water content. Alternatively, waste material is subjected to direct current (DC) which in the initial stage causes particles to migrate to the oppositely charged electrode (electrophoresis). Due to electro-osmosis, cake formation occurs as ions migrate to the oppositely charged electrode. This technology is suitable for use in combination with conventional filtration (Kim et al., 2014).

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4.6 Electroacoustic Dewatering

This is another method of dewatering waste where both electric field and ultrasound waves are used to increase the efficiency of dewatering. Electric field is used for electrophoresis and electro-osmosis whereas acoustic waves (sound waves) are used in maintaining electrical continuity throughout the waste material. The main advantage of using acoustic waves is that they decrease specific energy consumption, increases the filtration rate and helps to keep cathode clean (Hetherington et al., 2006).

4.7 Mechanical Freeze Thaw

In this process, the sludge is frozen followed by crushing and thawing under natural conditions. During freezing, the chemical bonds in the sludge are altered thus making removal of water easier.

The treated sludge is then subjected to conventional sludge dewatering equipment (Amin et al., 2012).

4.8 Hydrothermal Oxidation

This technology is also known as 'Supercritical water oxidation'. In this process, the water is heated and pressurized above the critical point at 374°C and 3,191 pounds per square inch (psi). Consequently, the solubility of organic substances and oxygen into water is significantly increased. The main advantage of this technology is that it decomposes organic matter completely and produces a high quality effluent (Amin et al., 2012).

4.9 Drying of Waste Material

Drying is done to remove the water from the waste residues collected from both domestic, industrial and agriculture waste. This reduces weight and volume with high solid percentage. Drying can be through direct or indirect heating. The different methods of drying are discussed below:

4.9.1 Belt Drying

It involves the use of two or more slow moving belts that are arranged in series. The air is supplied around the belts. The dewatered sludge is spread in the form of a thin layer on a belt to increase the surface area (Amin et al., 2012).

4.9.2 Direct Microwave Heating

This process involves the use of high-efficiency multi-mode microwave system which is specifically designed to remove moisture. It removes water and pathogens from dewatered sludge. This process is highly automated and can dry waste materials having an initial moisture content of 85% to a final moisture content of 10%. This technology has an added advantage that it has the capacity of about 100% pathogen without any change in its nutrient content (Amin et al., 2012).

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4.9.3 Flash Drying

This method can dry waste material to up to 90% or more solids. Sludge containing water is fed into a centrifuge machine where dewatering takes place and its solid content reach up to 25% concentration. This material is then discharged into thermal stage as a fine-grained spray. Once the particles of solid waste enter thermal cyclone chamber, they get dried up instantly. These dried particles are then taken out of the chamber in a fraction of second, with the help of sweep gas. The sweep gas, drawn through ventilator fan is reheated in hot gas generator before re-entering into dryer loop (Amin et al., 2012).

4.9.4 Fluidized Bed Dryer

After the wet cake is formed, it is passed through the fluidized bed dryer where it comes into contact with already dried granules. Indirect heating is then applied by means of tubular heat exchangers that are immersed in fluidized layer of solids. The major advantages of this technology are that it can dry the sewage material up to 90% solid content (Amin et al., 2012).

4.9.5 Chemical Drying

This process involves the drying of solids through chemical reaction. The dewatered waste material is allowed to react with ammonium salts or anhydrous ammonia and concentrated organic acids like sulphuric acid and phosphoric acid. The reaction of ammonia with organic acids generates heat and during this reaction sulphates and phosphates are produced. The heat produced from the reaction is utilized for drying of waste materials. During this process, hard granular materials are produced that can be mixed with plant nutrients to raise their nutritive value (Amin et al., 2012).

5. BIOREMEDIATION BY GENETIC ENGINEERING

Biotechnological technique like genetic engineering can be used for improving bioremediation of heavy metals and organic pollutants. Transgenic plants and associated bacteria can be used to create genetically modified organisms for bioremediation by over-expressing the genes responsible for their metal-binding proteins or peptides that in turn enhance their heavy metal accumulation and/or tolerance. Furthermore transgenic algae and microorganisms mutated with bioluminescence genes can be used in bio-monitoring of organic and inorganic pollution. There are several approaches for the construction of GEMs for bioremediation application. First approach is the identification of organisms suitable for modification with the relevant genes, *e.g*. aquatic microbes can be used to develop GEMs for bioremediation of aquatic sources. The use of such organisms would avoid the supplementation of nutrients to the inoculated environment, thereby reducing the costs incurred and maintenance required. Scientists have developed *Anabaena sp.* and Nostoc *ellipsosporum* by the insertion of linA (from *P. paucimobilus*) and fcbABC (from *Arthrobacter globiformis*) respectively (Kulshreshtha, 2013). The second approach is the pathway construction, extension and regulation. GEMs have developed by improving existing catabolic pathways or to extend these pathways to degrade some more compounds which are not possible to degrade by using wild strain. The complete catabolic pathway may be encoded by a single microorganism, or by a consortium of microorganisms, each performing one or more of the stages of bioremediation of

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xenobiotics. In this way, constructed GEMs possess the degradation capabilities of different microbial communities due to the alteration of gene sequences which further improve the efficiency and efficacy of the catabolic pathways (Kulshreshtha, 2013). Third approach is modification of enzyme specificity and affinity, e.g. *E. coli* strain is genetically modified to express a hybrid gene cluster for the degradation of trichloroethylene (TCE). Fourth approach is bioprocess development, monitoring, and control, and bioaffinity, bioreporter, sensor applications for chemical sensing, toxicity reduction, and end point analysis. Bioluminescence can be easily detected and do not require expensive devices, exogenous addition of chemicals or co-factors. Further, GEMs possess chemical sensors that allow the monitoring of contaminant bioavailability rather than just contaminant presence. Bioluminescence producing GEMs also help us to understand the spread of microbes in the polluted area and end point of the bioremediation (Kulshreshtha, 2013).

In a recent study, a *Pseudomonas putida* strain was genetically engineered for 1,2,3-trichloropropane bioremediation. 1,2,3-Trichloropropane (TCP) is a toxic compound that is recalcitrant to biodegradation in the environment. Attempts to isolate TCP-degrading organisms using enrichment cultivation have failed. Finally, the dehalogenase gene (dhaA31) was cloned and was introduced into the genome of strain MC4 using a transposon delivery system. Growth of the resulting engineered bacterium, *P. putida* MC4-5222, on TCP was observed, and all organic chlorine was released as chloride. The results demonstrated the successful use of a laboratory-evolved dehalogenase and genetic engineering to produce an effective, plasmid-free, and stable whole-cell biocatalyst for the aerobic bioremediation of a recalcitrant chlorinated hydrocarbon (Samin et al., 2014). Transgenic *Chlamydomonas* cells express metallothionin, a metal binding protein. These cells grow at normal rates in the presence of lethal concentrations of cadmium accumulating five-fold more cadmium compared to wild type cells. Mixotrophy in cyanobacteria and microalgae can provide many competitive advantages over bacteria and fungi in degrading persistent organic pollutants (POPs) (Subashchandrabose *et al.,* 2013).

6. BIOREMEDIATION USING EARTHWORMS (VERMICULTURE)

Earthworms could be used to extract toxic heavy metals, including cadmium and lead, from solid waste from domestic refuse collection and waste from vegetable and flower markets. Three species of earthworm, *Eudrilus eugeniae*, *Eisenia fetida* and *Perionyx excavates* are used to assist in the composting of urban waste and to extract heavy metals, cadmium, copper, lead, manganese, zinc, prior to subsequent processing. The process of vermicomposting in this way allows such waste materials to be remediated and the compost can then be used in growing human food without the risk of accumulating heavy metals in crops. Studies have shown that up to three-quarters of the various heavy metals can be removed by the worms from solid waste. The *E. eugeniae* species is the most effective worm at remediating solid waste and producing rich compost. Research has shown that the heavy metal content of such waste can be reduced to levels significantly below the permissible safe limits. The mechanism involved is because of worm's digestive system that is capable of detaching heavy metal ions from the complex aggregates between the ions and humic substances in the waste during the process of rotting. Various enzyme-driven processes leads to assimilation of the metal ions by the worms so that they are locked up in the organism's tissues rather than being released back into the compost as worm casts. The separation of dead worms from compost is a relatively straightforward process allowing the heavy metal to be removed from the organic waste (Science Daily, 2012). In a recent research, phenol bioremediation potential of Earthworms

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was studied. Earthworms were maintained under proper growth conditions. Different concentrations of phenol ranging from 10ppm to 50ppm were taken for the assays. All the bioremediation assays were done in the soil with phenol dispersed in water and remediation rates were observed for 24 hours, 48 hours, 72 hours, 96 hours and 120 hours. The initial concentration of phenol was increased eventually and the rate of bioremediation was estimated using 4-amino anti-pyrine method. The phenol degradation activity of the gut microflora of the earthworm along with the soil microflora was also observed on a formulated media. The amount of phenol bioremediated was found higher in case of earthworm and not the microflora solely. It was found to be 30 ppm in 48 hours when the initial concentration was 50 ppm (Kamarudheen et al., 2014). In another study, the earthworms' capacity to remediate the quality of soils polluted with heavy metals (Zn, Cu, Mn, Pb) as a result of using the swine residual water in agriculture ($50\ m^3\ ha^{-1}$) was distinguished. The study has been conducted in a Chernozem (FAO System), in a culture of *Zea mays* L. The collected data consisted of soil analyses and tissue analyses to establish the heavy metal uptake by earthworm species. Determination of the heavy metal contents of soil has been realized on two depth intervals: 0-10 cm and respectively 10-20 cm, through the method of flame atomic absorption spectrometry. Earthworm extraction was done using formaldehyde according to the methodology in force at six months since the residual water has been applied on soil. Both for earthworm number and earthworm weight there were significant differences (<0.05) between the values recorded in controls and treatments, i.e. the earthworm number considerably increased in the variants fertilized with swine residual water and also the earthworm weight, which confirm the earthworm preference for the organic matter provided by the residual water. Also there were significant differences (<0.05) between the three analyzed earthworm species regarding the accumulation process of the investigated microelements and, among them, *Lumbricus rubellus* showed in its tissues the lowest concentration of microelements and *Allolobophora rosea* the highest concentrations. There were also much lower concentrations of the studied microelements in the earthworm tissues as compared with the adjacent soil in all analyzed species, and among them there was recorded the lowest content of heavy metals in *Lumbricus castaneus*. This aspect and also the fact that this species has been the best represented as numeric abundance in the experimental soil confirm the good capacity of this species to tolerate the presence of the heavy metals in soil and to metabolize them with the soil ingestion within the feeding process. The results of this study support the idea claiming the earthworms' bioremediator potential of the soils polluted with heavy metals, as a possibility to restore their quality by maintaining in appropriate levels the earthworm populations in the agricultural lands. These findings also come to sustain the specialization of this role on earthworm species (Iordache & Borza, 2012).

7. DUCKWEEDS FOR PHYTOREMEDIATION

Effective wastewater treatments through conventional methods that rely on heavy aeration are expensive to install and operate. Duckweeds are capable of recovering or extracting nutrients or pollutants and are an excellent candidate for bio-remediation of wastewaters. Such plants grow very fast, utilizing wastewater nutrients and also yield cost effective protein-rich biomass as a by-product. Duckweeds being tiny surface floating plants are easy to harvest and have an appreciable amount of protein (15%–45% dry mass basis) and a lower fiber (7%–14% dry mass basis) content. Besides nutrient extraction, duckweeds have been found to reduce total suspended solids, biochemical oxygen demand (BOD), and chemical oxygen demand in wastewater significantly. Depending on the initial concentrations of nutrients, duckweed-covered

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systems can remove nitrate at daily rates of 120–590 mg NO_3^- m^{-2} (73%–97% of initial concentration) and phosphate at 14–74 mg PO_4m^{-2} (63%–99% of initial concentration). Removal efficiencies within 3 days of 96% and 99% have been reported for BOD and ammonia. Besides several genera of duckweeds (*Spirodela, Lemna, Wolffia*), other surface-floating aquatic plants like water hyacinth (*Eichhornia*) are well known for their phyto-remediation qualities (Gupta & Prakash, 2014). Duckweed culture is an eco-friendly approach of phyto-remediation which will not only help in free-of-cost extraction of nutrients in the form of protein-rich biomass but also bio-remediate the ponds, lakes, and other water bodies and make them a more suitable water resource for aquaculture. Wastewater-duckweed-carp poly-culture makes the perfect integrated package for pollution control and re-use of recovered nutrients. Moreover, in view of increased pressure on land over the years for production of food and fodder (due to ever increasing population, urbanization, industrialization, etc.), utilization of an alternate resource for the purpose makes sense. In this direction, duckweed culture holds ample scope not only for high quality food production through aquaculture but also releasing pressure on the underground water resources (Gupta & Prakash, 2014).

