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Advanced Oxidation Processes (AOPs) in Water and Wastewater Treatment

Hamidi Abdul Aziz and Salem S. Abu Amr

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Advanced Oxidation Processes (AOPs) in Water and Wastewater Treatment

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Dayang Haszelinna Abang Ali, Universiti Malaysia Sarawak, Malaysia

This chapter elaborates the importance of water and wastewater treatment to human, environment, and world. It further discusses the water-borne diseases and other effects without implementation of water and wastewater treatment system. The principles of treatments are elaborated in detail as well. The standard parameters and value needed to be checked and compiled by the water and wastewater treatment system are not forgotten. This chapter explains the sources of water pollution such as from geography, ecology, and industry site. It also includes thoughtful discussion on causative factors behind water pollution, either human or other activity. The chapter views the importance of clean water in a variety of economic aspects. Without clean water what will happen to the world economy?

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The legal and institutional framework, as well as the challenges and issues in water resources management, serves as the basis for the formulation of a policy framework that seeks to improve water resources management practices in the future. Recently, water resources 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 have reviewed several laws, including the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977, Environmental Quality (Prescribed Premises) (Raw Natural Rubber) Regulations 1978, and Environment Quality (Sewage and Industrial Effluent) Regulation 1979. Legal issues under the constitutional framework water management have also been reviewed. Exploring this topic generates an overview water management implementation in the context of Malaysia.

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Advanced oxidation processes (AOPs) have recently received attraction for treatment of different wastewaters. AOPs have an ability to oxidize a high quantity of refractory organic matters, traceable organic, or to increase wastewater biodegradability as a pre-treatment prior to an ensuing biological treatment. In this chapter, the fundamental mechanisms of different AOPs such as ozonation, hydrogen peroxide, UV, persulfate, and Fenton oxidation are summarized. The combination of different oxidation processes such as O3/H2O2, O3/UV, O3/Fenton+, O3/persulfate are evaluated. Several persulfate activation techniques are also summarized.

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As textile and dyeing industries increase, pollution due to effluent discharges from the same industries also increase and become of great concern to a healthy environment. In an attempt to understand the generation and treatment of textile wastewater, this chapter discusses the processes from which textiles are made, items of importance that are used in the production process which may account for the characteristics of the wastewater and persulfate, applied in the treatment of textile wastewater. Although these wastewaters are generally characterized by color, fluctuating pH, heat, salts, suspended solids (SS), the presence of metal ions, biological oxidation demand (BOD), and chemical oxygen demand (COD), color is the most obvious. The presence of color in the effluents from textile dyeing and finishing is due to the inefficient dyeing processes, resulting in unfixed forms of the dyestuff. To achieve the primary objective of obtaining a clean environment, there is a need for continuous monitoring of textile wastewater discharges, of which major concern is color.

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Petroleum wastewater generation is one of the main pollutants associated with oil refineries processes. The petroleum wastewater usually contains a complex variety of materials and organic compounds. Dedicated treatment facilities are required before the petroleum wastewater can be discharged to the environment. Researchers worldwide are still searching for a total solution to solve petroleum wastewater problem. In this chapter, different chemical treatment methods for the petroleum wastewater including coagulation-flocculation, Fenton and electro-Fenton oxidation, photocatalyst oxidation, and advanced oxidation processes are reviewed and discussed. Nevertheless, the efficiency of each process was also evaluated. It can be concluded that the performance of these processes is mainly attributed to petroleum wastewater type and initial organic concentrations whereas treatment performance weakens reported at higher initial concentrations of pollutants.

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This chapter presents a review on limited studies that have been conducted using advanced oxidation processes (AOPs) in treating biologically treated palm oil mill effluent. Palm oil mill effluent is the byproducts of palm oil production that is normally treated using a series of biological processes. However, despite being treated for a long period of retention time, the effluent still possesses high concentration of organics, nutrients, and highly colored, and will pollute the environment if not treated further. Advanced oxidation processes that utilized hydroxyl radicals as their oxidizing agents have the potential of further treating the biologically treated POME. Fenton oxidation, photocatalysis, and cavitation are the main AOPs that have been studied in polishing the biologically treated POME. Depending on the experimental conditions, the removal of organics, in terms of COD, TOC, and color, could reach up to more than 90%. Nevertheless, each of this process has its own limitations and further studies are needed to overcome these limitations.

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Municipal solid waste has continued to be a major problem in many nations of the world. The primary methods of treating landfill leachate include physical-chemical and biological treatment processes. Pressure-driven membrane processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO), are among the utmost promising and capable ways for treating landfill leachate. The concentrated leachate created from pressure-driven membrane processes typically represents 13%–30% of total incoming landfill leachate. Concentrated leachate is a dark brown solution with high levels of pollutants. Treating concentrated leachate is extremely difficult, and thus, a combined treatment system is suggested. In the present study, concentrated landfill leachate was treated using a combined treatment technique that included electro-ozonation. The removal efficacies of chemical oxygen demand (COD), color, and nickel were monitored at original pH (7.3) as well as current and voltage of 4 A and 9 V, respectively.

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Groundwater is the source of drinking water that needs to be maintained from pollution. Groundwater pollution is a major problem caused by human activities that are invaluable to human health. When high levels of organic and inorganic substances do not exceed the standard of drinking water, various studies have been made by researchers to overcome the problem. Various alternatives such as in-situ and ex-situ treatment have been carried out to eliminate pollutants from groundwater. Among the treatment, ozone becomes a major alternative because of its effectiveness in treating raw water. Ozone treatment has several advantages such as disinfectants, oxidize of organic and inorganic pollutant, and remove taste and color from groundwater. The performance of ozonation process becomes better when combined with other treatments. Therefore, application of ozone can replace chlorine because of its good potential to improve quality of groundwater effluent and comply drinking water standard adopted by World Health Organization.

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Antibiotics present in the environment are originated from pharmaceutical manufacturing processes or through wastes such as urine and feces. As antibiotics remain recalcitrant and persist in the treated water, consumption of treated water containing antibiotics raises a concern in the development of antibiotic resistance bacteria which would be later released to the environment. It might result in a vicious cycle which new antibiotics needs to be developed and dosage has to increase. Advanced oxidation processes (AOP) have been studied to effectively degrade antibiotics. During this process, hydroxyl radicals are formed to degrade organic compounds. Different APO are available in the literature such as photo-Fenton, Fenton, ozonation, sonolysis (UV), ultrasound combined with ozone, TiO2/direct photolysis, UV/H2O2, UV/ TiO2, UV/IGBT. To treat the high level of concentration of antibiotics, retention time of AOPs needs to be extended or/and OH● radicals need to be produced in a higher concentration for a complete mineralization.

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Landfill leachate is a hazardous pollutant generated from a landfill site. Discharge of landfill leachate has caused a major contamination to the environment and detrimental to human health. This chapter introduces an alternative method to treat recalcitrant pollutant in leachate by using ozonation with catalyst. The production of hydroxyl radical in ozonation was not enough to oxidize complex molecular structure in the leachate. Theoretically, the addition of catalyst enhances the capacity of radical and accelerates the chemical reaction. The effectiveness of ozonation with Fenton (O3/Fenton), hydrogen peroxide (O3/H2O2), and zirconium tetrachloride (O3/ZrCl4) in removing pollutant such as chemical oxygen demand (COD), color, and improvement of biodegradability by using this process were also discussed in this chapter. Comparison in term of treatment cost and benefits of the application of chemical as catalyst are briefly elaborated at the end of this chapter.

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Sanitary landfilling is the most acceptable method to eliminate solid urban wastes. However, it is known that sanitary landfill generates large amount of heavily polluted leachate. High concentrations of recalcitrant organics make its degradation more complicated and high concentration of organic material can be toxic and reduce bioremediation process. Landfill leachate treatment by advanced oxidation processes (AOPs) have been intensively studied with high successful rate for removing refractory pollutants (biological degradation) from leachate. Fenton reaction which is one basic AOPs is based on the addition of hydrogen peroxide to the leachate in the presence of ferrous salt as a catalyst. Because of that, many improvement and development of new Fenton-based methods have been reported in the literature. This review discussed the application of Fenton and related processes in terms of wide application in landfill leachate treatment. The effects of various operating parameters and their optimum ranges for organics contaminant removed were also discussed.

The presence of hazardous micropollutants in water and wastewater is one of the main concerns in water management system. This micropollutant exists in a low concentration, but there are possible hazards to humans and organisms living in the water. Moreover, its character that is recalcitrant to microbiological degradation makes it difficult to deal with. Advanced oxidation processes (AOPs) are efficient methods to remove low concentration micropollutants. AOPs are a set of processes consisting the production of very reactive oxygen species which able to destroy a wide range of organic compounds. The main principal mechanism in UV-based radical AOP treatment processes is the use ultraviolet light to initiate generation of hydroxyl radicals used to destroy persistent organic pollutants. Therefore, this chapter presents an overview on the principle of radical oxidant species generation and degradation mechanism by various type of UV based AOP in treating contaminants present in water and wastewater. The current application and possible improvement of the technology is also presented in this chapter.

Preface

Resources of fresh drinking water are the greatest vital reservoirs in the world. It is essential for all living organisms on the planet to have right to use suitable fresh water. Health risks associated with contaminated water and wastewater, pollution to aquatic environment and water scarcity issues contribute to the increase of advanced technologies implementation upon legislative impetus. The growing population and industrial developments have increased wastewater generation in recent years.

Wastewater can be defined as the flow of used water that is discharged from homes, businesses, industries, commercial activities, and institutions. This flow of used water is directed to treatment plants by a carefully designed and engineered network of pipes. Wastewater is further categorized and defined in accordance with its origin. Industrial wastewater is a complex organic and inorganic liquid that may pose adverse environmental impacts that depend on the characteristics of the materials that exist in these liquids. Wastewater pollutants are categorized into organic and inorganic matters, such as nitrogen, phosphorus, ammonia, iron chlorides, and heavy metals. A recent major problem of industrialized nations has been the environmental contamination caused by hazardous chemicals. Among the common sources of pollutants that are of concern in recent years include but not limited to the release of untreated or partially treated textile, palm oil, landfill leachate, petroleum, and pharmaceutical effluents. Pollution of pesticides on soil residue, waterways, rivers and crop fields have also been much given attention recently as its presence in environment has been increased over years.

Textile wastewater may degenerate the environment due to the high content of chemical substances, suspended solids and intense colour among other characteristics. Several point source water pollution have been traced due to the disposal of textile wastewater which have worked against the wellbeing of both human and aquatic lives. Downstream waters have also been negatively affected aesthetically (Yadav & Verma, 2014). Also, contamination of both surface and ground waters have made them unfit for irrigation and drinking (Marwari & Khan, 2012).

Palm oil is a major industry in Southeast Asia and its production is increasing rapidly with the growth of plantation areas across the countries including Malaysia, Indonesia and Thailand (Aris et al., 2008). The expansion of the oil palm industry comes with its environmental cost. The current extraction process of palm oil includes wet process and dry process. The wet process requires a large volume of water (Wu et al., 2009). It is estimated that the production of one-tonne crude palm oil utilizes 5 to 7.5 tonnes of water (Rupani et al., 2010). With such amount, the wastewater will pollute the environment if adequate treatment is not provided.

Due to rapid population growth, continuous economic development, industrialization, and urbanization, the generation of municipal and industrial solid waste is increasing. Landfilling is still the most suitable and applicable way for manage the huge amount of generated solid waste. However, large amount of leachate with high level of chemical, toxic and hazardous materials and heavy metals is generated from landfills and should be managed and treated well (Mojiri, 2014; Liermann, 2009; Visvanathan et al., 2000).

The petroleum wastewater is a complex organic liquid and can have enormously adverse environmental impacts, depending on the characteristics of the materials, which exist in them. In general, the pollutants in wastewater can be divided into organic matters and inorganic matters, which include nitrogen, phosphorus, ammonia and iron chlorides as well as heavy metals (Tengrui et al., 2007). A large amount of water is used during the petroleum refinery activities. Consequently, significant volumes of wastewater are generated.

Among the pharmaceutical wastes, antibiotics have received much attentions in recent years. Despite their vital importance in our daily life, antibiotics have been known to raise concern as a persistent water pollutant in the environment. The occurrence of antibiotics in the aquatic systems has biological impacts on the aquatic life and human health. The use of antibiotic chemical in the pharmaceutical products has reached an estimation from 100,000 to 200,00 tons per year (Kummerer, 2003). Conventional processes in the wastewater treatment plants (WWTP) are unable to degrade the recalcitrant components in antibiotics. Although antibiotics-contained water is safe for human consumption after treatment, bacteria become resistant to the antibiotics and the human immune system becomes weak. Furthermore, treated wastewater eventually ends up into the rivers or seas when they are not re-used for other purposes such as irrigation or for industrial purposes. Hence, further treatment is necessary.

Pesticides are commonly detected in soil residue, waterways, rivers and crop fields. There is an increase in use of pesticides due to the increase in plantations. It calls for strict and improved monitoring and/or alternatives in the eventual wastewater treatment process before discharge into the inland waterways and rivers (Naubi et al., 2016). The use of economical treatment methods which are sustainable irrespective of the concentration of pesticide wastewater at any given treatment plant is imperative. There are various types of advance oxidation processes which could remediate pesticide wastewater.

To this end, it is very important that definite steps should be taking to treat pollution of water at source, and to the required standard before an eventual discharge into either sewers or surface waters. Conventional treatments through classical physicochemical methods are insufficient for attaining the required levels of decontamination, especially given the presence of high concentrations of recalcitrant organics and organic materials. The majority of these pollutants are extremely toxic considering their physicochemical properties. These pollutants represent a risk to the health of humans and other living things when released into the aquatic environment. The selection of an appropriate treatment strategy is frequently difficult. Therefore, in order to meet the standards, suitable treatment alternatives should be established. The suitable technology may differ based on the type of wastewater produced. Even after treatment, the effluent characteristics are always hard to comply with the discharge standard.

Advanced oxidation processes (AOPs) have a capability of rapid degradation of recalcitrant pollutants in the aquatic environment. AOPs that utilize powerful hydroxyl or sulfate radicals as major oxidizing agents were first proposed in the 1980s for potable water treatment. Then, AOPs were broadly applied to treat various wastewater types because strong oxidants can readily degrade recalcitrant organic pollutants and remove certain inorganic pollutants in wastewater. AOPs have become increasingly popular in recent years.

This book aims to present an overview of the current state of knowledge and latest advances regarding the use of advanced oxidation to provide solutions for the control of various pollutants, hazardous substances and microbiological contaminants in water. Future trends and directions concerning various environmental applications of AOPs are presented in 14 chapters.

This book highlights the basic rule in water and wastewater management, particularly discussions on the importance of adhering to water management hierarchy in overall management systems. Related legislation on water and wastewater is discussed first, followed by an introduction to the AOPs. Various applications of AOPs in treating water and wastewater are then provided. Selected models in developed countries that can be possibly applied to developing countries are elaborated, and several key elements in achieving sustainable management for wastewater treatment are discussed. Among the processes discussed include using persulfate in textile wastewater, photocatalyst for petroleum wastewater treatment, AOP for palm oil mill effluent, electro-ozonation for concentrated landfill leachate, removal of Fe and Mn from groundwater, and treatment of pesticides and antibiotic effluent. Fenton, electro-Fenton, and sulfate- and UV-based radical AOPs are also discussed in subsequent chapters after the chapter on using photo catalyst techniques for petroleum wastewater treatment. All these clearly indicate the multi- and inter-disciplinary approach needed in the field of AOPs.

To date, there are some literatures focused only on general characteristics of some types of wastewater and discharge standards, other publications focused generally on some conventional treatment processes for wastewater. However, advanced treatment processes for specific types of wastewater such as textile, petroleum, pharmaceutical and other wastewater types has not been well documented. There are a lot of developments in wastewater treatment. However, there are still many gaps in knowledge in this area. This book will contribute in filling in some of the gaps. The book will help water and wastewater management authorities to proper manage their wastewater.

The target audience for the current book are scientist, researcher, student, engineer, professionals, practitioner from leading organizations and companies such as water association and authorities, water and wastewater management companies, solid waste landfills operators, legislators, etc. The book is also meant for all concerned with the fundamental, engineering and applied aspects of oxidation techniques involving ozone and related oxidants and/or UV techniques, photocatalyst applications, persulfate and Fenton oxidation, and all interested in environmental protection.

It is quite rewarding to see generous contribution of the authors with different backgrounds that shared their experiences in this book on the advancements of AOPs. We are also indebted to all the reviewers who helped in making this book an excellent reference material of AOPs.

ORGANIZATION OF THE BOOK

This book is organized into 14 chapters. A brief description of each chapter is presented as follows.

Chapter 1, "Introduction to Water and Wastewater Treatment," identifies general water composition, distribution, treatment, and management. The concepts and objectives of water and wastewater treatment are also reviewed.

Chapter 2 is "Legislations of Water and Wastewater Treatment." In this chapter, several laws and regulations on water and wastewater are summarized, especially in relation to Malaysia's Environmental Quality Act (Act 127) of 1974.

Chapter 3 is "Advanced Oxidation Processes for Water and Wastewater Treatment: An Introduction." In this chapter, the fundamental mechanisms of different advanced oxidation processes, such as ozonation, hydrogen peroxide, UV, persulfate, and Fenton oxidation, are summarized. The combination of various oxidation processes, such as O_3/H_2O_2, O_3/UV, O_3/Fenton+, and O_3/persulfate, is evaluated. Several persulfate activation techniques are also summarized.

Chapter 4 is "Persulfate in Textile Wastewater Treatment." In this chapter, the fundamental, mechanism, and application of persulfate oxidation and activation are discussed.

Chapter 5, "Advanced Oxidation Processes for Treating Petroleum Wastewater," includes the mechanisms and performances of advanced oxidation processes.

Chapter 6, "Applications of Advanced Oxidation Processes in Palm Oil Mill Effluent Treatment," focuses on advanced oxidation processes for palm oil mill effluent. The general composition of palm oil wastewater and the characterization of new conventional and advanced techniques for palm oil wastewater treatment are summarized.

Chapter 7, "Concentrated Landfill Leachate Treatment by Electro-Ozonation," focuses on utilization of electro-ozonation technology for concentrated landfill leachate treatment.

Chapter 8, "Photocatalysis (TiO_2/solar) in Water and Wastewater Treatment," discusses and revises the application of photocatalysis (TiO_2/solar) in water and wastewater treatment. The mechanism of photocatalysis, characteristics of semiconductor photocatalyst, differences between suspended and immobilized photocatalyst systems, comparison of the use of natural sunlight and commercial lamp, and the features of the reactor involved are covered. Potential advantages and limitations and the application of photocatalysis in water and wastewater are also described.

Chapter 9, "Groundwater Treatment via Ozonation," outlines ozone applications in groundwater treatment. The causes and problems of groundwater pollution, which affects the quality of drinking water, are identified. Several case studies on groundwater pollution problems throughout the world are included.

Chapter 10, "Overview of Antibiotic Treatment Using Advanced Oxidation Process," provides an overview of antibiotic treatment by using advanced oxidation processes. Different advanced oxidation processes available in the literature are revised and discussed.

Chapter 11, "Comparative Study of Advanced Oxidation Processes for Treating Pesticide Wastewater," focuses on advanced oxidation processes for treating pesticide wastewater using different advanced oxidation process technologies. The treatment costs for each process are compared.

Chapter 12, "Ozonation With Catalysts in Landfill Leachate Treatment," introduces an alternative method for treating recalcitrant pollutant in leachate through ozonation with a catalyst. The effectiveness of ozonation with Fenton (O_3/Fenton), hydrogen peroxide (O_3/H_2O_2), and zirconium tetrachloride ($O_3/ZrCl_4$) in removing pollutants, such as chemical oxygen demand, color, and biodegradability improvement by using such processes, is analyzed. Comparison of treatment costs and benefits is performed.

Chapter 13 is "Advanced Oxidation Processes for Landfill Leachate Treatment." The advanced oxidation processes for landfill leachate treatment are the focus of this chapter. The effects of various operating parameters and their optimum ranges for organic contaminant removal are discussed.

Chapter 14 is "Application of UV-Based Advanced Oxidation Processes in Water and Wastewater Treatment." The main principal mechanism of UV-based radical advanced oxidation processes is discussed in this chapter. UV light is used to generate hydroxyl radicals for destroying persistent organic pollutants. The current application and possible improvement of the technology are also presented.