8. MUSHROOMS AND BIOREMEDIATION

Spent mushroom compost is generated as waste after the harvesting of mushroom crop. Recently, it is proposed to call it as "post mushroom substrate" because it is not really spent and has many uses. The composition of spent mushroom substrate varies depending on the type of mushroom to be cultivated and substrate used. It is proved as an excellent source of humus, although much of its nitrogen content has been used up by the growing mushrooms. It remains a good source of general nutrients (N, P, K along with trace elements) which makes it well suited for supporting plant growth (Svoboda et al., 2002). Mushrooms are found to possess the two basic abilities of biodegradation and bioaccumulation for the bioremediation of waste. Biodegradation ability of mushrooms is due to the presence of many enzymes involved in the degradation of pollutants and solid waste residues though the extent and safe level is unknown. Moreover, mushrooms are known for the bioaccumulation of pollutants or heavy metals from the habitat in which they are growing. Mushroom possesses a very effective mechanism that enables them to take up some trace elements from the substrate. Heavy metal accumulation ability of mushroom has been studied by the number of authors (Kala & Svoboda, 2000; Svoboda et al., 2002; Kulshreshtha & Sharma, 2014).

9. BIOREMEDIATION OF PLASTIC AND RUBBER BY ENDOPHYTIC FUNGI

The massive and rapid accumulation of plastic and rubber waste is a problem that cannot be ignored. While there has been an enormous boom in synthetic polymer production, methods of treating these materials after disposal have not been able to keep up. Since several types of plastic and rubber contain the same chemical bonds that are found in natural plant polymers, specific attention is given to the ability of endophytes, organisms that grow symbiotically inside plants, to degrade synthetic plastic and rubber. The endophytic fungus *Pestalotiopsis microspore* has previously been identified in the degradation of the plastic polyester polyurethane. This fungus secretes a small enzyme that is responsible for plastic degradation (Legaspi & Elaine, 2014).

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10. BIOREMEDIATION THROUGH MICROBES: GROWTH PARAMETERS

Most bioremediation systems work under aerobic conditions, but recalcitrant molecules are degraded by microbial organisms only under anaerobic conditions. Bioremediation depends on various parameters: nature of pollutants, soil structure, pH, moisture content and hydrogeology, nutritional state, microbial diversity of the site, temperature and oxidation-reduction (redox-potential) (Dua *et al.,* 2002). In bioremediation processes, microorganisms use the contaminants as nutrient or energy sources (Tang *et al.,* 2007). Bioremediation activity through microbes is stimulated by supplementing nutrients (nitrogen and phosphorus), electron acceptors (oxygen), and substrates (methane, phenol, and toluene), or by introducing microorganisms with desired catalytic capabilities (Ma *et al*., 2007; Baldwin *et al.,* 2008). Plant and soil microbes develop a rhizospheric zone which is also used as a tool for accelerating the rate of degradation or to remove contaminants. In addition to this, aromatic compounds are persistent environmental pollutants that are widely distributed in the biosphere due to anthropogenic activities. These compounds are highly toxic to living beings; therefore, many of them have been listed as priority pollutants by Environmental Protection Agency. Microbial degradation has emerged as an effective technology to remove these compounds from environment. Many microbial enzymes such as oxygenases, dehalogenases, reductases, hydroxylases and dehydrogenases are involved in the degradation of these environmental pollutants. Among them, oxygenases are the key enzymes for aerobic biodegradation of aromatic compounds because they are involved in the initial reaction of degradation and also catalyze the ring cleavage of the aromatic compounds which is the essential step for the complete mineralization of these compounds (Arora *et al.,* 2009). Oxygenases catalyze insertion of one or two oxygen atoms into the substrates. Two classes of oxygenases have been identified based on number of oxygen atom used in the oxidation: mono-oxygenases and dioxygenases. Monooxygenases incorporate one atom of the oxygen into the substrate whereas dioxygenases add both atoms of the oxygen (Arora *et al.,* 2009).

11. PROS AND CONS OF BIOREMEDIATION

Bioremediation is a natural process and is therefore perceived by the public as an acceptable waste treatment process for contaminated material such as soil. The residues for the treatment are usually harmless products and include carbon dioxide, water and cell biomass. Theoretically, bioremediation is useful for the complete destruction of a wide variety of contaminants. Many compounds that are legally considered to be hazardous can be transformed to harmless products. This eliminates the chance of future liability associated with treatment and disposal of contaminated material. In bioremediation, there is no need of transferring contaminants from one environmental medium to another and the complete destruction of target pollutants is possible. Bioremediation can also be carried out on site, without causing a major disruption of normal activities. This also eliminates the need to transport quantities of waste off site and the potential threats to human health and the environment that can arise during transportation. Bioremediation can prove less expensive than other technologies that are used for clean-up of hazardous waste (Dua et al., 2002).

The major con of bioremediation is that the process is limited to those compounds that are biodegradable. Not all compounds are susceptible to rapid and complete degradation. There are some concerns that the products of biodegradation may be more persistent or toxic than the parent compound. Biodegradation process is a natural phenomenon and is highly specific. There are major site factors required

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for complete biodegradation that include the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients and contaminants. Biodegradation is often difficult to extrapolate from bench and pilot-scale studies to full-scale field operations. Research is needed to develop and engineer bioremediation technologies that are appropriate for sites with complex mixtures of contaminants that are not evenly dispersed in the environment. Contaminants may be present as solids, liquids, and gases. Bioremediation often takes longer than other treatment options, such as excavation and removal of soil or incineration. Regulatory uncertainty remains regarding acceptable performance criteria for bioremediation. There is no accepted definition of "clean", evaluating performance of bioremediation is difficult, and there are no acceptable endpoints for bioremediation treatments (Dua et al., 2002).

12. CONCLUSION

Environmental pollution affects quality of life and environmental ecosystem. Since decades, many attempts are being done to reduce environmental pollution. Among these attempts bioremediation is one of the good remedial techniques. Bioremediation technique involves the use of microorganisms to reduce the toxicity of harmful wastes and heavy metals from contaminated wastes water. Some other methods of bioremediation are by using earthworms (vermiculture), duckweeds and mushrooms, thermophilic fermentation or by genetically engineered microbes including endophytic fungi for biodegrading plastic wastes. Recently bioremediation is used in combination with other physical and chemical methods such as plasma incineration, pyrolysis, conditioning, electro-coagulation, electroacoustic dewatering, mechanical freeze thaw, hydrothermal oxidation, flash drying, microwave heating, fluidized bed dryer, and chemical drying. Bioremediation can thus be proved as a problem solving approach in the field of solid waste by detoxifying wastes. Due to its cost effectiveness and lesser environmental impact, it offers an attractive and more conventional clean-up technology.

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Chapter 76
Modeling of Polypropylene Modified Bitumen Mix Design Results Using Regression Analysis

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ABSTRACT

This study investigates the effects of mixing Polypropylene waste plastics in the bituminous mix for the design of Flexible Pavement. Since, obtaining Marshall Test results from the bituminous mix is time-consuming, so if the practitioners measure the values of stability and flow by mechanical testing, other computations can be done by applying simple mathematical calculations. So, this study carried out stability and flow tests on different specimens made with varying bitumen and polypropylene plastic content. From the initial test results, the optimum bitumen and plastic contents are found. Further, the test results obtained from Marshall Test are modelled by identifying various input variables, which are various physical properties of the mix such as plastic content, bitumen content, air voids and unit weight. The regression modeling framework is adopted in this study to predict the Marshall stability and flow value. Since the developed models have yielded good results, these can be effectively used in parameter estimation, and thus aids the future researchers.

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INTRODUCTION

The rapid growth in industrialization coupled with population growth has led to enormous rise in production of various types of wastes worldwide. In a recent study concerning the top 20 countries that have dumped the most plastic waste into the oceans, India (at 12th) is one of the worst performers. It has dumped up to 0.24 million tons of plastic waste into the ocean every year, thereby polluting the natural resources. One recent study (2014-15) reported that approximately 8 kg of waste plastics dumped by the each individual in India. These plastic wastes are needed to be recycled, if not, it gets disposed by the available waste disposal techniques like Land filling and Incineration. Though these techniques have been widely in use but these too have certain impacts on the environment which are discussed as under.

Land filling refers to a process of disposal wherein the waste materials are buried in a specific area that is situated far away from the city. This process has certain impacts on the environment like affecting water recharge, reducing soil microbial activity, and also it leads to drainage and water line clogging. Such clogging in turn leads to production of gases such as methane, which affects Greenhouse effect. Also, land availability for filling is a major point of concern. Further, Incineration refers to a process of burning the wastes above 700°C. Incineration of polymers like polypropylene, polystyrene, etc. evolves gases like CO_2, CO etc. which in turn causes global warming, pollution. If polyvinyl chloride mixes with the waste, it results in the production of Chlorine, HCl and sometimes Dioxin which is a carcinogenic and a poisonous gas. In fact, this process requires scientific monitoring and it can accentuate pollution problems, if strict standards aren't being enforced.

Since both landfilling and incineration have certain negative impact on the environment. Under these circumstances, an alternate use for the waste plastics is the need of the hour. Several investigations in India and many other countries have revealed that properties of bituminous mixes can be enhanced to meet the present requirements of pavement with the inculcation of certain additives in bituminous mixes. These additives are termed as "Bitumen Modifiers" and the bitumen that is premixed with these modifiers is termed as "Modified Bitumen". Modified bitumen is expected to provide higher strength and durability depending upon the type of additives used and modification process involved. The time period of next renewal is expected to be extended by 50 percent in case of surfacing with modified bitumen in comparison to normal period specified for conventional bituminous mix. Certain Performance analysis studies undertaken under the protection of Central Road Research Institute, New Delhi; Highway Research Station, Chennai; Rubber Board, Kottayam (Kerala); Ministry of Road Transport and Highways, New Delhi; Kerala Public Works Department and Gujarat Engineering Research Institute, Vadodara have revealed that the usage of Modified Bitumen in construction as well as maintenance of bituminous roads is quite cost effective, when life-cycle cost is taken under consideration.

Plastic waste when mixed with hot bitumen, it melts to form an oily coat over the aggregate and the mixture is laid over the road surface as similar as a normal tar road. The plastic waste can be effectively used as a binder material in flexible pavements. They may be used to enhance strength, enhance fatigue resistance to deformation and thus makes the pavements more durable. Plastic coated bitumen can result in higher stiffness than that of conventional bitumen, but without undergoing a large increase in flexibility.

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PAST RESEARCH ON MODIFIED BITUMEN

Since last few decades, researchers are focussing more on usage of modified bitumen in pavement construction. In this process, modifying the properties of bitumen by using waste plastics is gaining importance due to its nature of enhancing the strength and economical mix. Kumar et al. (2003) reported that there occurs comparatively plastic bitumen blends less than that of neat bitumen, as observed during thin film oven test, which in turn controls the premature failure of a flexible pavement due to cracking. There is significant improvement in the indirect tensile strength and a considerable reduction in the rutting characteristic of the modified mixes prepared as compared to conventional ones. It has been reported that the Marshall Stability value of modified bituminous mix modified with 5 per cent of waste plastics increased by about 23%. Vasudevan et al. (2006) reported that even though Plastics-Modified-Bitumen (PMB) improves the quality of the roads and associated properties, the process (dry or wet process of mixing) of using these plastics for blending decides the enhanced strength of the bonding. Dry process is far better process than wet process. They also reported that polymer will not be leaching out after laying the road using waste plastic coated aggregate bitumen mix. Rajmane et al (2007) conducted a study on effective utilization of waste plastic in construction of flexible pavement for improving their performance and have found out that Plastic roads would be a boon for India's hot and extremely humid climate, where temperatures frequently cross 50°C and torrential rains create havoc, leaving most of the roads with big potholes.

Vasudevan (2007) has emphasized upon the use of dry process of mixing over wet process because bitumen binding strength in the Wet process is less compared to Dry Process. Reena Gupta et al (2011) worked upon a novel approach to improve road quality by utilizing plastic waste in road construction and have found out that no toxic gas is produced as the maximum temperature to coat the aggregates is 150-160 degree C in technology related to dry process of plastic waste utilization. Jalal J. Jafar (2015) under his study for Utilisation of Waste Plastic in Bituminous Mix for Improved Performance of Roads has proposed a mechanism to explain the effect of the chemical additives on the increase in the stiffness of the bituminous mixture which attributed to an increase in the bonding forces between the aggregates and the bitumen. Further, SerkanTapkın et al (2009) conducted a study on Prediction of Marshall test results for polypropylene modified dense bituminous mixtures using neural networks and have found that the addition of polypropylene fibres results in the improved Marshall Stabilities and Marshall Quotient values.