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Chapter 1

Introduction to Water and Wastewater Treatment

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ABSTRACT

This chapter elaborates the importance of water and wastewater treatment to human, environment, and world. It further discusses the water-borne diseases and other effects without implementation of water and wastewater treatment system. The principles of treatments are elaborated in detail as well. The standard parameters and value needed to be checked and compiled by the water and wastewater treatment system are not forgotten. This chapter explains the sources of water pollution such as from geography, ecology, and industry site. It also includes thoughtful discussion on causative factors behind water pollution, either human or other activity. The chapter views the importance of clean water in a variety of economic aspects. Without clean water what will happen to the world economy?

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INTRODUCTION TO WATER AND WASTEWATER TREATMENT

There are about 332.5 million cubic miles of water on earth, but only less than one percent is easily accessible for domestic and industrial application as fresh water (Proverbs et al., 2016). The freshwater resource is often regarded as infinite supply because water purifies and replenishes itself through the hydrologic cycle. However, it is not necessarily true if the water resources keep being polluted or drained faster than it can be restored. Moreover, only two-thirds of the accessible water is suitable for consumption, while the remnants are not consumable due to pollution and other factors. Diminishing water resource is indeed a growing concern all over the world, and thus it is necessary to have clean and safe water accessibility to secure healthy population. The public awareness combined with prevention and treatment action will avert environmental problems and water-related human diseases. Water and wastewater treatment are the mitigation available when dealing with inaccessible water caused by pollution. The treatment technology imitates the 'hydrologic cycle' which purposes are to clean, purify and restore water for drinking or in accordance with the regulated water quality standards.

Water and Disease

Disease is a particular abnormal condition that affects part or all of an organism and consists of a disorder of a structure or function. Disease is not solely a direct outcome of physical injury as it may be caused by external factors such as pathogens (bacteria, virus or vectors) or by internal dysfunctions, particularly the immune system such as immunodeficiency or hypersensitivity. The polluted water can cause a wide range of diseases across the globes which include several life-threatening diseases. In fact, the World Health Organization (WHO) has reported that waterborne disease is the deadliest killer in the world. The target group is the low immunity people namely young children, elders and sick individuals. Number of case reported is higher in developing countries, in which 80% of illnesses are due to water-borne diseases with diarrhea causing dehydration as the top killer among children (Fonyuy, 2014). Water although regarded as renewable resource, safe and protected fresh water, is indeed finite and should not be taken for granted.

Contaminated water which contributes to diseases is often associated with biological factor or presence of pathogenic microorganisms, and thus known as water-borne diseases. Nevertheless, chemicals such as organic substances, inorganic substances, and radionuclides are also noteworthy factors. These chemicals may be introduced into the water from improper waste management, uncontrolled mining and poor agricultural practice. Many of these substances are not harmful to humans or present in low concentrations which hardly cause health effects. However, some of the substances are known to cause serious health effects at low concentrations, and treatment is needed to remove them or to reduce their concentration in drinking water.

Infection may occur through direct or indirect exposures involving these two groups of contaminants. Direct infection which involves biological factor arises through consumption of water which is infested with pathogenic microorganisms such as *Salmonella typhi*, *Shigella* spp., *Campylobacter* spp., *Vibrio cholera*, and many more (Guillot & Loret, 2009). On the other hand, the indirect route is through vectors lurking in the contaminated water. These vectors may live in the water or part of their life cycles requires water as a breeding ground. For example, vectors which carry water-borne diseases are mosquitoes, snails, flies, fleas and tick. For chemical inducing diseases, the direct route is through consumption of toxic water which comprises harmful chemicals such as heavy metals, nitrates, pesticides and disinfection by-products. Indirect route is through consuming marine life which tends to bioaccumulate harmful chemicals in their body system. When human consumes the infected organism, the accumulation of toxic substances continues in the body until specific symptoms are developed corresponding to specific contaminants.

Water for Life

Earth is a life-sustaining and nourishing planet due to the presence of water. Water is responsible for the complex processes of the Earth's climate and its interaction with atmosphere, ocean, and land. Furthermore, water is able to replenish and distribute itself through a phenomenon called hydrologic cycle. Water is the only known natural substance that exists in the form of solid (ice), liquid and gas (steam) phases in temperature and pressure that can be discovered on the surface of the earth. Chemically, water is an inorganic compound consists of H_2O molecules and usually comprises a major part of any living organism. Due to the unique properties of water, it benefits living organisms by serving as a biochemical solvent, thermal buffer and living environment.

Furthermore, water is a polar molecule which has two opposite charges of positive terminal (hydrogen) and negative terminal (oxygen). Due to its polarity, water can form electrostatic interactions with polar molecules and ions. This property allows water to dissolve in a wide range of solutes. In addition, it is also able to dissolve in more solutes than any other solvent, granting the name universal solvent. Polar compounds namely sugars, amino acids, short nucleic acids and proteins dissolve in water. However, biological molecules such as non-polar lipids (fats and oils) and large polymers (polysaccharide, large proteins and DNA) do not dissolved in water. Regardless of the solubility, water can serve as an excellent solvent for biochemical reactions and facilitate the transportation of dissolved compounds through the cells.

Water which has high specific capacity for liquid, latent heat of vaporisation and latent heat of fusion permits it to regulate the temperature within a tolerable range suitable to most living organisms. For example, the energy required for one gram of water to increase its temperature by one degree is 4.2 kJ/g/°C. As cells are majorly consist of water, it will take a high amount of energy to raise its temperature significantly. This prevents extreme surrounding temperature and allows stable temperature for most biochemical reaction to occur. Latent heat of vaporisation allows the sweating mechanism to absorb heat from the body and remove it during cooling. While high latent heat of fusion will allow the survival of aquatic organism in cold climate since ice will not form until a large amount of heat is released from water. These water properties facilitate various processes which occur naturally in the environment.

Water provides home for aquatic organisms. The ability of free oxygen (O_2) to dissolve in water allows the respiration of marine life which similar to the organisms on land. Fish obtains oxygen through their adapted gills while, aquatic plants and phytoplankton require dissolved oxygen when sunlight is unavailable for photosynthesis. The density of ice which is lower than the density of water in liquid form allows fish and crustacean in cold climate to survive underneath the floating ice. The floating ice also acts as a barrier to prevent the lower part of the lake from completely frozen due to extreme cold temperature. While the surface tension of water held by cohesion force allows small insect such as strider to walk on the surface of the water.

Types and Sources of Water in the World

Generally, the water on earth can be categorised into two distinct categories based on salinity namely saltwater and freshwater. Saltwater constitutes 97 percent of the total of water on the earth is the largest water reservoir in the world (Islam, 2008). Nevertheless, it is not directly accessible due to high content of salt. Saltwater has an average salinity of 3.5 percent which is equivalent to 35 gram of salt per liter of water. Removing salt from saltwater requires high capital and energy, and thus saltwater remains as non-favorable water resource. However, at the region of arid climate where freshwater is very limited, desalination is the preferred method to obtain fresh water. Reverse osmosis is a more feasible desalination method compared to distillation as it is more economical and less destructive to environment if applied properly.

Freshwater is low salinity water with concentration lower than one gram salt per liter of water. From three percent of freshwater resource, only one-thirds is accessible for human consumption. Most of the freshwater is non-accessible in the form of icecaps and glaciers. The readily accessible source of freshwater is divisible into surface water and groundwater. Surface water includes water expose to atmosphere and results from surface runoff. Sources of surface water are river, lake, wells nearby river and direct rain catchment. While groundwater is formed when water seeps through soils and permeable rocks and then accumulates within an underground space called aquifers. Generally, groundwater stores nearly 43 times more water than surface water. The extraction of groundwater is made available through man-made well, Artesian well, spring, and geyser.

Sources of Wastewater

Wastewater is a contaminated water commonly generated from human activities. The characteristics of a wastewater varies in different localities depending on types of industries and its level of activity, climate (storm water pattern), population density and separation efficiency of each wastewater sources. Wastewater originates from five major sources namely, human and animal, household, industry, storm water runoff and infiltration or inflow. The term municipal wastewater is used for the collection of all sources except storm water runoff.

Human and animal wastes include the solid and liquid discharge as a byproduct from human and animal excretion system especially from gastrointestinal system. This organic waste is consist of water, protein, non-digested fats, bacterial biomass, ash and fibres. The water contaminated by faeces and urine may host millions of living pathogenic microorganisms which may cause deadly water-borne diseases. Besides the release of strong and intolerable odour, the water contaminated by this source will also threaten environment and food supply.

Household waste is another source of wastewater. It may consist of soap, grease, food, and bodily waste from the sink, toilet, shower and washing machine. Nutrient such as nitrogen, phosphorus and organic material from household waste can disrupt the balance of natural ecosystem while pathogenic microbes can cause diseases. Domestic wastewater usually comprises a minor amount of impurities which is less than 0.2%. This wastewater can be classified as low strength wastewater with general range of COD less than 2000 mg/L (Lee *et al.*, 2016).

Industrial waste contain high concentration of metals and toxic chemicals in accordance to specific industry. This waste may has extreme level of pH, temperature and excess nutrient that affect the environment adversely. The treatment for industrial wastewater usually includes dechlorination process, treatment of recalcitrant water and removal of toxic compounds from the waste effluent. The strength of industrial wastewater is ranged from medium to high strength with COD greater than 2000 mg/L (Lee *et al.*, 2016).

Storm water is the precipitation that is not absorbed by ground and therefore it flowed over roads, carried all the drifted contaminants and are transported through storm water drain. It may be channelled either through a separate storm water system or through a combine system where it is later treated along with municipal wastewater. The separate sewer system is more preferable since it prevents sewer overflow, reduce flooding, allows resource tapping and optimise the performance of wastewater treatment itself. Stormwater system usually planned through ‘risk-based design’ such as probable maximum flood caused by the probable maximum precipitation for rare events.

Lastly, infiltration and inflow is also a source of wastewater. It happens due to defective and improperly sealed sewer systems which permit groundwater to enter through cracks, breaks or unsealed joints. The problems lie with mixing of clear water in sanitary sewer that should be conveyed in separate storm sewer. Generally, infiltration and inflow occurs in every sewer systems but only at small amounts which is expected and tolerated. However, it may be considered problematic when it causes increasing load in sanitary sewer system and then leads to overflow and flooding of the sewer system.

History of Water and Wastewater Treatment

The importance of water treatment has been recognised since ancient time. As early as 2000 BC, the people of India have used charcoal to filter water and copper pots to preserve it. The Egyptian dating to 1500 BC may have used filtration through wick siphon and coagulation using chemical alum to improve clarity of water. Other treatments such as boiling, placing hot metals in the water and sand filtration were the common treatment which have been recommended for thousands of years. In 500 BC, Hippocrates who famously known as ‘Father of Western Medicine’ found the healing properties of water and he invented a water filter which known as Hippocrates sleeve. The filter was aimed to reduce sediments which could cause unwanted colour and odour.