Though the above studies reported substantial literature on utilization of waste plastics for modifying the properties of bitumen in order to enhance the strength of the bitumen mix, still there is a scope for investigating the changes in properties of bitumen after adding the polypropylene plastics.

PROVEN CASE STUDIES ON UTILIZATION OF MODIFIED BITUMEN IN INDIA

Several live projects have been reported in India for effective utilization of modified bitumen in flexible pavement design. Some of the studies are reported in this section.

1. Laboratory studies have been carried out at the Centre for Transportation Engineering of Bangalore University, in which the waste plastic was used as an additive to heated bitumen in different proportions (ranges from zero to 12% by weight of bitumen). The results from these laboratory inves-

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tigations reported that, the addition of waste plastic of about 8.8% by weight of bitumen, helps in substantially enhancing the strength, stability, fatigue life and many other desirable properties of bituminous mix, even during adverse water-logging conditions. The addition of 8.0% by weight of waste plastic for the preparation of modified bitumen resulted in a saving of 0.4% bitumen by weight of the mix or about 9.6% bitumen per cubic meter of bituminous mix.

2. In the state of Tamil Nadu, length of roads around 1000 m in various stretches have been constructed using waste plastic as an additive to bituminous mix under the scheme of "1000 km Plastic Tar Road", and it was found that, the performance characteristics of all the road stretches are satisfactory.
3. The performance characteristics of the road stretches constructed using waste plastic in Karnataka are also found to be satisfactory.

The construction of roads using Waste Plastics in the above states was based on the guidelines developed by Bangalore University and College of Engineering, Madurai. However, standard specifications are not available on the use of waste Plastic in Bituminous road Construction. So in this regard, IRC was specially requested by NRRDA for the preparation of such Guidelines for enabling the construction of these Rural Roads under PMGSY using Waste Plastic. In order to facilitate the development of Guidelines for this, an Expert Group was appointed by NRRDA for the preparation of interim guidelines for the usage of plastics which would be sent to IRC for further approval.

It is quite evident that the above studies reported on utilizing the waste plastics in flexible pavement design, but most of these studies followed the laborious experiments for calculating the Marshall Stability and flow value. Hence, by keeping this in mind, this study concentrated on developing a model for the estimation of Marshall Stability, so that the model results serves as an aid for future researches in this area.

GOALS AND OBJECTIVES

Motivation behind the study is too efficiently utilise the waste plastic in a constructive and a cost effective manner so that it can be beneficial to the society. Main objective of the current project work are:

1. To identify the optimum proportion of waste plastic that is to be added in the bituminous mix for getting the desired strength.
2. To compare the experimental results with the conventional pavement details and perform the analysis.
3. To prepare a statistical model to analyse the parameter dependencies and generate a relation between dependent and independent variables.
4. To assess the extent with which various physical properties of constituents affecting the stability and flow.

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METHODOLOGY

Plastic Aggregate Bitumen Interaction Model

The shredded plastics when sprayed over the hot aggregate melt and spread over the aggregate in the form of a thin coating at the aggregate surface. When the aggregate is heated around 160°C, the coated plastics remains in the softened state. Over these coated aggregates, hot bitumen (heated at 160°C) is added. The added bitumen then spreads over the aggregate. At this temperature both the coated plastics and bitumen are in the liquid state and so are capable of easy diffusion at the interphase. This process is further aided by the increase in contact area. These observations may be reported as follows- Waste polymers i.e. polypropylene are hydrocarbons with long chains and the bitumen is a complex mixture of asphaltenes and maltenes that are also long-chain hydro carbons. When bitumen gets mixed with plastic coated aggregate a percentage of bitumen diffuses through the plastic layer and binds with aggregates. The plastic layer has already strongly bonded with aggregates. During this phase, a three-dimensional internally cross linked network structure develops between bitumen constitutes and polymer molecules. Therefore, the bonding becomes stronger and removal of bonded bitumen becomes hard.

Materials Used in the Study

1. **Aggregate:** Stones passing through 12.5mm sieve and retained on 10mm sieve; Sand.
2. **Bitumen:** VG30 Bitumen Grade.
3. **Waste Plastic:** Polypropylene (PP) waste plastic in the shredded form (2.36 to 4.75mm).

Process Description

As indicated in the flow chart, the primary step is the material procurement wherein the different constituents like aggregates, bitumen and waste plastic are collected in the desired form and quantity. Aggregates composed of stones that are retained on 10 mm sieve but passed through 12.5 mm sieve; and sand. The grade of bitumen used in this study is VG30 grade bitumen (i.e. 50-70 penetration grade bitumen). Polypropylene waste plastics have been used in shredded form (2.36mm to 4.75mm). Shredding of these plastics has been done in a plastic factory in Vellore. The choice of Polypropylene types of waste plastics was based on the availability, suitability and its efficient properties. Not all types of waste plastics can be used in flexible pavement design. Plastics like Polyvinyl chloride can't be used for this purpose due to the release of harmful gases on its applications.

The next step is to find out various physical properties of the constituents, using laboratory testing. These physical properties of constituents are tested in order to assure that the selected constituents are suitable pavement design. Following this, Marshall Specimens have been prepared varying the percentages of plastic and bitumen and then the results obtained from the modified bitumen have been compared with that of conventional bitumen. The main objective of this test was to obtain the Optimum contents of Bitumen and Plastic in order to get the desired strength. Post analysis have been done using Regression modeling that yielded a relationship between parameters and this relationship was then used to perform sensitivity analysis.

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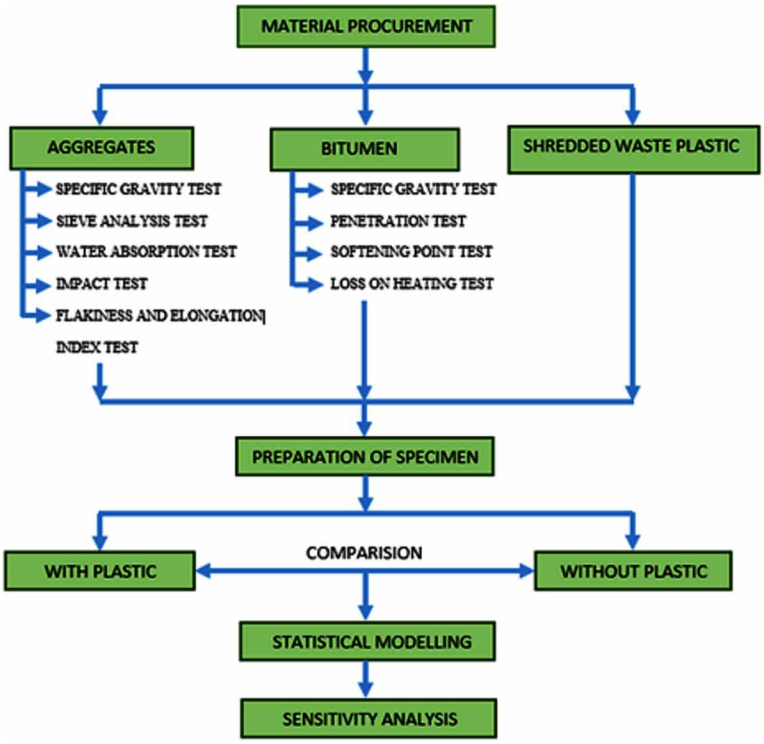
Figure 1. Shows the detailed methodology which was followed in this study



Processes for Manufacturing Bituminous Mix Using Waste Plastic

There are two different processes namely, dry process and wet process used for design of bituminous mix flexible pavement. However, this study uses the dry Process of Mixing due to following reasons:

1. Advantage of Dry Process Over Wet Process:
    a. Harmful gases are not evolved in dry process as no burning of the plastic waste is done.
    b. Dry process is simple while the wet process is complex.
    c. Ease in handling in case of dry process as the dealing is done with the normal dry shredded waste plastic unlike the wet process wherein the dealing is done with the hot molten waste plastic.
    d. Unlike wet process, there is no risk of uneven mixing of molten plastic and bitumen and thus there will not be any loose binding of aggregates.

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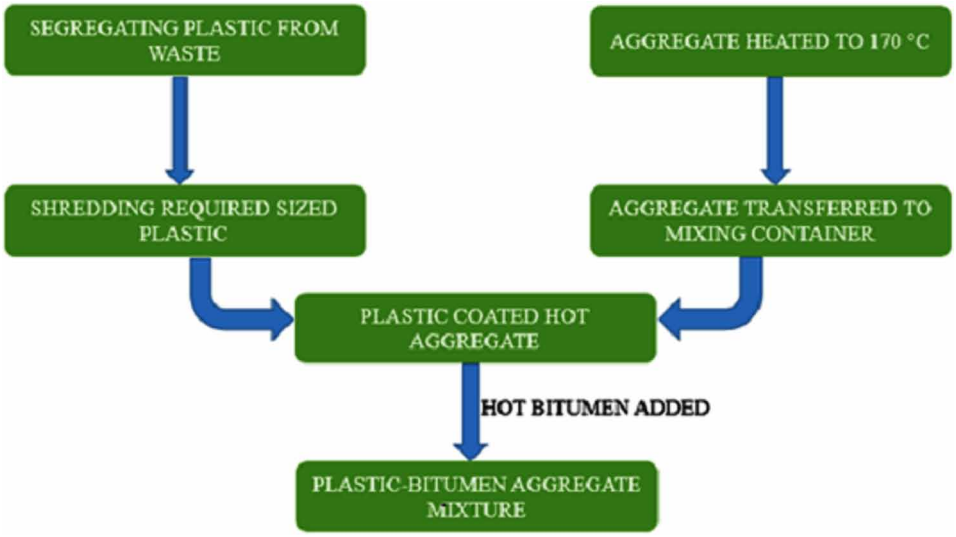
Figure 2. Shows the steps involved in dry process of mixing



EXPERIMENTATION

Tests on Aggregates

1. **Specific Gravity:** It is the ratio of the weight of a given volume of aggregate to the weight of an equal volume of water. It is considered to be a measure of strength or quality of the material. Stones having low specific gravity are generally weaker than those with higher specific gravity values. The specific gravity of coarse aggregates used is found out to be 2.5g/cc. The specific gravity of aggregates normally used in road construction ranges from about 2.5 to 3 with an average of about 2.68.
2. **Sieve Analysis Test:** A sieve analysis (or gradation test) is a laboratory procedure used to assess the particle size distribution (also called gradation) of a granular material. The size distribution is of critical importance as it is an indicative to the way the material performs when in use.
3. **Water Absorption Test:** Aggregate absorption is the increase in mass due to water in the pores present in the material. Aggregate absorption is a useful quality measure because:
   a. High values of water absorption can indicate non-durable aggregate.
   b. Absorption also indicates the amount of asphalt binder the aggregate will absorb.
   c. Water absorption is found out to be 0.9%. According to IRC, the maximum allowable limit of water absorption for any aggregate used in highway construction should not exceed 2% by weight of aggregates.
4. **Impact Test:** Aggregates should be tested for their resistance against shock or impact loads caused due to the movement of vehicles at high speeds. Aggregate impact strength is found out to be 11.64%. According to IRC, the maximum allowable aggregate impact is 30%.

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5. **Flakiness and Elongation Test:** Flakiness index is the percentage by weight of flaky aggregates whose least thickness is less than 0.6 times the average size of the aggregate. Elongation index is the percentage by weight of aggregates whose longest dimension is more than 1.8 times the average size of aggregate. The combined flakiness and elongation index is found out to be 24%. According to IRC, the maximum allowable combined flakiness and elongation indices is 30%.

Tests on Bitumen

1. **Specific Gravity:** It is the ratio of mass of a given volume of bitumen to the mass of an equal volume of water, both taken at a specified temperature. The specific gravity of pure bitumen ranges from 0.97 to 1.02. The specific gravity of bitumen used is found out to be 0.99 g/cc. According to Indian standards (BIS), minimum specific gravity of paving bitumen at 27℃ shall be 0.99.
2. **Penetration Test:** Penetration value is a measure of hardness or consistency of bituminous material. It is the vertical distance penetrated or traversed by the point of a standard needle into the bituminous material under specific conditions of load, temperature and time. This distance is measured in one tenths of a millimetre. This test is an indicative of consistency of bitumen. Higher penetration values implies softer grade bitumen. Penetration value of bitumen used is found out to be 52.
3. **Softening Point Test:** The Softening Point of bitumen is the temperature at which the substance attains particular degree of softening. As per IS: 334-1982, it is the temperature in ℃ at which a standard ball passes through a sample of bitumen in a mould and falls through a height of 2.5 cm, when heated under glycerine or water at specified conditions of test. The binder should possess sufficient fluidity before its application in road uses. The softening point is an indicative of the temperature up to which a bituminous binder should be heated for various road-use applications. The softening point of bitumen used is found out to be 35℃.
4. **Loss on Heating Test:** The loss in weight (exclusive of water) of bituminous materials when heated is called loss on heating of bituminous materials. The loss on heating is observed to be 0.4%. According to IRC, the maximum allowable value of matter loss by heating should not exceed 1%.