In post-classical period (200-1500), lack of information on water treatment was known. Then, in 1627, Sir Francis Bacon became the first acknowledged scientist to show interest on desalination process. He hypothesised that if he dug a hole nearby a seashore, the seawater that was filtered through multiple layers of sand should be pure and salt-free water. Although his hypothesis failed, he heralded the forthcoming water filtration researches. In 1700s the first domestic water filter made of wool, sponge and charcoal was utilised (Hubbell, 2011). The history continued as Robert Thom designed the first water purification plant at Scotland in 1804. The water was treated using slow sand filtration and then distributed using horse-drawn vehicle.

In 1849, London was struck by the worst epidemic in its history. The cholera outbreak claimed 14,137 lives and infected many others (Streiner *et al.*, 2010). However, it was not until 1854, John Snow managed to demonstrate cholera was a water-borne disease and not due to miasma. The addition of chlorine to disinfect cholera-causing water was also his notable work. Following the remarkable success, the government of Great Britain implemented sand filter and chlorination for public consumption. Therefore, it dictated the establishment of the first water regulation by a government in the world (Spielvogel, 2007). In the late 1880s, Louis Pasteur solved John Snow’s puzzle with his germ theory of disease which help scientists to relate diseases with microorganisms.

Starting 1914 drinking water standards were implemented for drinking water supplies in United States which specified the permissible limits of bacterial count. Later, the Public Health Service revised the standard several times with minor modification until in 1960s, when it was realised that rapid industrial and agricultural growth have created many xenobiotic compounds. These new man-made chemicals were able to invade water supplies through factory discharge, farm field runoff and leaking disposal tanks. Although treatment such as aeration, flocculation and activated carbon adsorption presented at the time, they were either underused or ineffective at removing these new chemical contaminants.

The increase consciousness towards chemical contamination has led to the establishment of Safe Drinking Water Act 1974. In 1980s, improvements were made in membrane development for reverse osmosis filtration while other disinfectant such as ozone and chloramine has started to flourish. Some treatments were driven by existence of chlorine-resistant pathogenic microorganism that can cause diseases such as hepatitis, gastroenteritis, pneumonia and cryptosporidiosis. Today, most treatment plant still utilised the method from thousands of years ago (coagulation, filtration and chlorination) but advanced techniques such as membrane filtration, advanced oxidation, ion exchange and others are also being employed in some modern water treatment plant.

TYPE OF WATER AND WASTEWATER TREATMENT

Wastewater discharge and drinking water need a proper treatment before it could be taken or released. The processes in water treatment are very important to ensure the water quality follows the standard guideline of drinking water from world health organization (WHO). In fact, guidelines for wastewater treatment have been provided by the Ministry of Environment or local authority for each country which are categorized into Standard A and Standard B. Standard A refers to the discharge of wastewater released at before catchment area or water treatment plant (WTP), while Standard B refers to the wastewater discharge after WTP according to stream flow.

Treatment of water and wastewater can be divided into physical, biological and chemical treatment processes. In the early stage of selection method of water and wastewater treatment, the understanding on the processing, designs, schematics, and specifications are crucial. It is also vital to comprehend the interrelation of various processes and correct order of these processes in relation to each other for effective treatment. Undeniably, the treatment of wastewater depends upon the impurities present. The impurities can present physically, chemically and biologically, and therefore the treatments should be given accordingly to physical, chemical and biological treatment.

Physical Treatments

Among the physical treatment units are screen, clarifier, and grit chamber, which use physical process such as gravity settling and mechanical straining mechanism for removal of impurities. Mechanical straining takes place in screens, while gravity settling takes place in clarifiers. Clarifiers are also known as sedimentation basin or settling tanks. The objective of preliminary treatment is to remove the coarse solids and other large materials often found in raw wastewater. Removal of these materials is necessary to enhance the operation and maintenance of subsequent treatment units (Hench et al, 2003).

Screening

Screening is the process for removal of larger particles which can interfere with subsequent equipment or process. Screening devices can be broadly classified as coarse or fine (Gogate and Pandit, 2004). Smaller size openings generate more screenings and more contaminants on screening. The screened matter need to be handled, stored, and disposed. For design of screening, the bar spacing, materials of construction and dimensions need to be carefully measured. Besides that, the channel depth, width and approach velocity also among the consideration subjects (Bürger *et al.,* 2011). The screen processes also need to consider restriction of wind, aesthetics improvement and odor reduction. Overall, the primary screen aims to protect equipment from rags, wood and other debris. Furthermore, it also helps to reduce interference with in-plant flow and performance.

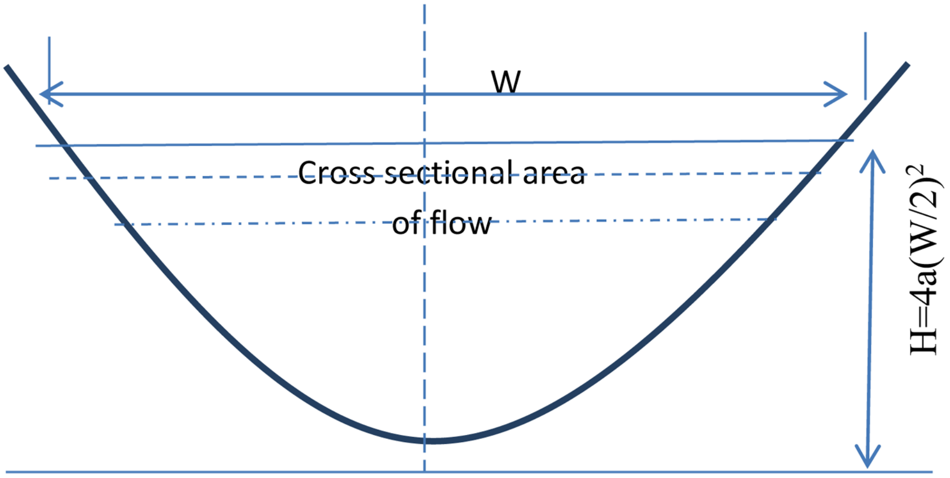
Grit Removal

Grit removal is commonly provided at all treatment plants for removing non putrescible materials and heavier than organic matter. It protects moving mechanical equipment and pumps from unnecessary wear and abrasion, and thus prevents clogging in the pipes. It also prevents cementing effect on the bottom of the tanks and at the same time reduces the accumulation of inert materials in the tanks (Gogate and Pandit, 2004).

Velocity-Controlled Grit Channel (Horizontal Flow)

This is the oldest type of grit removal process (Figure 1). The velocity should be maintained as close to 0.25 – 0.35 m/s to provide sufficient time for grit particles to settle. The parabolic shape gives the best flow pattern and the length of channel governed by the depth required by the settling velocity. The grit removal process is basically removed by using buckets, scrappers or plows.

Figure 1. Ideal parabolic cross section of grit chamber



Aerated Grit Chamber

Aerated grit chamber has been developed after the discovery of grit accumulations in spiral flow aeration tank. It consists of a spiral-flow aeration tank, where the spiral velocity is controlled and induced by the dimensions of the tank and the quantity of air supplied. The grit hopper is about 0.9 m deep with steeply sloping sides. Using this technique, the grit removal is removed by screw conveyors, tubular conveyors, jet pumps and air lifts.

Mechanical Grit Removal (Vortex)

It is a mechanically induced vortex to capture grit at the center. Normally, it is a proprietary design which consists of a cylindrical tank, and the flow enters tangentially creating a vortex-flow pattern. The centrifugal and gravitational forces cause the grit to separate. This method removes the grit by airlifts.

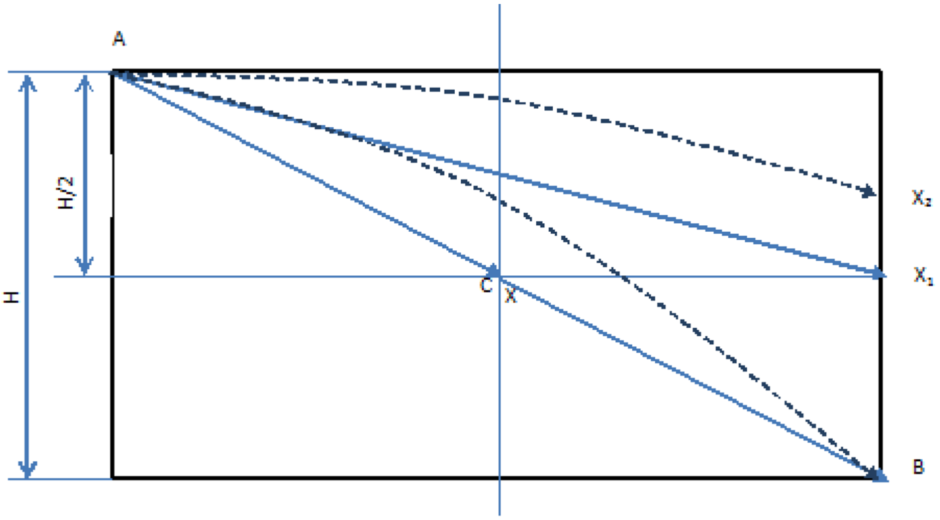
Sedimentation

Sedimentation is the removal process of solid particles from the suspension by gravity settling. The clarification process is similar to sedimentation, but it refers to the function of producing a clarified effluent, and thickening process settles the concentrated and compacted impurities on the floor of a tank and in sludge hoppers (Bürger *et al.,* 2011). There are four classes of settlement:

- **Class I:** Unhindered settling of discrete particles
- **Class II:** Settling of dilute suspensions of flocculent articles
- **Class III:** Hindered settling or zone setting
- **Class IV:** Compression settling (Compaction)

Figure 2 shows theoretical effect of tank depth on removal of discrete and flocculants particles. Flocculent particles are particles which interact with other particles in their vicinity. Organic suspended solids and the floc particles generated by chemical coagulation and flocculation of water, with a broad spectrum of sizes and surface characteristics are example for these flocculent particles. Different-sized particles settle at different rates so that larger particles will overtake or collide with smaller particles. As a result, it may coalescence into larger aggregates with an increasing settling velocity and then the typical path of a flocculent particle is curved, representing the increasing velocity with depth. There is significant requirement of settling tanks for treating flocculent suspensions is, therefore, that the depth must be great enough to allow particle agglomeration to occur. This is in contrast to the behavior of discrete particles whose settling behavior is independent of depth. The effect of tank depth on removal efficiency is shown in Figure 2. If the tank depth is reduced by half, the retention time is halved and the depth reached by each type of particle during that time is reduced. Nevertheless the discrete particle will again just reach the bottom of the reduced depth tank, whereas the flocculent particle will not have reached the tank floor and will be drawn off in the tank outflow. This is a summary of mechanism occurs inside a sedimentation tank. However, it is generally considered that the overall effect of reducing settling tank depth is to reduce removal efficiency when treating flocculent particles. This is proven by observation of X_2 at reduced tank depth, flocculent particle 'misses' sludge zone and carried off. While, X_1 successfully enters sludge zone though reduction of tank depth.

Figure 2. Theoretical effect of tank depth on removal of discrete (straight line) and flocculants (dashed line) particles



For above case (class II settlement), it is commonly done in the primary sedimentation tank. The primary sedimentation tank only applicable for short detention times usage during the hot climates as to avoid odor and rising sludge. There are three types of sedimentation tank namely rectangular, circular and up flow, but rectangular sedimentation tank tends to be favorable as it is more conducive and effective. These primary tanks are designed to remove settleable solid (90 – 95%), suspended solid (50 – 70%), total solid (10 – 15%) and BOD (25 – 35%).

Biological Treatments

Biological treatment is also known as secondary treatment where the process involves biological treatment during secondary sedimentation (Gogate and Pandit, 2004). The treatment of wastewater subsequent to the removal of suspended solids by microorganisms such as algae, fungi, or bacteria under aerobic or anaerobic conditions during which organic matter in wastewater is oxidized or incorporated into cells that can be eliminated by removal process or sedimentation (Bürger et al., 2011). The settled wastewater is introduced into a specially designed bioreactor where under aerobic or anaerobic conditions the organic matter is utilized by aerobic and anaerobic microorganisms (Gogate and Pandit, 2004). The bioreactor is designed according to bioenvironmental conditions for the microorganisms to reproduce and use the digest organic matter as energy for themselves. The oxygen and food, in the form of settled wastewater, are supplied to the microorganisms, and thus the biological oxidation process of dissolved organic matter will be maintained. The biological process mostly involves bacteria that form the basic trophic level (the position level of an organism occupies in a food chain) of the food chain inside the bioreactor.

The bioconversion of organic matter into thick bacterial biomass can fundamentally purify the wastewater (Malandra, *et al.,* 2003). Later, it is crucial to separate the microbial biomass from the treated wastewater through sedimentation. This secondary sedimentation is basically similar to primary sedimentation except that the sludge contains bacterial cells rather than fecal solids. The microorganism really plays a great role for the biological removal of organic matter from the settled wastewater, especially the heterotrophic bacteria (Bürger *et al.,* 2011). These microorganisms are able to decompose the organic matter through biological oxidation and biosynthesis. The biological oxidation forms some end-products, such as minerals, which remain in the solution of water and are discharged with the treated effluent (Eq 1). Meanwhile, the biosynthesis phase is a transformation of the colloidal and dissolved organic matter into new cells that form denser biomass that can be removed by sedimentation (Eq. 2).

Oxidation:

$$\text{COHNS} + O_2 + \text{Bacteria} \rightarrow CO_2 + NH_3 + \text{other end product} \quad (1)$$

(Organic matter)

Biosynthesis:

$$\text{COHNS} + O_2 + \text{Bacteria} \rightarrow C_5H_7NO_2 \quad (2)$$

(Organic matter)

Biological Treatment Principles

There are core principals need to be considered during the biological treatment as follows:

1. The biological systems are very sensitive for extreme variations in hydraulic loads. Diurnal variations of greater than 250% are problematic because they will create biomass loss in the clarifiers.
2. Temperature is a significant factor for the growth rate of microorganisms. A 10°C reduction in wastewater temperature will drastically decrease the biological reaction rates to half.
3. BOD removal can achieve up to 95% efficiency, but large tanks are required in order to eliminate the entire BOD, which is not feasible.
4. It seems impossible for biological treatment systems to handle “shock loads” efficiently. Equalization is necessary if the variation in strength of the wastewater is more than 150% or if the wastewater at its peak concentration exceeding 1,000 $mg.L^{-1}$ BOD.
5. The carbon: nitrogen: phosphorus (C: N: P) ratio of wastewater is usually ideal. The C: N: P ratio of industrial wastewaters should range from 100:20:1 to 100:5:1 for a most advantageous biological process.
6. Oils and solids need to undergo pretreatment prior to biological treatment as they may negatively affect the performance of wastewater treatment.
7. Toxic and biological-resistant materials require special consideration and may require pretreatment before being introduced into a biological treatment system.

Aerobic Treatment

Commonly, aeration has been used to remove trace organic volatile compounds (VOCs) in water. It has also been implemented to transfer a substance, such as oxygen, from air or a gas phase into water in a process called “gas adsorption” or “oxidation”, i.e., to oxidize iron and/or manganese [Pant and Adholeya, 2007]. Aeration produces gases such as CO_2 and H_2S. Air stripping has been also utilized effectively to remove NH_3 from wastewater and to remove volatile tastes and other substances in water. Kimochi research group mentioned that aerobic treatment with biowastes is effective in reducing harmful gaseous emissions as greenhouse gases (CH_4 and N_2O) and ammonia (Shannon *et a.,* 2008).

Oxidation Pond

Oxidation ponds are aerobic systems where the oxygen required by the heterotrophic bacteria (an organism that unable to use carbon and organic carbon for growth) is provided not only via transfer from the atmosphere, but also from photosynthetic algae (Kimochi *et al.,* 1998) The algae are restricted to the euphotic zone (sunlight zone), only a few centimeters deep. Ponds are constructed to a depth of between 1.2 and 1.8 m to ensure maximum penetration of sunlight and appear dark green in color due to dense algal development (Craggs *et al.,* 2012).

Aeration Lagoons

The depth of aeration lagoons is deeper (3–4 m) compared to oxidation ponds, where oxygen is supplied by aerators, but not by the photosynthetic activity of algae as in the oxidation ponds (Conkle *et al.,* 2008). The roles of the aerators are to keep the microbial biomass suspended, ensure sufficient dissolved oxygen and allows maximal aerobic activity. On the other hand, bubble aeration is commonly used where the bubbles are generated by compressing air pumped through plastic tubing laid through the base of the lagoon. A predominant bacterial biomass increases and neither sedimentation nor sludge return, this procedure counts on adequate mixed liquor formed in the lagoon (Michael *et al.* 2013). Therefore, the aeration lagoons are suitable for degradable wastewater such as wastewaters of food industries. The treatment level, strength, and temperature of the influent will determine the hydraulic retention time (HRT) (ranges from 3 to 8 days). Generally, HRT of about 5 days at 20°C achieves 85% removal of BOD in household wastewater. However, if the temperature declines by 10°C, then the BOD removal will decrease to 65% (Uhlmann, 1979).

Anaerobic Treatment

The anaerobic treatments are employed to treat wastewaters which are rich in biodegradable organic matter (BOD >500 mg L^{-1}) and for further treatment of sedimentation sludge (Leitão *et al.*, 2006). A huge volume of organic wastewater containing large amounts of biodegradable materials are contributed from the agricultural and food processing industries. These wastewaters are difficult to be treated aerobically due to the troubles and expenses of fulfilment of the elevated oxygen demand to preserve the aerobic conditions. In contrast, anaerobic degradation occurs in the absence of oxygen. Although the anaerobic treatment is time-consuming, it has a multitude of advantages in treating strong organic wastewaters (Rajeshwari *et al.,* 2000). These advantages include elevated levels of purification, aptitude to handle high organic loads, generating small amounts of sludge that are usually very stable, and production of methane (inert combustible gas) as end-product. Anaerobic digestion is a complex multistep process in terms of chemistry and microbiology. Organic materials are degraded into basic constituents, finally to methane gas under the absence of an electron acceptor such as oxygen.

Anaerobic Digester

Lettinga *et al.* (1980) illustrated the structures and constructions of the anaerobic digesters and the use of building materials. Currently, there are plenty expert system for planning and designing biogas plants. Figure 3 shows different types of anaerobic digesters. The anaerobic treatment is conducted without oxygen. It is different from an anoxic process, which is a reduced environment in contrast to an environment without oxygen. Both processes are anoxic, but anaerobic is an environment beyond anoxic where the oxidation reduction potential (ORP) values are highly negative. In the anaerobic process, nitrate is reduced to ammonia and nitrogen gas, and sulfate (SO_3^{2-}) is reduced to hydrogen sulfide (H_2S) (Shannon *et al.,* 2008). Phosphate is also reduced because it is often transformed through the ADP–ATP chain.

Activated Sludge

The activated sludge process is a mixture of thick bacterial population suspended in the wastewater under aerobic conditions. Excessive nutrients and oxygen, plus high rates of bacterial metabolism growth and respiration can be achieved, which result in the consumption of the available organic matter to either oxidized end-products (e.g., CO_2, NO_3^-, SO_4^{2-}, and PO_4^{3-}) or biosynthesis of new microorganisms (Leitão *et al.,* 2006). There are five phases for the activated sludge process which are bioreactor, activated sludge, aeration and mixing system, sedimentation tank, and returned sludge (Holenda *et al.,* 2008). The treatment of wastewater using biological process commonly uses activated sludge process due to lower operational cost (Figure 4). However, a huge quantity of surplus sludge is produced in wastewater treatment plants (WWTPs) which become an enormous burden in both economical and environmental aspects. The excess sludge contains a lot of moisture and not easy to treat. The by-products of WWTPs are dewatered, dried, and finally burnt into ashes. Some are used in farm lands as compost fertilizer. However, it is suggested that the dried by-products of WWTPs are fed into the pyrolysis process rather than the burning process (Werle and Wilk, 2010).