Tests Results

From the tests conducted, it can be obtained that the given materials meet the desired specifications and hence can be successfully used in further study.

Table 1. The test results for bitumen tests

S. No.	Tests	Results	Permissible Limits	IS Code
1	Specific gravity test	0.99 g/cc	0.97 g/cc to 1.02 g/cc	IS 1202
2	Penetration test	52	50 to 70 (VG30)	IS 1203
3	Softening point test	35℃	40℃ to 50 ℃	IS 1205
4	Loss on heating test	0.4%	≤ 1%	IS 1212

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Table 2. The test results for aggregate tests

S. No.	Tests	Results	Permissible Limits	IS Code
1	Specific gravity test	2.5 g/cc	2.5 to 3.0	IS 2386 Part II
2	Sieve analysis test	Uniformly graded	-	IS 2386 Part I
3	Water absorption test	0.9%	≤ 2%	IS 2386 Part III
4	Impact test	11.64%	≤ 30%	IS 2386 Part IV
5	Flakiness and elongation index test	24%	≤ 30%	IS 2386 Part I

Marshall Test

This test is used to measure the resistance to plastic deformation of a compacted cylindrical specimen of bituminous mixture when the specimen is diametrically loaded at a deformation rate of 5 cm per minute. The Marshall stability of a mix is defined as the maximum load carrying capacity of the specimen at a standard test temperature of 60°C. The flow value is defined as the deformation that the test specimen undergoes during loading up to the maximum load. Flow is measured in 0.25 mm units. In this test, Marshall Specimens are prepared varying the bitumen and the plastic content in order to find the optimum bitumen content and the optimum plastic content. All the samples are prepared as per the guidelines given in ASTM D1559. Cylindrical moulds (10cm diameter and 7.5cm in height) consisting of a base plate and collar extension have been used.

Steps of Design

1. Determine the proportion of coarse and fine aggregates to be used as per the desired grading.
2. Determine the specific gravity of each of the constituents: aggregate constitutes, bitumen and the waste plastic.
3. Prepare the trial mixes by varying the bitumen and the plastic content.
4. Measure the specific gravity of compacted specimens.
5. Perform the stability test on specimens.
6. Compute percentage air voids, voids filled with bitumen and voids in mineral aggregates for each specimen.
7. Record the optimum bitumen content and the optimum plastic content from the data obtained.
8. Evaluate the design and perform analysis.

Formulae Used in the Study

$$G_m = \frac{W_a}{W_a - W_w} \tag{1}$$

where,

G_m = Bulk or actual specific gravity (g/cc)

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W_a = Weight of compacted specimen in air (Kg)
W_w = Weight of compacted specimen in water (Kg)

$$G_t = \frac{W_1 + W_2 + W_3 + W_b}{\frac{W_1}{G_1} + \frac{W_2}{G_2} + \frac{W_3}{G_3} + \frac{W_b}{G_b}} \quad (2)$$

where,

G_t = Theoretical specific gravity (g/cc)
W_1 = Weight of coarse aggregate (Kg)
W_2 = Weight of fine aggregate (Kg)
W_3 = Weight of filler (Kg)
W_b = Weight of bitumen in total mix (Kg)
G_1 = Specific gravity of coarse aggregate (g/cc)
G_2 = Specific gravity of fine aggregate (g/cc)
G_3 = Specific gravity of filler (g/cc)
G_b = Specific gravity of bitumen (g/cc)

$$V_v = \frac{G_t - G_m}{G_t} * 100 \quad (3)$$

where, V_v = Percent air voids in the mix (%)

$$V_b = \frac{\frac{W_b}{G_b}}{\frac{\sum W}{G_m}} * 100 \quad (4)$$

where, V_b = Percent bitumen content in the mix (%)

$$VMA = V_v + V_b \quad (5)$$

where, VMA = Volume of voids in the mineral aggregates (%)

$$VFB = \frac{V_b}{VMA} * 100 \quad (6)$$

where, VFB = Voids filled with bitumen (%)

Tables 3-6 show the Marshall Test results.

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Table 3. Marshall test results for specimens without plastic

Bitumen Content (%)	Air Voids (%)	VFB (%)	VMA (%)	Unit Weight (Kg/ m3)	Stability (Kg)	Flow (mm)
3	8.988	53.258	19.229	2378	1120	2.73
4.5	4.886	72.701	17.898	2442	1210	2.92
6	3.196	82.746	18.524	2446	780	4.94
7.5	2.882	86.291	21.023	2416	670	7.37

Table 4. Marshall test result for specimens modified with 3% of polypropylene plastics

Bitumen Content (%)	Air Voids (%)	VFB (%)	VMA (%)	Unit Weight (Kg/ m3)	Stability (Kg)	Flow (mm)
3	9.226	52.899	19.588	2356	1210	2.94
4.5	5.567	66.152	18.319	2416	1430	3.5
6	3.298	82.094	18.418	2450	940	4.82
7.5	2.996	85.688	20.933	2424	730	7.2

Table 5. Marshall test result for specimens modified with 4.5% of polypropylene plastics

Bitumen Content (%)	Air Voids (%)	VFB (%)	VMA (%)	Unit Weight (Kg/ m3)	Stability (Kg)	Flow (mm)
3	9.896	50.564	20.018	2354	1240	3.89
4.5	7.015	64.546	19.786	2391	**1450**	3.57
6	4.219	78.795	19.896	2421	950	4.02
7.5	3.159	85.201	21.346	2412	790	4.91

Table 6. Marshall test result for specimens modified with 6% of polypropylene plastics

Bitumen Content (%)	Air Voids (%)	VFB (%)	VMA (%)	Unit Weight (Kg/ m3)	Stability (Kg)	Flow (mm)
3	10.998	46.987	21.016	2329	1230	3.27
4.5	7.777	60.244	20.746	2355	**1370**	3.58
6	5.886	71.821	20.888	2384	890	4.04
7.5	4.998	77.177	21.899	2378	650	5.5

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Result Analysis and Discussion

Based on the Marshall Test Results, variation of unit weight, air voids, VFB, VMA, stability and flow for each of the plastic content, is plotted against Bitumen content and the analysis is performed as under.

It is quite evident from the Figure 3 and Figure 7 that at the lower bitumen contents, unit weight as well as the stability are less but with the increase in bitumen content, these values attains a peak and afterwards reflects a decreasing trend. At lower bitumen contents, specimens fails at lower loads because the quantity of bitumen mixed with aggregates is not sufficient enough to develop efficient bonding between aggregates to withstand applied loads. On the other hand, specimens with excess quantity of bitumen also fail at smaller loads due to a thick film of bitumen at the interface of aggregates which prevents the effective transmission of loads onto the aggregates. Hence, only at a particular quantity of bitumen (optimum content), maximum values of unit weight as well as Marshall Stability are observed.

From the Figure 4 and Figure 5, it can be observed that as the bitumen content increases, Voids filled with bitumen also increases which in turn leads to decrease in air voids present in the specimen as more and more bitumen tends to fill empty voids in the specimen.

As the bitumen content increases, a slight variation is observed in the values of Voids in mineral aggregates, as reflected in Figure 6. This variation attributes to the adjustment of mineral aggregates with the increased bitumen content.

Flow is the measure of the deformation caused due to applied loads. From the Figure 8, it is observed that the flow increases with the increase in bitumen content because of the presence of a thick bitumen film around aggregates that prevents strong aggregate interlocking.

From the Figure 7, as the maximum stability occurs at 4.5% bitumen content, therefore the Optimum Bitumen Content is 4.5%. Then a curve is plotted between stability and plastic content at the optimum bitumen content and it is observed from the Figure 9 that the maximum stability value occurs at 4.5% plastic content, so the optimum plastic content is 4.5%.

Figure 3. Variation in unit weight with bitumen content

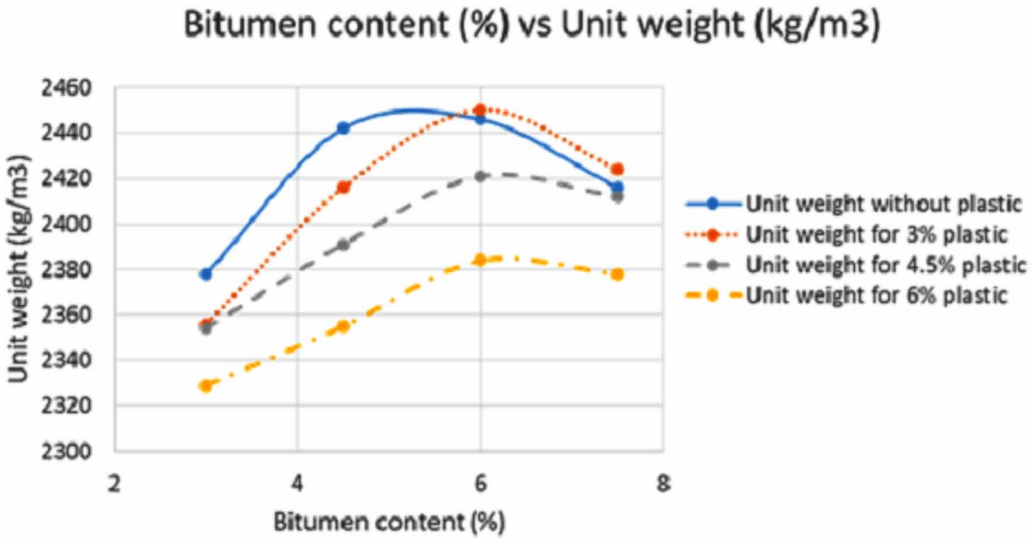

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Figure 4. Variation in VFB with bitumen content

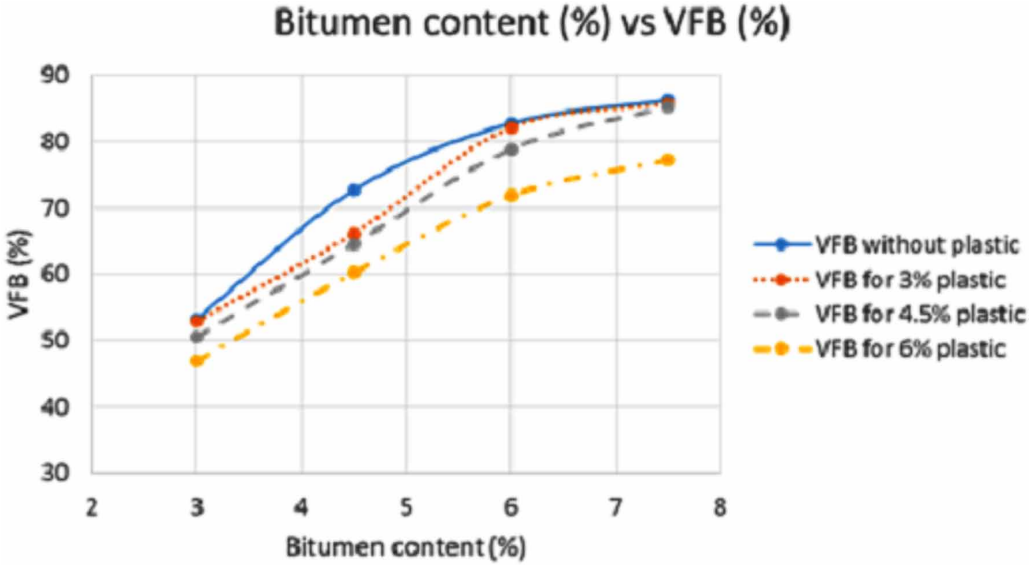
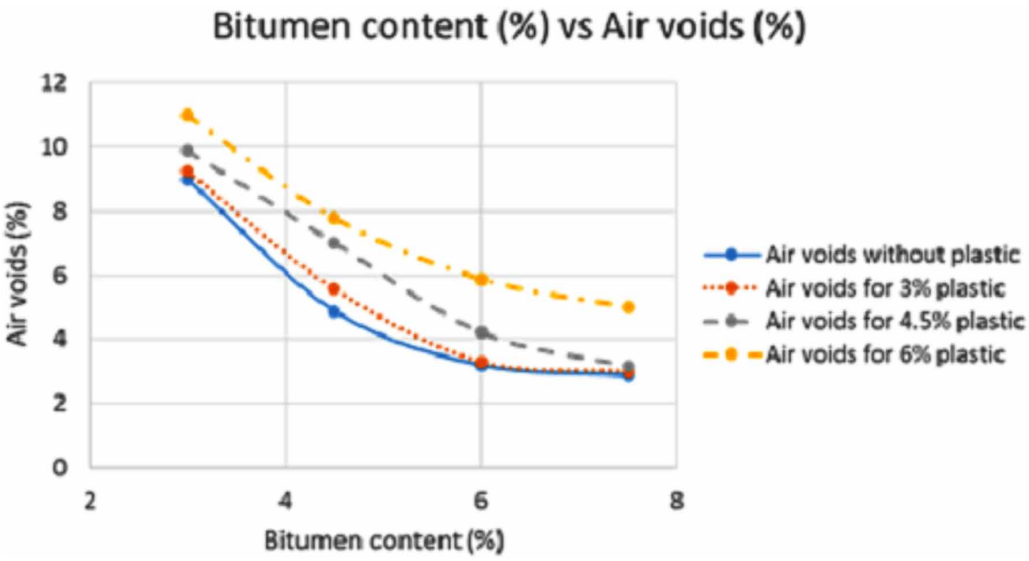


Figure 5. Variation in air voids with bitumen content



MODELLING OF MARSHALL STABILITY AND FLOW

Regression Analysis

Regression analysis is the technique employed here to model Marshall Stability and flow. Regression analysis is a statistical tool in order to assess the relationship between variables. Regression analysis is widely used for prediction and forecasting purposes. Usually, it is used to ascertain the causal effect of

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Figure 6. Variation in VMA with bitumen content

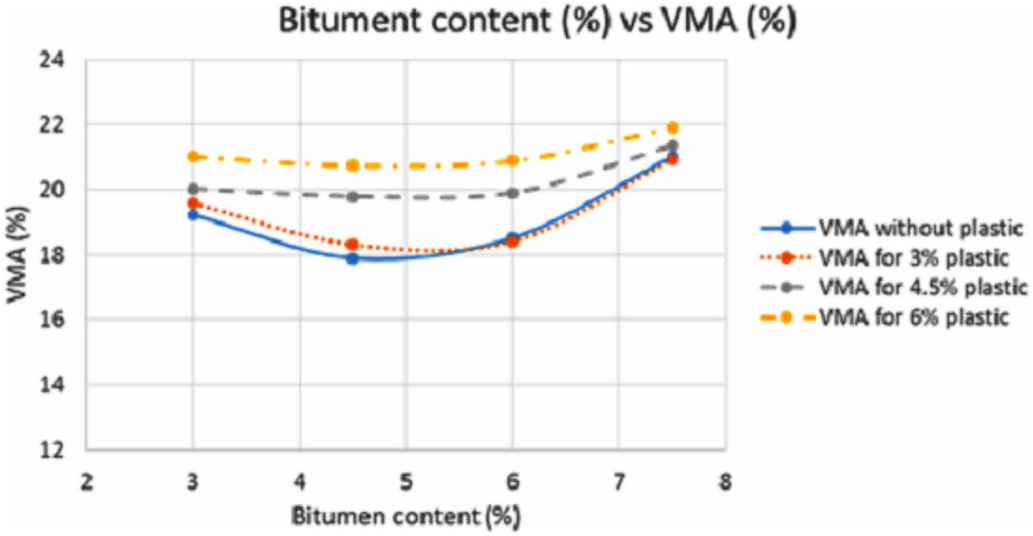
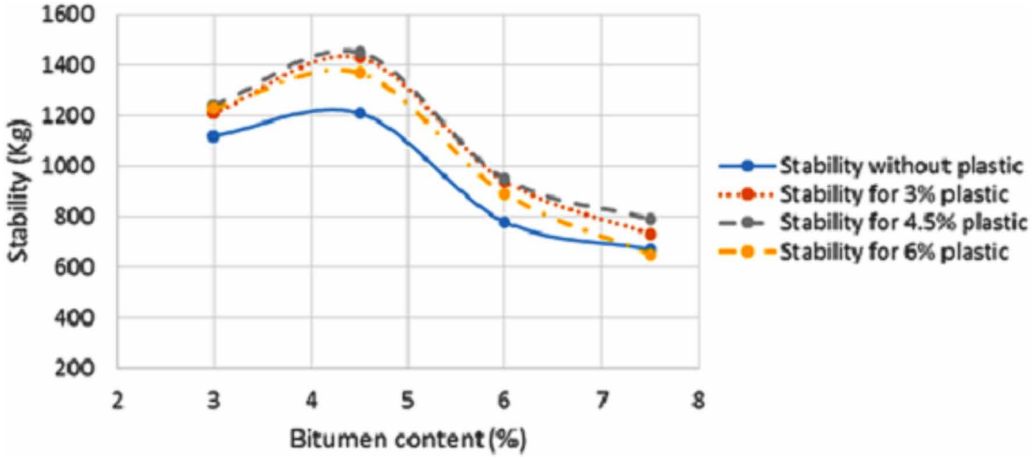


Figure 7. Variation in stability with bitumen content



one variable upon another, as for example, the effect of increase in price of a commodity upon its demand, or the effect of change in money supply upon inflation rates. To explore such issues, the data on the underlying variables of interest is assembled and regression is employed to predict the quantitative effect of the causal variables upon the variable that those variable influence. This analysis is also used to assess the 'statistical significance' of the estimated relationships, i.e. the degree of confidence that the true relationship is close to the estimated relationship.

This study inculcated the use of 'Multiple Linear Regression model' since there are multiple parameters involved. Multiple regression analysis is a powerful tool used for predicting the unknown value of a variable from the known value of two or more variables, also termed as 'predictors'.

More precisely, multiple regression analysis helps to predict the value of Y for given values of X_1, X_2, …, X_n.

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Figure 8. Variation in flow with bitumen content

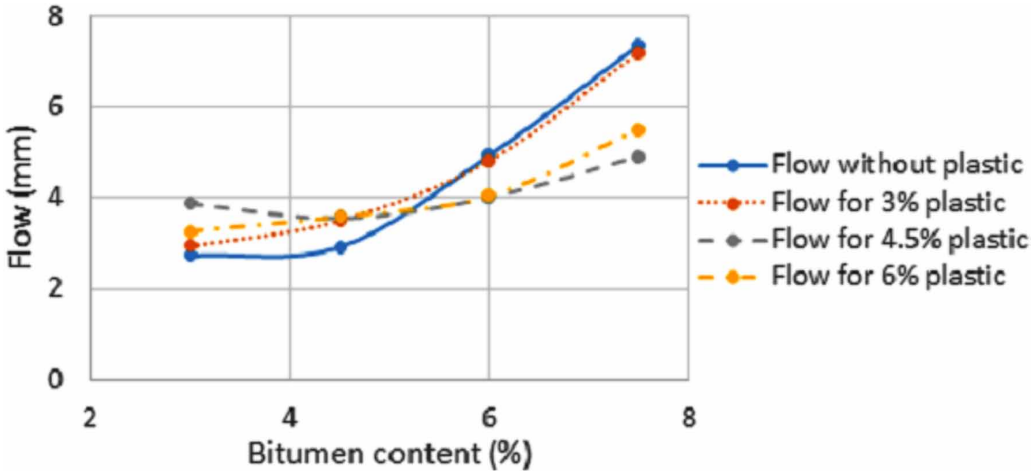
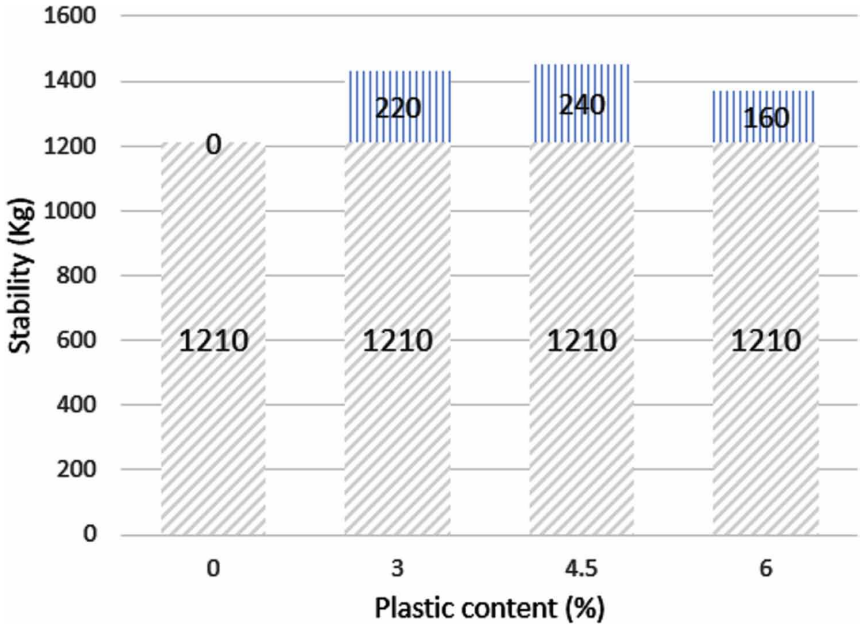


Figure 9. Variation in stability with plastic content



Dependent and Independent Variables

In multiple regression model, there is one dependent variable and two or more independent variables. A dependent variable is one whose value is to be predicted and the independent variables are those whose values are used for prediction. These independent variables are also referred to as 'exploratory' variables.

In general, a multiple regression equation of Y on X_1, X_2, …, X_n is of the form:

$$Y = b_0 + b_1X_1 + b_2X_2 + \ldots + b_nX_n \quad (7)$$

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where, Y = Dependent variable and X_i = Independent variables (where, i = 1, 2,….n).

Interpretation of Regression Coefficients

Here, b_0 is the intercept and b_1, b_2,….b_n are analogous to the slope in linear regression equation and are also termed as 'regression coefficients'. These could be indicated in similar way as slope. Thus, if b_i = 10, then it implies that Y will increase by 10 units if X_i increased by 1 unit. The appropriateness of the multiple regression model as a whole can be tested by using the t-test in the ANOVA (Analysis of Variance) table. A significant 't value' indicates a linear relationship between Y and at least one of the X's.

Test for Model Significance

In order to assess prediction ability of the developed regression equation, a good practice is to look upon 'Coefficient of Determination' (R^2 value). R^2 lies between 0 and 1. The closer is the value of R^2 to 1, the better is the developed model and its prediction.

In order to assess, if the independent variables chosen individually influences the dependent variable significantly or statistically, to test the null hypothesis that the relevant regression coefficient is zero; a t-test is required.

If the t-test of a regression coefficient is significant, it indicates that the concerned independent influences Y significantly while controlling for other independent variables.

Assumptions for Multiple Linear Regression

1. Multiple regression technique does not test if the data are linear. On the contrary, it proceeds by the assumption that the relationship between the Y and each of the X_i's is linear. Hence, it is a good practice to always look at the scatter plots of (Y, X_i), i= 1, 2,…,n. If any of the plots suggests non linearity, one must use a suitable transformation to attain linearity.
2. Another important assumption is the absence of multicollinearity i.e. the independent variables are not related among themselves. However, this can be tested by the computation of the correlation coefficient between each pair of independent variables.
3. Other assumptions include those of normality and homoscedasticity (i.e. the variance around the regression line is same for all values of the predictor variable (X_i)).
4. Multiple regression analysis is generally useful when one is interested in predicting a continuous dependent variable from a number of independent variables. In the case, the dependent variable is dichotomous, then the logistic regression should be used.

For this study, the dependence of Marshall Stability and Flow upon different variables is assessed. Herein, parameters are chosen based on the correlations between them i.e. there should be significant correlation between dependent and independent variables.