During activated sludge process, inside the aeration tank there are suspended solids, where the concentration of the suspended solids is known as mixed liquor suspended solids (MLSS), measured in milligrams per liter (mg L^{-1}) (Leitão *et al.,* 2006). Mixed liquor is a mixture of raw wastewater and

Figure 3. Typical anaerobic digester reactors types: (a) Mixed Anaerobic digester, (b) UASB reactor, (c) AFB or EGSB reactor and (d) Upflow AF

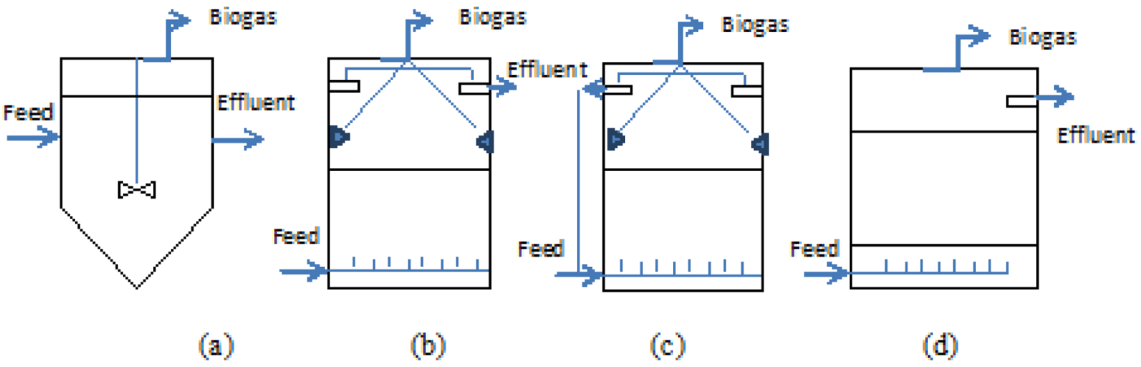
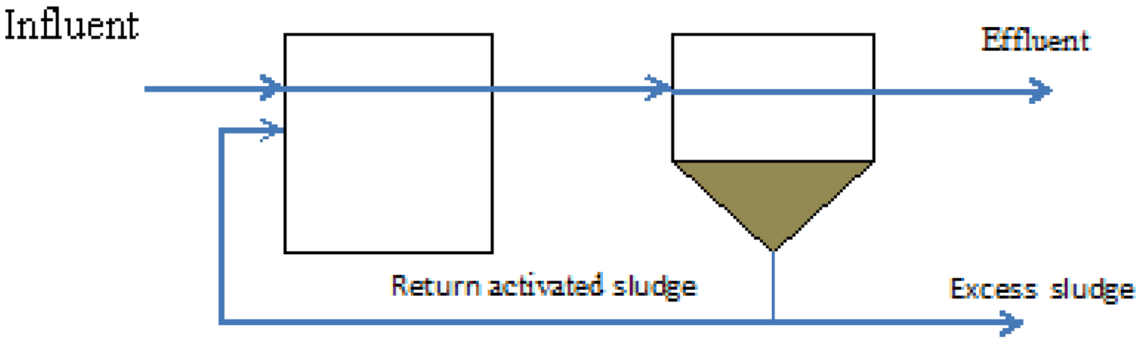


Figure 4. Activated sludge processes



activated sludge in an aeration tank. MLSS consists mainly of microorganisms and non-biodegradable suspended solids. MLSS is the effective and active portion of the activated sludge process which ensure that there is sufficient quantity of viable biomass available to degrade the supplied quantity of organic pollutants at any time. This is called as Food to Microorganism Ratio (F/M Ratio) or food to mass ratio. If this ratio is kept at the right level, then the biomass will be able to digest high quantities of food, which reduces the loss of remaining food in the effluent (Schwarz *et al.*, 2006). In other words, more digestion of the food will lower the BOD values in the treated effluent. It is important for the MLSS to remove the BOD in order to cleanse the wastewater for further usage and hygiene. Raw sewage is introduced into the wastewater treatment process with a concentration of several hundred mg L^{-1} of BOD. The concentration of BOD in wastewater is reduced to less than 2 mg L^{-1} after being treated with MLSS and other treatment methods, which is considered as safe for use (Schwarz *et al.,* 2006).

Chemical Treatments

During early evolution stage of wastewater treatment technologies, chemical treatment has come first before biological treatment. Currently, the biological treatment precedes chemical treatment in the treatment process and now considered as a tertiary treatment. The mostly implemented chemical treatment processes are chemical precipitation, neutralization, adsorption, disinfection, and ion exchange.

Chemical Precipitation

The dissolved inorganic matter can be eliminated by adding an acid or alkali, by changing the temperature, or by precipitation as solid. The precipitation can be eliminated by sedimentation, flotation, or other solid removal processes (Harper and Kingham, 1992). Even though chemical precipitation (coagulation, flocculation) is still implemented, it is highly suggested to replace the chemical precipitation process by phytoremediation. The bioremediation and phytoremediation help in reducing the usage of chemicals, which is in line with the green environment concern.

Neutralization

Neutralization refers to controlling the pH of the wastewater whether it is acidic or alkaline to keep the pH around 7. The lack of sufficient alkalinity will require the addition of a base (Table 1) to adjust the pH to the acceptable range. Lime (CaO), calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3), also known as soda ash, are the most common chemicals used to adjust the pH (Ahn *et al.,* 2008). The lack of sufficient acidity will require the addition of an acid to adjust the pH to the acceptable range. Sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3) are the most common chemicals used to adjust the pH.

Adsorption

Adsorption is one of the methods frequently applied in the wastewater treatment. However, too many people confuse between adsorption and absorption. Absorption method is not frequently applied in the wastewater treatment as it is not economic and practical. In addition, adsorption is easily found in the water or wastewater treatment. Figure 5 explains the difference between absorption and adsorption. Adsorption is a physical process where soluble molecules (adsorbate) are removed by attachment to the surface of a solid substrate (adsorbent). Adsorbents should have an extremely high specific surface area. Activated alumina, clay colloids, hydroxides, resins, and activated carbon are among example of adsorbents. The surface of the adsorbent should be free of adsorbate. Therefore, the adsorbent should be activated before use. There are many types of organic materials which can be eliminated by adsorption, such as detergents and toxic compounds. The most popular used adsorbent is activated carbon, produced from pyrolytic carbonization process of biomass. Activated carbon is the most applied adsorbent and is a sort of carbon processed to be riddled with small, low-volume pores that broaden the surface area vacant for adsorption. The high level of microporosity is represented by 1 g of activated carbon which has a surface area larger than 500 m^2, which is determined by gas adsorption. To reuse the carbon, thermal oxidation or steam oxidation can be applied. Otherwise, soaking with acid of alkaline also can be applied.

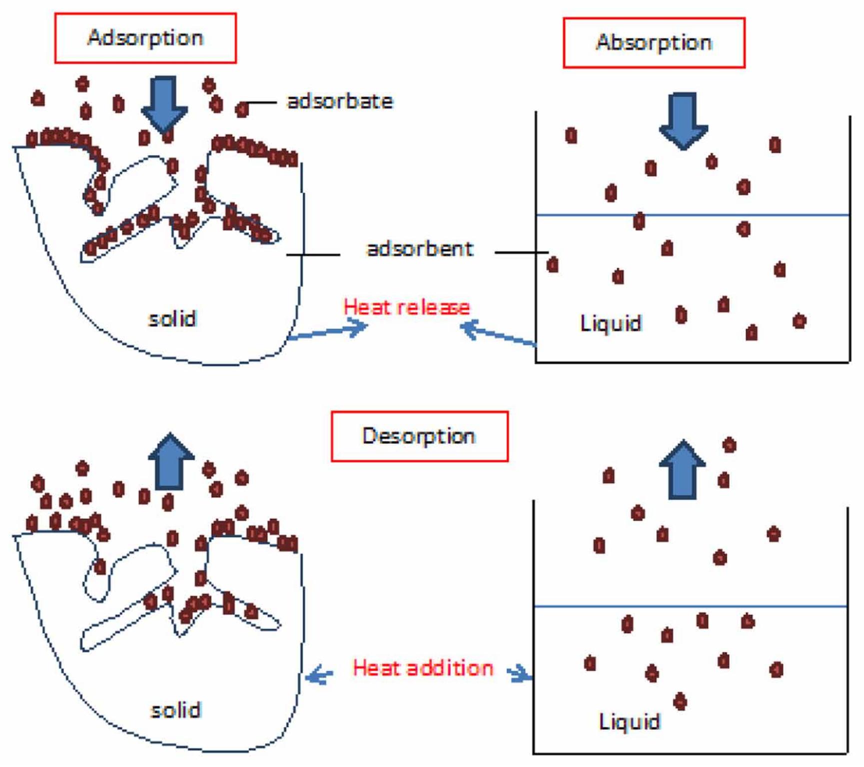
Disinfection

The disinfection of wastewater is the final treatment step of the tertiary treatment process. The aim of disinfection is to exterminate or at least inactivate the pathogens. The justifications behind effluent

Table 1. Neutralization Reaction [Ahn et al., 2008]

To Neutralize Sulfuric Acid With
Lime: $H_2SO_4 + CaO \leftrightarrow CaSO_4 + H_2O$ Calcium hydroxide: $H_2SO_4 + Ca(OH)_2 \leftrightarrow CaSO_4 + H_2O$ Sodium hydroxide: $H_2SO_4 + NaOH \leftrightarrow NaSO_4 + 2H_2O$ Soda Ash: $H_2SO_4 + Na_2CO_3 \leftrightarrow Na_2SO_4 + H_2O + CO_2$
To Neutralize Hydrochloric Acid With
Lime: $2HCL + CaO \leftrightarrow CalCl_2 + H_2O$ Calcium hydroxide: $HCl + Ca(OH)_2 \leftrightarrow CaCl_2 + H_2O$ Sodium hydroxide $HCl + NaOH \leftrightarrow NaCl + H_2O$ Soda Ash: $HCl + Na_2CO_3 \leftrightarrow NaCl + H_2O + CO_2$