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Figure 10. The table of correlations between the parameters involved

		Plastic_content	Bitumen_content	Air_voids	VFB	VMA	Unit_weight	Stability	Flow
Plastic_content	Pearson Correlation	1	.000	.326	-.248	.625**	-.579*	.150	-.140
	Sig. (2-tailed)		1.000	.218	.354	.010	.019	.578	.604
	N	16	16	16	16	16	16	16	16
Bitumen_content	Pearson Correlation	.000	1	-.889**	.936**	.402	.577*	-.820**	.836**
	Sig. (2-tailed)	1.000		.000	.000	.123	.019	.000	.000
	N	16	16	16	16	16	16	16	16
Air_voids	Pearson Correlation	.326	-.889**	1	-.989**	.049	-.879**	.673**	-.694**
	Sig. (2-tailed)	.218	.000		.000	.857	.000	.004	.003
	N	16	16	16	16	16	16	16	16
VFB	Pearson Correlation	-.248	.936**	-.989**	1	.076	.819**	-.748**	.751**
	Sig. (2-tailed)	.354	.000	.000		.781	.000	.001	.001
	N	16	16	16	16	16	16	16	16
VMA	Pearson Correlation	.625**	.402	.049	.076	1	-.498*	-.421	.449
	Sig. (2-tailed)	.010	.123	.857	.781		.050	.104	.081
	N	16	16	16	16	16	16	16	16
Unit_weight	Pearson Correlation	-.579*	.577*	-.879**	.819**	-.498*	1	-.405	.398
	Sig. (2-tailed)	.019	.019	.000	.000	.050		.120	.126
	N	16	16	16	16	16	16	16	16
Stability	Pearson Correlation	.150	-.820**	.673**	-.748**	-.421	-.405	1	-.785**
	Sig. (2-tailed)	.578	.000	.004	.001	.104	.120		.000
	N	16	16	16	16	16	16	16	16
Flow	Pearson Correlation	-.140	.836**	-.694**	.751**	.449	.398	-.785**	1
	Sig. (2-tailed)	.604	.000	.003	.001	.081	.126	.000	
	N	16	16	16	16	16	16	16	16

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 7. Gives the regression model for stability

Variables	Coefficients	Standard Error	t Stat
Constant	20.31579	7.381433	2.752283
Plastic Content	0.042882	0.008386	5.113287
Bitumen Content	-0.40602	0.063546	-6.38942
Air voids	-0.25557	0.067728	-3.77347
Unit weight	-0.00659	0.002793	-2.36032

Note: For a variable to be significant, the corresponding absolute t stat value should be greater than 2.131 i.e. the t stat value corresponding to 95% Confidence level and 15 degrees of freedom.

The multiple regression equation for stability is:

Stability = 20.31579 + 0.042882 * (Plastic Content) – 0.40602 * (Bitumen Content) – 0.25557 * (Air Voids) – 0.00659 * (Unit Weight)

The multiple regression equation for flow is:

Flow = -4.701225554 – 0.208519892 * (Plastic Content) + 1.344323532 * (Bitumen Content) + 0.476473045 * (Air Voids)

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Figure 11. The regression plot for stability

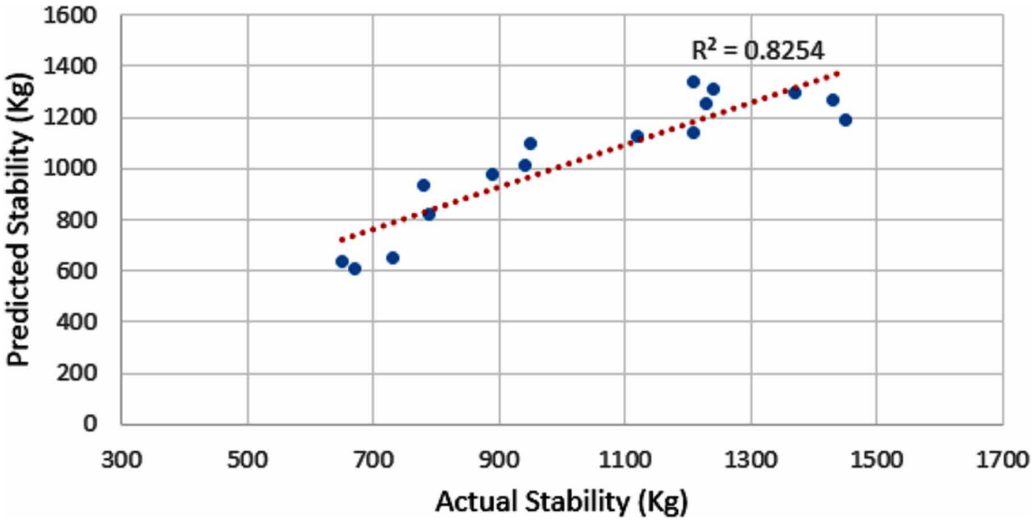
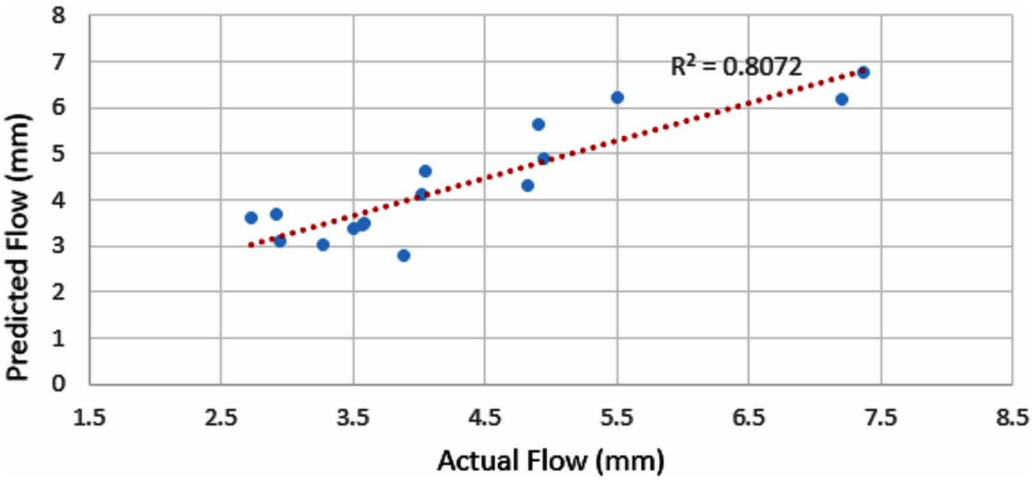


Table 8. The regression model for flow

Variables	Coefficients	Standard Error	t Stat
Constant	-4.701225554	1.320386109	-3.560493043
Plastic Content	-0.208519892	0.044535712	-4.682082834
Bitumen Content	1.344323532	0.157989793	8.508926473
Air voids	0.476473045	0.106305775	4.482099337

Note: For a variable to be significant, the corresponding absolute t stat value should be greater than 2.131 i.e. the t stat value corresponding to 95% Confidence level and 15 degrees of freedom.

Figure 12. Shows the regression plot for flow



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CONCLUSION AND FUTURE SCOPE OF WORK

Conclusion

This study explored the effective utilization of waste plastic (polypropylene) as a binder replacement in the flexible pavement design as the obtained results in case of plastic additive reflects higher strength values as compared to the conventional bituminous mixes. A considerable improvement in other pavement properties is also observed. The use of waste plastics not only helps in enhancing pavement properties, it also aids in curbing the waste disposal. The key findings of the study are the optimum bitumen content of 4.5% and the optimum plastic content of 4.5%. The modelling approach adopted in the study has produced quite satisfactory results. This regression modelling also shows that Bitumen Content is the most significant parameter affecting Marshall Stability and Flow. Since the Coefficient of determination values of both the models are close to 1, which means the predicted results are quite closer to the actual results, so the developed models can be efficiently used for prediction. These models can aid future researchers to obtain the Marshall Stability and Flow values directly from the physical properties of materials which will save a lot of time spent in conducting cumbersome and laborious tests.

Future Research Directions

The findings and the approach from this study can be extended in exploring the efficient utilization of other types of waste plastics as well as the other types of wastes from different industries. Besides, due to availability of less data, the study is limited to Regression modelling, however with the increase in the number of data collection, further advanced modelling can also be adopted to model Marshall Stability and flow which may validate the results more accurately.

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Chapter 77
Reverse Logistics in the Electronics Waste Industry

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ABSTRACT

Recently, due to the rapid world population growth, decreasing of natural resources and raw materials, increasing environmental awareness, interesting for wasting raw materials, using produced products more efficiently, and reusing of sources is rapidly increasing. Nowadays, reverse logistics as an important business strategy for profitable and sustainability is becoming important. The effective implementation of reverse logistics gives companies a competitive advantage in sectors. Due to mentioned reasons firms intend to incorporate reverse logistics activities such as the recovery, remanufacturing, recycling or disposal. Reverse logistics has become increasingly important as a profitable and sustainable business strategy. Therefore, more and more manufacturers have adapted the practice of recovering value from returned products and integrate product recovery activities into their processes. The electronic industry is one of the fastest growing manufacturing industries and the main purpose of this chapter is to explore the opportunities for waste returns within this sector.

INTRODUCTION

In recent years, the number of studies about the recovery of the limited sources increase due to rapid population growth, climatic changes, depletion of natural resources and increasing environmental awareness. Reverse Logistics (RL) has become attractive because of raised consumer awareness, the green laws performed by the governments, request of the producers to reduce the cost with lower business capital, increasing of the usage of the recovered containers, increasing of the request of services, raising the quality, re-production, fixing etc. (Sengul, 2009). Also today in many countries, the firms are responsible to collect some of their products back. According to the regulation came into force in Germany in

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1991, the firms are responsible to recycle 65%-70% of the packages of their products. Beside the legal sanctions, the consumers are being more conscious every day and they are being more sensitive on environment. Also the green image has become an important selling factor for companies. That situation is forcing many firms to find new ways of recycling and recollecting of their products. The effective implementation of reverse logistics provides competitive advantage to the firms in their sector. Also the economic factors like needing less source of the recycled products compared to new ones is playing an important role in the development of the products. Because of this situation, a logistic network providing an affective flow only to forward is not enough, also proper reverse logistic structures are needed to be installed which provide possibilities for flowing of used and improved products for recovering of the used products. Today, the reverse logistic activities are gaining more importance for the firms as a profitable and sustainable business strategy. Because of that kind of reasons, the firms include the reverse logistics into their systems which provides recovering of the products from customers into the production, recycling of them or disposing of them. The goal is minimizing the harmful impacts of the used products to the environment, reducing the productions cost, gaining competitive advantage, etc. gaining maximum benefits from the used products. Because of all these reasons, the firms like Fuji Film, Hewlett–Packard, IBM Europe and Xerox, etc. have already voluntarily performed participation in the activities of recycling (Qiang et al., 2013).

In the reverse logistics network, there are more units than the ones in the forward logistics network. Supply chain including reverse flow, in addition to all the elements of advanced logistics network, includes 3rd party logistics companies which perform duty as demand point, secondary markets, disposal centers, collecting points and more. Transportation of the products from the customers to the facilities, determination of the settlements for submitting them in to the market from here, plants and the quantity of the products which will be carried, which recycling strategy will be performed to the products are important decisions which must be taken.

In this work, first, the basic elements of the reverse logistics issue have been explained. In pursuit of explaining the activities of the firms performed in the scope of the reverse logistics by the firms, the decision steps and the reasons of the application. At the last part, general characteristics of electrical and electronic goods, their recycling processes under the reverse logistics are described.

REVERSE LOGISTICS

Definition and Scope of the Reverse Logistics

There are different descriptions for “Reverse Logistics” in literature. First terms about the concept of the reverse logistics in scientific literature have been used in 1970’s years by Guiltinan and Nwokoye (1974) and Ginter and Starling (1978). In 1980’s years, the reverse logistics is described as reverse flow opposite to the forward flow in the traditional supply chain, in other words it is described as a wrong way flow (De Brito, 2004). The Council of Logistics Management, has made it first know description on the reverse logistics in 1990’s years. The concept of reverse logistics is “planning, execution and control processes for the purpose of recovering the information of the raw materials, the inventories still in process, the finished goods from the point of consumption to the point of production or disposing them in the correct way” (Yongsheng & Shouyang, 2008).

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Pohlen and Farris (1992) has described "RL" as the flow of the product in distribution channel from the consumers to the producers. The RL description of the USA Reverse Logistics Executive Council is as so: "planning, execution and control processes for the purpose of regaining the information of the raw materials, the in-process inventory, the finished goods from the point of consumption to the point of production or disposing them in a proper way." The reverse logistics activities have an important share in all logistic activities (Rogers & Tibben-Lembke, 1999). Stock (1992) has described the reverse logistics as "the role of the logistics in product returns, reducing sources, recovery, material substitution, reusing of the materials, disposing and burning of the wastes, repairing and remanufacturing. The reverse logistics can be examined from different points. Basically it can be characterized in three ways and the proper description can be defined according to this (Fleischmann, 2000):

1. The reverse logistics is being accepted as the growing element of the logistic systems. The supply chains had been traditionally described as an one-way structure. As Ganeshan et al. (1998) has described as "the most know description of the supply chain is the system consist of the supplier, producer, retailer and costumers. In this system the product flowing is from the supplier to the customer and the information flowing in both ways." The reverse logistics is described as reverse product flowing. But in the organizations it is seen that the material flow is not characterized to below and the logistic network is developed. In this situation, it is not proper to separate the reverse flows from the whole picture.
2. The reverse logistics is being considered as the flow of second products which of original usage has been completed or not able to used. For this reason, the reverse logistics is mentioning about planned and really realized derivatives of past usage. The goal is increasing the economic value of the products released by disposing or some regaining forms.
3. The reverse logistics term is mainly described the receiver side. So, we can say that the reverse logistics is a special situation of the supply logistics.