Figure 5. A comparison between absorption and adsorption

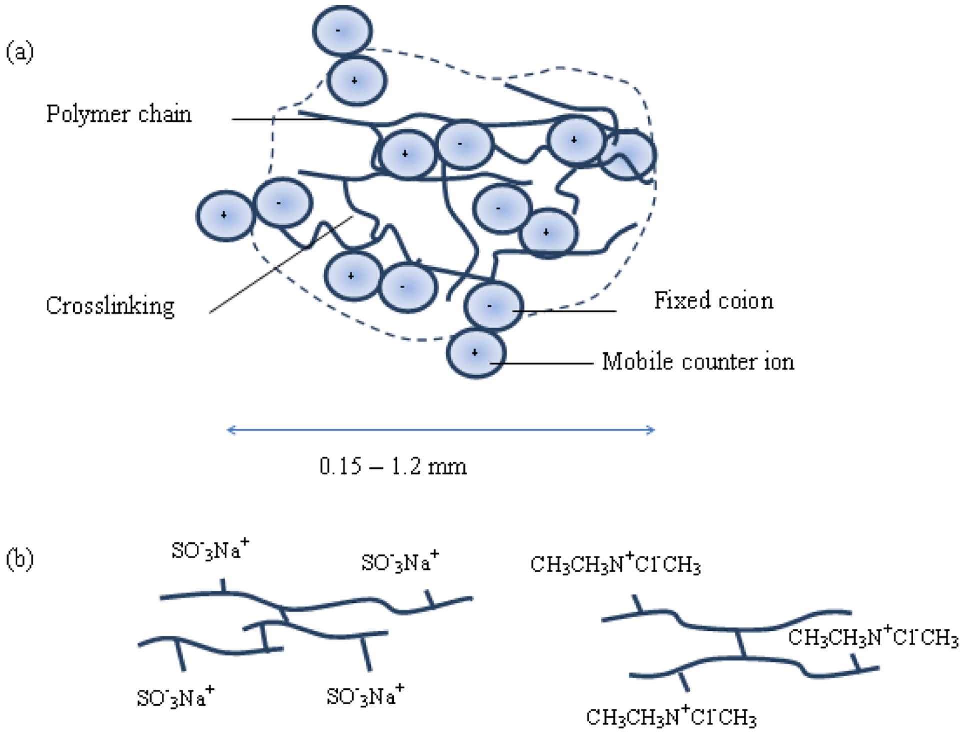


disinfection are to protect public health by destroying or inactivating the pathogens such as microbes, viruses, and protozoan, and to meet the wastewater effluent standards. The purpose of disinfection is to protect the microbial wastewater quality. The ideal disinfectant should have bacterial toxicity, inexpensive, not dangerous to handle, and should have reliable means of detecting the presence of a residual. The chemical disinfection agents include chlorine, ozone, ultraviolet radiation, chlorine dioxide, and bromine (Haas *et al.,* 1982).

Ion Exchange

Ion exchange (IX) is a reversible reaction in which a charged ion in a solution is exchanged with a similarly charged ion which is electrostatically attached to an immobile solid particle (Rengaraj *et al.*, 2001). The famous of ion exchange method in wastewater treatment is softening, where polyvalent cations (e.g., calcium and magnesium) are exchanged with sodium. Practically, wastewater is introduced into a bed of resin. The resin is made by converting a polymerization of organic compounds into a porous matrix. Sodium is commonly exchanged with cations in the solution. When the bed becomes saturated with the exchanged ions it will be directly shut. To regenerate the bed, it needs a concentrated solution of sodium passing through the bed (Weiss *et al.,* 1966). Figure 6 shows the schematic illustration of organic cation-exchange bead.

Figure 6. Schematic of organic cation-exchange bead: (a) The bead is shown as polystyrene polymer cross-linked with divinyl benzene with fixed coions (minus charge) balanced by mobile positively charged counterions (positive charge), (b) strong cation exchange resin on left (Na^- form) and strong-base on right (Cl^- form)



Integrated Treatments

Tertiary and/or advanced wastewater treatment is implemented when specific wastewater constituents which cannot be removed by secondary treatment must be removed. For nitrogen, phosphorus, additional suspended solids, refractory organics, heavy metals and dissolved solids it is necessary to have individual treatment processes. The advanced treatment processes are sometimes combined with primary or secondary treatment (e.g., chemical addition to primary clarifiers or aeration basins to remove phosphorus) or used in place of secondary treatment (e.g., overland flow treatment of primary effluent). It is also called as integrated treatment.

For example, for phosphorus removal, commonly secondary treatment removes only about 1-2 mg/l of phosphorus, so a huge volume of phosphorus is discharged in the final effluent, causing eutrophication of lakes and natural water stream. Generally, it appears as orthophosphate, polyphosphate and organically bound phosphorus. Phosphorus is significantly needed by microbes to synthesis, transport and maintain the energy, as well as it is stored for subsequent use by microbes. During secondary treatment process about 10 to 30% of influent phosphorus is removed (Metcalf & Eddy, 2003). Currently, phosphate removal is done by using chemical precipitation and the cost is expensive. Besides that, it also can cause an increase of sludge volume up to 40%. To overcome the problem, biological phosphate removal (BPR) is introduced, which is accomplished by sequencing and producing the appropriate environmental condition in the reactors. Treatment technologies presently available for phosphorus removal include (de-Bashan & Bashan, 2004):

1. **Physical:** Filtration for particulate phosphorus and membrane technologies
2. **Chemical:** Precipitation and physical-chemical adsorption
3. **Biological:** Assimilation and enhanced biological phosphorus removal (EBPR)

Advanced Oxidation Process

Some compounds in municipal and industrial wastewater (synthetic or natural-origin) may cause several problems in biological treatment because of their recalcitrant properties and toxic effect to the microorganisms. Advanced oxidation process is a treatment that involves reaction of strong oxidising agents or irradiation with organic and inorganic contaminants. This process will first mineralise or render recalcitrant molecules as biodegradable compounds. The increase production of biodegradable compounds will result in more operative and successful microbial process. Therefore, advance oxidation process is often employed as a supporting process to inefficient biological treatment.

The principle behind "advanced oxidation process" was established by Glaze et al. (1987). It has been introduced that the objective of AOP is to generate hydroxyl radical (OH·) for oxidation process of water contaminants. For inorganic compounds, oxidation can be described as the removal of electrons to produce higher oxidation state such as Fe^{2+} to Fe^{3+}. For organic compounds, it involves the production of oxygenated compounds such as carbonyl compounds, organic acids and alcohols. The hydroxyl radical has preferable features such as high oxidation potential (2.8V), easy to produce in natural water condition, short shelf life and relatively non-selective electrophilic oxidant (Naddeo *et al.,* 2011). Hydroxyl radicals decompose organic contaminants through four main pathways: radical addition, hydrogen abstraction, electron transfer and radical combination (Deng & Zhao, 2015).

Generally, hydroxyl radical-AOPs are divisible into three groups namely: (1) UV based (2) ozone based and (3) Fenton based (Deng & Zhao, 2015). The main step in UV based AOP is the electronic excitation of the substrate followed by the electron transfer from the excited substrate to ground state molecular oxygen (O_2). Through homolytic breakage, free radicals are formed and further reaction with dissolved oxygen generates peroxide radicals. With the reaction of OH^-, H_2O and O^{2-} at the surface of catalyst, positive state of valence band, and negative electrons can further form hydroxyl radicals. In the presence of oxidants such as H_2O_2 or O_3, additional OH· may be yielded under UV irradiation.

Iron is the most frequently used metals in activation of H_2O_2 to produce OH· in water. Therefore, the AOP involving iron is called Fenton process. Dark Fenton reaction proceeds under acidic conditions as according to classical Fenton radical mechanism. The iron can initially be in either Fe^{2+} and Fe^{3+} states. The overall degradation efficiency does not depend on the initial oxidation state of iron. Based on the classical Fenton process, three modified processes are proposed: Fenton-like reaction, photo-Fenton reaction and electro-Fenton reaction (Deng & Zhao, 2015).

Ozone is a strong oxidant with high oxidation potential of 2.07 V. However, direct O_3 oxidation is a selective reaction, which demands ionised and dissociated form of organic compounds rather than natural form. The pH of water is crucial since hydroxide ions initiate ozone decomposition. In the presence of other oxidants or irradiation the OH· can be significantly increased. To date, three known pathways for ozone based AOP are ozonation, O_3/H_2O_2 and photolysis of H_2O_2.

QUALITY WATER AND WASTEWATER

Quality water and wastewater can be assessed through the general parameters for water and wastewater. Parameters for water especially drinking water is different with wastewater, and every single parameter is needed to evaluate water and wastewater quality. High concentration of parameters shows that quality of water and wastewater becomes lower. For example, high content of $CaCO_3$ in the drinking water will simulate kidney stones disease, then the water quality is considered low. The same situation for wastewater because it will discharge to stream and has a potential to contaminate water resources and harmful to living creature and environment.

Parameters Assessment for Drinking Water Quality

To ensure that the water is safe for human consumption and livestock use, water supplies should be analysed and checked to ensure they meet the satisfactory levels for bacterial and chemical composition. The local health department in most countries can conduct a microbiological test and chemical or mineral analysis. The testing procedure is not the same for all contaminants. Unfortunately, no single water test can provide information on all possible contaminants (Petrović *et al.*, 2003).

Mineral Analysis

A mineral analysis determines the inorganic composition found in water. A typical mineral analysis will give the content in parts per million (milligrams per liter) of mineral elements such as calcium, magnesium, manganese, iron, copper and zinc. The analysis also provides result of the acidity or pH of the water and the hardness, expressed in parts per million or grains per gallon (Baban, 1993). At the same time, it gives the concentration of nitrate, sulfates and other chemical compounds. Large amounts of minerals and other impurities may pose a health hazard. For instance, nitrate contamination can cause health problems for infants and ruminant animals, sulfates can have a laxative effect in humans, and arsenic may cause cancer if consumed over a long period of time. Minerals at high concentrations can also affect the appearance and use of the water. Hard water is due to high levels of calcium and magnesium. Iron may leave red stains on plumbing fixtures, equipment and laundry. Suspended silt makes water look muddy or cloudy and dissolved gases may give water a bad taste and/or odour (Petrović *et al.,* 2003).

Microbial Tests

A microbiological test determines the risk of the water contamination by disease-causing microorganisms (pathogens). However, to test the drinking water for all possible pathogens is really complex, time consuming and expensive. Instead, water is commonly tested for indicator microorganisms such as total coliform and *E. coli* bacteria because if they are present in water, the condition of the well and its surrounding environment may support the presence of other disease-causing microorganisms (van *et al.*, 1989). Thus, a positive water test result for total coliform only or both total coliform and *E. coli* indicate the possible existence of various disease-causing microorganisms. Coliform is a name of a group which comprises many bacteria. Most coliform bacteria do not cause disease and they are lavish in soils, waters, and vegetation. The presence of this bacteria in drinking water indicates that disease-causing organisms could be contaminating the water system. *E. coli* is a special type of coliform bacteria that most likely originates from a fecal source. Most *E. coli* bacteria are also harmless and are found in great quantities in the intestines of people and warm-blooded animals. However, some *E. coli* strains can cause illness. The presence of *E. coli* in a drinking water sample almost always indicates recent fecal contamination by sewage or manure, meaning there is a greater risk that pathogens are present (LeJeune *et al.,* 2001).