The reverse logistics is the process of efficient and effective planning, execution and control processes of the second material stores, flow of the material and concerned information for the purpose of regaining of the material or disposing in a proper way in the opposite way to the traditional supply chain (Fleischmann et al., 2001). The reverse logistics is a fact helping to the green logistic activities. Performing scientific methods on the problems about environment and developing methods which will solve these problems has become important for many disciplines, and modern logistic management has taken place in the disciplines concerned with the environment (Erol et al., 2006). The reverse logistics is concern with the remanufacturing, recycling or safe disposal processes of the products moving to the start point of the supply chain because of various reasons (Erol et al., 2008) (see Table 1).

The traditional production cycle has been started to be described as recovery production cycle after entering of the reverse logistics logic into the business structure. In summary, descriptions of RL, has been changed over time from the emphasis of reverse flowing to environmental responsibility. As a result, all these definitions and passed time show us that the reverse logistics has extended its area (De Brito, 2004).

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Table 1. Products and the waste samples created by them

Product	Potential Waste
Box Drink	Aluminum box
Detergent	Plastic-based box or package
Ball-point pen	Plastic or metallic sections
Cellphone	Integrated circuit, wire, battery, plastic
Computer	Wire, monitor, cabinet, led
Newspaper	Used paper
Automobile	Engine, metallic parts, tire, plastic, wire

THE ACTIVITIES OF THE REVERSE LOGISTICS

The activities concern with reusing in the scope of the reverse logistics include the following steps:

Collecting

All activities are concerned with the collection of the used products or materials from the consumers for processing and transporting to the place for processing (Fleischmann et al., 2000; Sengul, 2009). For example, collecting back the used carpets from carpet sellers and the used photocopy machines from the users (Fleischmann et al., 2000). The collecting process includes obtaining, transporting and storage of the used products (Kumar & Malegeant, 2006). The collecting work is done by the own facilities of the establishment or the 3rd part providers (Demirel and Gokcen, 2008a).

Inspection and Sorting

Includes the activities determining whether the collected products are proper to re-usage or not and how they can be used. Performing inspection and sorting activities on collected products for several recovery and disposing operations before sending to the producer firm. These operations are also called as local eliminating. The local eliminating is being performed to at the collecting point of the returned products. In this step the decision between reprocessing of the product or disposing is taken (Flesichmann, 2000). In the stage of inspection and sorting, testing, disassembly, separating into small parts, sorting and storage operations are performed (Fleischmann et al., 2000).

Reprocessing or Direct Recovery

The direct recovery is sending again the products to the selling points and again usage without performing any treatment on them. The reprocessing is converting a used product into usable product again. This stage includes different options like recycling, repair and re-manufacturing. In addition to that options, it can also include the steps of cleaning, renovation and re-assembling too. We can give examples as nylon recycling from used carpets, new part production from used photocopy machines and cleaning the waste construction sand for the reprocessing (Fleischmann et al., 2000).

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The most important difference separating the reverse logistic systems is occurring at this stage (Demirel & Gokcen, 2008a). The reprocessing is the stage in the reverse logistic web which needs the highest investment. Especially the cost of the operations of the re-manufacturing and the recycle is high. The main difference show itself in the stage of the reprocessing. According to this, the processes of the product recovery can be lined as following (Thierry et al., 1995):

- **Repairing:** The goal of the repairing is making the returned product workable or usable (Thierry et al., 1995). The repairing operation of the product includes the repairing of the broken or damaged parts and changing them (Karacay, 2005). The quality of repaired product is less than the quality of a new product (Wadhwa et al., 2009).
- **Refurbishing:** The goal of the product innovation is increasing the quality level of the used product to a certain quality level (Thierry et al., 1995). The facilities of refurbish maintain the quality of the returned products nearly as same as the quality level of a new product (Jarayaman et al., 2003). Generally this operations is performed on expensive products (like military and commercial planes). In the product innovation operations the broken parts are changed with new ones or old parts are changed with ones having more quality according to technology (Sengul, 2009).
- **Re-Manufacturing:** The goal of the re-manufacturing is increasing the quality level of the used product up to the quality level of a new product. All parts of the used product are demounted and all modules and parts are controlled. The worn, outdated and demode parts and modules according to the current technology are changed with new ones. The repairable parts and modules are repaired and tested (Thierry et al., 1995). The re-manufacturing is known as main recovery option because of feasibility and its benefits (Lu & Bostel, 2007).
- **Cannibalization:** The first three options provide highly rated reusage in recovery activities. In here the reusage possibility is limited. The main goal is taking limited numbered usable parts from the used product or component (Thierry et al., 1995).
- **Recycling:** In the product recovery options mentioned above, the main goal is preserving the functions and properties of the used products and components as good as possible. In recycling operation, the products loose its functions and properties. The recycling is obtaining material from used products (Thierry et al., 1995). In the recycling operation the material is regained without preserving the structure of the product (Thierry et al., 1995). The recycling operations are performed on many used products. For example, in many countries like USA, England, Germany, nearly all metallic parts composing 75% of the weight of the scrapped cars are being performed to recycling (Thierry et al., 1995).

Disposing

In this stage needed operations are performed for valueless products which can not be reused because of the technology or economic reasons. The valueless of a waste or scrap depends on not creating any value by reusage of it as technically or economically or not being worth to process. The rejected products in the stage of inspection and sorting because they need very much repairing and the products which can not be used because their expire date has passed can be disposed. There are some options like removal, soil burying and incineration (Fleischmann et al., 2000).

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Returning Recourses in Reverse Logistics

If the products don't perform their functions, there is no need for them, then they will be sent back or thrown. We can list the typical reasons of the products as errors, damage caused during transport, the introduction of new models, product replacement with another product, refunds, repairs, recall and incorrect deliveries (Min et al., 2006). At the same time, several returning reasons of the products in the supply chain hierarchy from the production stage to the delivering step to the consumers can be collected in three main groups as following (Dekker et al., 2004):

- **Production Returns:** Sometimes the needed quality can't be gained in the production stage or retaking of the products and components which must be recycled can be described as productions returns.
- **Distribution Returns:** That includes all returns occurred in the stage of distribution in the reverse logistics. That is a reverse distribution activity including product recalls, withdrawal of the product from customers (Jarayaman et al., 2003). The recalls caused by the safety or health risks at the products are initiated by the manufacturer or supplier. Business to business (B2B) commercial returns are caused by the returning options concern with the contract between the retailer and the parent company. Damaged product deliveries, defective products, out-of-lifecycle products, seasonal products which couldn't sold, etc. can be given as example to that category.
- **Returns from the Customers:** These returns consist of the returns after the product has reached to the customer because of several reasons. Warranty returns, service returns (repair, replacement parts), end of usage returns can be evaluated in this scope.

Decision Stages in Reverse Logistics

Transportation of the products from the customers to the facilities for recycling, determination of the settlements for remarketing them from that place, facilities and the amount to be transported between each plant are the important decisions which must be taken (Fleischmann et al., 1997). The periodic decisions in the reverse logistics can be lined as following (De Brito, 2004; Srivastava, 2008b):

- **Long Term Decisions:** Plant layout, facility planning, capacity and design,
- **Middle Term Decisions:** Integration of the operations and choosing which information and technology system will be used,
- **Short Term Decisions:** Inventory, vehicle routing, schedules for re-manufacturing.

Strategic decisions are taken by senior management, tactical decisions are taken by middle level management and the operational decisions are taken by the lower-level management (Sengul, 2009). The reasons of performing the reverse logistics by the companies can be summed under three general titles:

- **Economical Factors:** In today's world in which the competition conditions have become hard, the economic factor play triggering role for the improvement of the products. The companies are trying to find new ways to reduce the production costs. The reverse logistics program can provide direct benefits for the companies by reducing the amount of the raw materials, adding value to the product by recycling or reducing the disposal cost. The indirect benefits of the reverse logistics are

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as green (environmental) image, improved customer satisfaction, preparation for the laws which will be valid in the future and market protection (Fleischmann, 2000; De Brito, 2004). The investigations show that the re-manufacturing has 25% less cost instead of new production (Linton & Johston, 2000). Previously performing recycling operations of the firms will provide advantage to them for adopting the laws which will be applied in the future (Louwers et al., 1999). The product recycling methods can be performed to make close relations with the customers having environmental sensitivity. So, the firms can gain indirect economic benefit by the established green image (Buyukozkan and Vardaloglu, 2008; Fleischmann et al., 2000).

The direct and indirect benefits of the reverse logistics provided to the firms can be summed as following (Dekker et al., 2004):

- **Direct Benefits:** Reducing the amount of the used materials, reducing the production costs, adding value to the products by recycling.
- **Indirect Benefits:** Laws which will come into force, protecting the market share, green image, developing customer / supplier relationships.
- **Legal Regulations:** Legal regulations are another factor which forces the firms to perform the reverse logistics. These laws force the firms to return and recycle the used products in a certain ratio (Dekker et al., 2004; De Brito, 2004). Nowadays the return products have big importance and responsibilities are given to the producers for the products which have completed their life cycle (Fleischmann et al., 2001). In many countries, companies are being held responsible with collecting back a certain part of the products they produce. Especially the European Union gives importance to the development and implementation of "green laws" for the reduction of the environmental impact even for the elimination (Sengul, 2009). In the scope of the "Germany Waste and Packaging Law" which has entered into force in 1991 in Germany, manufacturers, distributors and retailers must recycle minimum 60%-75% of their packaging wastes (Fleischmann et al., 1997). Again in this country, the manufacturers are responsible for the disposal of the electronic products which have completed their life time (Jarayaman et al., 2003). In Turkey "Packaging and Packaging Waste Control Regulation" has entered into force in the date of 07.30.2004. In the European Union, in January 2003, the "The Waste Electrical and Electronic Equipment " (WEEE) directive (EC, 2003a) has been issued for collecting the electrical and electronic products and supporting recycling of the products like this type. Also the " The Restriction of Hazardous Substances" (RoHS), (2002/95/EC numbered directive) has been issued by the European Union and the usage amount of six hazardous materials (chromium, cadmium, lead, polybrominated biphenyls, mercury and polybrominated diphenyl ether) has been limited at the all production stages of the electrical and electronic devices (EC, 2003b). Because of the laws, every product bought by the government must have recycled materials in Japan. In Netherland, the manufactures are responsible of collecting used refrigerators, washing machines, freezers, televisions and electronic tools and all packages of these products, treating them and providing recycling of them.

Generally these legal regulations are at the way of collecting the products at the end of their life cycle, reusing of them, waste management and encumbering the responsibilities about this on manufacturers, reducing the amount of the wastes, increasing the recycle amount of the products and materials. Some of the legal regulations in our country are as following: Control Regulation of Medical Wastes, Control

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Regulation of Tires which have completed their life time, Control Regulation of Solid Wastes, Control Regulation of Vegetable Waste Oil, Control Regulation of Waste Batteries and Accumulators, Control Regulation of Packaging Wastes, Control Regulation of Hazardous Wastes etc.

- **Environmental Sensitivity:** Environmental sensitivity is one of the performing reasons of the reverse logistics. Including the environmental goals into the reverse logistics applications and strategic plans of the firm provides competitive advantage to the firm according to its competitors. In recent years, the interest in environmental management in supply chain management has been increased (Ravi et al., 2005). As the result of this, producing environment friendly products and recycling of the products has become an important market component (Sengul, 2009). In addition to this, (Ravi et al., 2005) has mentioned from firm citizenship concern with the values required for responsibility of the firms or organizations on the reverse logistics as another performing reason of the reverse logistics. The reverse logistics help improving of the firm image. At this point, Nike firm is converting the used shoes to the materials used in installing of the basketball courts and jogging trails. And this application makes a positive affect to raise the brand value.

DIFFERENCES BETWEEN FORWARD LOGISTICS AND REVERSE LOGISTICS

There are some differences between forward logistics and reverse logistics. At the same time, the reverse logistics cannot be the symmetric reflection of the forward logistics (Fleischmann et al., 1997). The basic difference between the reverse logistics and the forward logistics including some uncertainties of the reverse logistics because of its structure about used products. There are uncertainties about the amount, quality and timing of the returned products, furthermore different return ratios are valid for each products of the firm. In the forward logistics the factors like time, quantity, quality are controllable, so they can be guessed. This is the main property separating these two ones. The differences between forward logistics and reverse logistics can be summed as shown in Table 2 (Tibben-Lembke and Roger, 2002).

Table 2. Differences between forward logistics and reverse logistics

Forward Logistics	Reverse Logistics
Estimates are relatively clear	It is more difficult to make estimations
Transporting is from one center to many centers	Transporting is from many centers to one center
Product quality is uniform	Product quality is not uniform
Product packaging is uniform	Package of the product is damaged
Following route is certain	Following route is not certain
Channels are standardized	It is directed with expectations
Prices are standard	Prices are affected by many factors
Costs are under control with accounting system	Costs are less certain
Consistent inventory management	Inconsistent inventory management
Agreements between actors are clear and simple	Agreements between actors are completed according to conditions
Marketing methods are certain	Marketing methods change according to some conditions
Real-time information is available for tracking items	The traceability process level is lower

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RECYCLING OF ELECTRIC-ELECTRONIC WASTES

Electrical and Electronic Equipment (EEE) are one of the most rapidly grown sector in the world (Hischier et al., 2005). Accordingly in recent years, there is a rapid increasing in the production of EEE all over the world. Rapid technological developments and continuously provision of the new products to the market increase the usage of these equipments in daily life in the modern world. Parallel to this situation, The Waste Electrical and Electronic Equipment (WEEE) occur which can cause to new environmental problems (He et al., 2006; Achillas et al., 2012).

EEE are the equipments needing electric current or electromagnetic field, generating that kind of current and area, transmitting, measuring and designed not to exceed usage of 1000 volts alternating current or 1500 volt direct current for their main functions according to EU's Directive 2002/96/EC regulation (Bereketli et al., 2011). WEEE are the wastes of several electric and electronic equipment and materials which don't provide any benefit to their owners or have completed their usage life time, has become inactive because of breakdown etc. (Widmer et al., 2005). According to EU's Directive 2002/96/EC regulation, WEEE are the waste electrical and electronic equipment including all components, subassemblies, consumables which are part of the equipment when the equipment is thrown (Widmer et al., 2005). As an alternative, e-waste term is widespreadly used instead of WEEE (Chancerel and Rotter, 2009).

United Nations Environment Program has calculated that in every year 50 million tons of WEEE are produced all over the world (Bereketli et al., 2011). According to the foresight of European Union Commission, 45% increasing in the amount of e-wastes is predicted between 1995-2020 in European countries (Hischier et al., 2005). In 1998 in West Europe, 6 million tons of WEEE occurred and 3%-5% ratio of increasing at this amount is expected (Cui & Forssberg, 2003). According to the declaration of United Nations University in 2005, 27 countries which are members of European Union have produced 8.3–9.1 million tons e-wastes (Oliveira et al., 2012). It is expected that in 2015 the amount of the e-wastes will be 12 million tons annually. That means 14 kg WEEE per person (Gutierrez et al., 2008). In 2004 in USA, 315 millions items of computers have been completed their life time (He et al., 2006).

In Table 3, the amount of the WEEE produced per person in some countries of the world (Ongondo et al., 2011).

According to 2002/96/EC directives European Parliament and WEEE Council (January 2003) have described WEEE product categories as following (Widmer et al., 2005):

1. Large household appliances e.g. fridges, cookers, microwaves, washing machines and dishwashers.
2. Small household appliances e.g. vacuum cleaners, irons, toasters and clocks.
3. IT and telecommunications equipment e.g. personal computers, copying equipment, telephones and pocket calculators.
4. Consumer equipment and photovoltaic panels e.g. radios, televisions, hi-fi equipment, camcorders ad musical instruments.
5. Lighting equipment e.g. straight and compact fluorescent tubes and high intensity discharge lamps.
6. Electrical and electronic tools – e.g. drills, saws and sewing machines, electric lawnmowers.
7. Toys, leisure and sports equipment e.g. electric rains, games consoles and running machines.
8. Medical devices e.g. (non infected) dialysis machines, analysers, medical freezers and cardiology equipment.
9. Monitoring and control instruments e .g. smoke detectors, thermostats and heating regulators.
10. Automatic dispensers e.g. hot drinks dispensers and money dispensers.

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Table 3. The amount of the WEEE produced per person in some countries

Country	Annual WEEE Amounts Per Person (kg)
Germany	13.3
England	15.8
Switzerland	9.0
China	1.7
India	0.4
Japan	6.7
Kenya	0.2
South Africa	1.2
Argentina	2.5
Brazil	3.5
USA	7.5
Canada	2.7

In additionally, categories of EEE covered by this directive as follows (EC, 2003a):

1. Temperature exchange equipment.
2. Screens, monitors, and equipment containing screens having a surface greater than 100 cm2.
3. Lamps.
4. Large equipment (any external dimension more than 50 cm) including, but not limited to: Household appliances; IT and telecommunication equipment; consumer equipment; luminaires; equipment reproducing sound or images, musical equipment; electrical and electronic tools; toys, leisure and sports equipment; medical devices; monitoring and control instruments; automatic dispensers; equipment for the generation of electric currents. This category does not include equipment included in categories 1 to 3.
5. Small equipment (no external dimension more than 50 cm) including, but not limited to: Household appliances; consumer equipment; luminaires; equipment reproducing sound or images, musical equipment; electrical and electronic tools; toys, leisure and sports equipment; medical devices; monitoring and control instruments; automatic dispensers; equipment for the generation of electric currents. This category does not include equipment included in categories 1 to 3 and 6.
6. Small IT and telecommunication equipment (no external dimension more than 50 cm).

There are three different ways of treatment of WEEE. These are recovery, recycling and disposal options explained in previous sections (Gomes et al., 2011).

Characteristics of WEEE Products in Terms of Recycling

WEEE has a heterogeneous and complex structure in terms of material and component. Developing an affective and qualified environment friendly recycling system is concern with having knowledge of physical properties of valuable materials, harmful wastes and their components. These properties can be classified as following (Cui & Forssberg, 2003):

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Hazardous components: WEEE has inhomogeneous and complex structure in terms of their components and materials (He et al., 2006). These components and materials include precious materials like iron, steel, copper, aluminum, metal, gold, silver, palladium, platinum, plastic, etc. and also there are wastes which are harmful for human health and environment (Wang et al., 2012). If e-wastes are not performed recycling and disposing processes under control, they will be harmful affects for human health and environment. For example, in the content of consumer electronic products 40% ratio of lead material which has harmful effects to the human brain and also triggers to allergic reactions and cancer (Widmer et al., 2005). The harmful materials in WEEE are cadmium, cathode ray tubes, mercury containing components, such as switches, asbestos waste, toner cartridges, liquid, paste and color toner, liquid crystal imagers, and gas discharge lamps, etc. (Cui & Forssberg, 2003; He et al., 2006).

Material composition: In the structure of EEE's there are many different materials more than one thousand. There are considerably precious materials in the structure of WEEE's (Widmer et al., 2005). The basic economic trigger of the recycling of the electronic wastes is the precious materials in them. At the same time, the proportion of the precious metal in the EEE illustrates a growing trend toward reduction (Cui & Forssberg, 2003). In the first generation of computers there was 4 gr gold. Today that amount is nearly 1 gr. One ton of WEEE includes 0,2 ton of copper (Widmer et al., 2005).

Physical properties: As a component of the precious materials, WEEE includes metals as copper, aluminum, gold and also plastic. The key factor in developing mechanic recycling system is effective material separation process based on the differences in physical characteristics (Cui & Forssberg, 2003).

Particle size, shape and separation properties: Particle size, shape, mechanical recycling properties have an important role in mechanical recycling processes. There is a specific particle size range in which nearly all mechanical recycling processes are effective (Cui & Forssberg, 2003).

Examining of E-Wastes (WEEE) in Terms of Regulations

Many countries are preparing regulations for supporting recycling and reducing the amount of disposal (Bereketli et al., 2011). In Europe the situations like disposal of electronic equipment, laying down specific recycling targets, retaking obligations of the products are determined by legal regulations (Thierry et al., 1995). There are two directives as WEEE (EC, 2003a) and RoHS (EC, 2003b) which have been come into force in EU at the date of 13 February 2003 concern with the waste of electrical and electronic equipment (Allsopp et al., 2006). Since the date of 1 January 2006 electrical and electronic products which will be produced and sold in the borders of EU will be proper to RoHS and WEEE regulations.

RoHS

RoHS (Restricting the use of Hazardous Substances) are the rules limiting the usage amount of the hazardous materials in electrical and electronic equipment to prevent the harm of the electrical and electronic equipment given to the environment dictated by EU. The six materials limited in the scope of RoHS are cadmium, mercury, chromium, polibrominl biphenyl, polibrominl diphenyl ether and lead (He et al., 2006). In Table 4 the ratio of materials limited for usage in the scope of RoHS can be seen.

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Table 4. The ratio of materials limited for usage in the scope of RoHS

Material	Amount (As Weight in a Homogeneous Material)
Mercury (Hg)	0.1%
Hexavalent chromium (Cr^{6+})	0.1%
Polybrominated biphenyls (PBB)	0.1%
Polybrominated diphenyl ether (PBDE)	0.1%
Lead (Pb)	0.1%
Cadmium (Cd)	0.01%

WEEE Directives

WEEE-The Waste of Electrical and Electronic Equipment Directives (Directive 2002/96/EC) provides recollecting of the products of the manufacturers and importers in EU and disposal of them without giving any harm to the environment (Ongondo et al., 2011). This directive includes manufacturers, distributors, consumers and all actors in the process of WEEE treating. It has been issued based on 175/1 article of European Treaty and it is only for increasing the environmental protection works. The responsibilities loaded on the actors with WEEE Directive are as following (EC, 2003a):

- Ministries are responsible for checking and controlling e-waste collecting and recycling activities of manufacturers, electronic products retailers, local units, recycling centers.
- Municipalities are responsible for providing every kind of support for the recycling of electrical and electronic equipment and serving to that process. Also they are responsible for providing the collection of domestic wastes and e-wastes separately and controlling the activities of collection and recycle centers.
- Producers are responsible for providing the recycle of a certain percentage of manufactured products, creating the appropriate conditions for the easy implementation of recycling, conducting research and development work on the subject, produced goods to designed to be suitable for recycling, giving priority to be derived from the recycling of raw materials. Also they are responsible for financing e-waste management and sending the products and/or parts which can't be recycled to the companies that provide recycling services.
- Recycling companies (the reverse logistic service suppliers) are responsible for taking certificate of conformity from the ministry, having the proper and developed technology for recycling activities.
- Electronic products distributors are responsible for collecting old and electrical and electronic products removed from usage and components from consumers free of charge or sending to the manufacturers or recycling companies free of charge.
- Consumers are responsible for leaving the electrical and electronic devices which they want to dispose in proper way in the private centers.

The goal of the WEEE directive is reducing the disposal ratio of EEE and healing the environmental performance of EEE products (He et al., 2006). WEEE recycling options have the goal of increasing of the recycling and reducing of the disposal.

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KEY TERMS AND DEFINITIONS

Electrical and Electronic Equipment (EEE): Electrical and Electronic Equipment is defined as equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields.

Logistics Management: As defined by the Council of Supply Chain Management Professionals (CSCMP): "Logistics management is that part of supply chain management that plans, implements, and controls the efficient, effective forward and reverse flow and storage of goods, services, and related infor-

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mation between the point of origin and the point of consumption in order to meet customers' requirements. Logistics management activities typically include inbound and outbound transportation management, fleet management, warehousing, materials handling, order fulfillment, logistics network design, inventory management, supply/demand planning, and management of third party logistics services providers.

Reconditioning: When a product is cleaned and repaired to return it to a "like new" state.

Recycling: When a product is reduced to its basic elements, which are reused.

Refurbishing: Similar to reconditioning, except with perhaps more work involved in repairing the product.

Remanufacturing: Similar to refurbishing, but requiring more extensive work; often requires completely disassembling the product.

Reuse: Using a product again for a purpose similar to the one for which it was designed.

Reverse Logistics: A specialized segment of logistics focusing on the movement and management of products and resources after the sale and after delivery to the customer. Includes product returns for repair and/or credit.

Supply Chain: Starting with unprocessed raw materials and ending with the final customer using the finished goods, the supply chain links many companies together.

Waste Electrical and Electronic Equipment (WEEE): Waste Electrical and Electronic Equipment is defined as EEE which has reached end of life (waste); including all components, subassemblies and consumables which are part of the product at the time of discarding.

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