Standard WHO (World Health Organization) for Drinking Water

WHO creates international standard on water quality and human health in the form of guidelines for the basis of regulation and standard setting world-wide. The Guidelines for Drinking-Water Quality (GDWQ) encourage the protection of public health by supporting the development of locally relevant standards and regulations (health based targets), adoption of preventive risk management approaches covering catchment to consumer (Water Safety Plans) (Petrović *et al.,* 2003). There are two tests to verify safety of the drinking water which are microbial water quality and chemical quality test as described below.

Microbial Water Quality

For microbial water quality is likely to include microbiological testing. In most cases, it will involve the analysis of faecal indicator microorganisms, but in some situations it may also include assessment of specific pathogen densities (van *et al.*, 1989). The tests are testing of water source, water immediately after treatment, water in distribution systems or stored household water. The microbial quality of drinking-water includes testing for *Escherichia coli* as an indicator of faecal pollution. *E. coli* provides conclusive evidence of recent faecal pollution and should not present in drinking-water (Edberg *et al.,* 2000).

In practice, testing for thermo-tolerant coliform bacteria can be an acceptable alternative in many circumstances. Even though *E. coli* is a useful indicator, but it has some limitations. Enteric viruses and protozoa are more resistant to disinfection; thus, the absence of *E. coli* will not necessarily represent freedom from these organisms. Under certain cases, it may be necessary to include more resistant microorganisms, such as bacteriophages and/or bacterial spores. This may include the use of source water known to be contaminated with enteric viruses and parasites or high levels of viral and parasitic diseases in the community (Baban, 1993). Water quality can vary rapidly, and all systems are subject to occasional failure. For example, rainfall can greatly increase the levels of microbial contamination in source of water, and water-borne outbreaks. Results of analytical testing must be interpreted by considering these effects.

Chemical Water Quality

Assessment of the chemical quality of drinking water depends on comparison of the analysis results of water quality the standard values. For additives (i.e., chemical which is derived from materials and chemicals used for drinking water), the priority is placed on the direct control of the quality of these products. While for controlling drinking water additives, testing procedures typically assess the contribution of the additive to drinking water and take account of variations over time in deriving a value that can be compared with the guideline value.

The main concern for most chemicals is their long-term exposure. However, some hazardous chemicals present in drinking water are of concern due to effect of exposure over a short period. Whilst the concentration of the chemical of interest varies widely, even a series of analytical results may fail to fully identify and describe the public health risk (e.g., nitrate, which is associated with methaemoglobinaemia in bottle-fed infants). In controlling such hazards, consideration must be given to fundamental factors such as fertilizer use in agriculture and trends in detected concentrations, since these will indicate whether a significant problem may arise in the future. Other hazards may arise intermittently, often associated with seasonal activity or seasonal conditions. One of the examples is the occurrence of blooms of toxic cyanobacteria in surface water. A guideline value signifies the concentration of a constituent that does not exceed tolerable risk to the health of the consumer over a lifetime of consumption. Guidelines for some chemical contaminants (e.g., lead, nitrate) are set to be protective for susceptible subpopulations. These guidelines are also protective for general population over a lifetime.

National Drinking-Water Policy

The aim of national drinking-water laws and standards is to ensure that the consumer enjoys safe potable water. Effective control of drinking-water quality is supported ideally by adequate legislation, standards and codes, and their enforcement (Malandra *et al.,* 2003). The precise nature of the legislation in each country will depend on national, constitutional and other considerations. It will generally outline the responsibility and authority of a number of agencies and describe the relationship between them. The national regulations, adjusted as necessary, should be applicable to all water supplies.

In countries where universal access to safe drinking-water at an acceptable level of service has not been achieved, policy should refer to expressed targets for increases in access. Such policy statements should be consistent with achievement of the Millennium Development Goals of the United Nations (UN) Millennium Declaration and should take into account levels of acceptable access on the Right to Water of the UN Committee on Economic, Social and Cultural Rights. Drinking-water supply policy should normally outline the requirements for protection of water sources and resources, the need for appropriate treatment, preventive maintenance within distribution systems and requirements to support maintaining water safety after collection from communal sources. Table 2 shows the national guidelines for raw drinking water quality for Malaysia.

Parameters Assessment for Wastewater Discharge

The quality of effluent discharged from treatment plants into receiving waters need to follow the established standards. These take the form of acceptable upper limits for various effluent contaminants. Sample of effluents from treatment plants are taken regularly and analyzed in laboratories to ensure that these standards are followed and the treatment plants are operated efficiently. There is a need to measure the pollutants in sewage in order to better understand and thus facilitate the treatment of sewage. Besides that, the data are used to examine the effects of effluent or treated sewage toward the environment. Table 1 illustrates the standard for quality of effluent from Indah Water Consortium (IWK).

WATER POLLUTION SOURCES

Geography

Contamination of water resources due to geography factor has been noticed by many environmentalists, scientists and researchers. Level of landscape leads this issue to critical view. Water from rain can

Table 2. Malaysia guidelines for raw drinking water quality (revised December 2000)

Parameter	Symbol	Benchmark (mg/l)
Sulphate	SO_4	250
Hardness	CaCO3	500
Nitrate	NO3	10
Coliform	-	Must be not detected in any 100 ml sample
Manganese	Mn	0.1
Chromium	Cr	0.05
Zinc	Zn	3
Arsenic	As	0.01
Selenium	Se	0.01
Chloride	Cl	250
Phenolics	-	0.002
Total dissolved solids	-	1000
Iron	Fe	0.3
Copper	Cu	1.0
Lead	Pb	0.01
Cadmium	Cd	0.003
Mercury	Hg	0.001

cause runoff phenomena if land cannot absorb more water. The nearby creeks, stream or ponds will be in contented by the excess liquid flows via the surface of the land. Runoff not only occurs from natural processes, but it could come from human activity as well. Runoff will bring all toxics, soil, silt, clay and contaminated materials in the land to the creeks, stream or ponds.

The best example of runoff contributed by natural process is snowmelt. Due to saturated water from heavy snow in the mountains, runoff will occur and it will flow into streams, rivers and lakes. Other causes of runoff from natural processes are glaciers and rain. In certain condition, runoff will not occur because of saturated water from the land, but this phenomenon may occur caused by other sources of liquid. The best example in this situation is the volcanic eruption of which toxic chemicals enter the waterways through natural disaster. The gasses released by volcanic eruption will eventually precipitate in water for certain time and contributes to water contamination. In addition, worse condition of runoff will occur during the rainy season when saturated water in the land channels all precipitate materials in the land to waterways.

In geography aspect, human activity also contributes to contamination via runoff phenomena. The water contamination is divisible into two sources namely point sources and non-point sources. The point sources pollution is runoff of contaminated water from industry such as sewage treatment plant, factory, or even household. Population, type of industry and amount of raining per year need to be considered before designing an open wastewater treatment plant to avoid runoff contamination by point sources from entering the waterways. Meanwhile, the non-point sources can come from any sources which are very difficult to identify, and possibly most of the runoff not directly channel to waterways, but the runoff combined with rainwater and irrigation wash chemicals will flow into local streams of urban, suburban,

Table 3. Standard "A" and "B" for public sewage treatment facilities from IWK Malaysia (Halim et al., 2010)

Parameter	Standard A (mg/L)	Standard B (mg/L)
Temperature (celcius)	40	40
pH Value	6.0 – 9.0	5.5 – 9.0
Biological Oxygen Demand	20	50
Chemical Oxygen Demand	50	100
Suspended Solids	50	100
Mercury	0.005	0.05
Cadmium	0.01	0.02
Chromium	0.05	0.05
Arsenic	0.05	0.10
Cyanide	0.05	0.10
Lead	0.10	0.5
Copper	0.20	1.0
Manganese	0.20	1.0
Nickel	0.20	1.0
Tin	0.20	1.0
Zinc	0.20	1.0
Boron	1.0	1.0
Iron (Fe)	1.0	4.0
Phenol	1.0	5.0
Free chlorine	0.001	1.0
Sulphide	0.5	0.5
Oil and Grease	Not detectable	10.0

or rural areas instead. Commonly, runoff from non-point sources contains lawn fertilizer, pesticides, and even spilled gasoline from a car. Mitigation for nonpoint source pollution may include improvement of storm water systems, limitation of pesticides application, and development of wetland.

Ecological

Degradation and eutrophication are two examples of pollution from ecological system or process. Although ecology refers to natural process, but some of the pollutants via ecological process are from human activity, for example degradation. The degradation process is due to interaction of fungi, enzyme, algae, bacteria or any kind of tiny microorganism process with organic waste originated from human activity. In fact, the degradation process of domestic wastewater is a natural ecological process, but the sources of wastewater are from human activity. Degradation of organic waste such as garden waste or organic matter will increase the amount of amino acid, fatty acid and nitrogen in the sample. Then, the runoff will bring all of those chemicals to the water body and finally it will contaminate the stream, lake or glacier.

The enrichment nutrient in the water due to runoff will cause eutrophication phenomena. Eutrophication occurs when the environment becomes enriched with nutrients such as the amount of biological oxygen demand (BOD), total nitrogen (TN) and total phosphorus (TP). The enrichment of nutrients will encourage algae growth in the water surface. The habitats of marine will destroy because of algal bloom and consequently decrease the content of oxygen, prevent penetration into water and finally will decline the quality of water. Some of algae or bacteria (but pretend to be algae) which involve in the eutrophication phenomena have a tendency to produce toxic, for example cynobacteria. Cynobacteria produces toxicity during the growth process and directly it will make the water become toxic and not suitable for living creature. Cynobacteria is one of the bacteria species, but it pretends like algae having greenish colour.

Fertiliser is one of the materials often used as source of eutrophication. Fertilisers are normally used in farming, but occasionally fertilisers which are not absorbed by plants will cause runoff into nearby water sources causing an increase in nutrient levels. Then, it will cause phytoplankton to grow and reproduce more rapidly and finally resulting in algal blooms. Rapid growth of algae in the water will disrupt normal ecosystem function and cause many problems. Algae will compete with marine life by consuming oxygen in the water and eventually lead to fatality of many aquatic organisms such as fish which also needs oxygen in the water to live. Too much algae covering the surface of water will block the penetration of sunlight through underwater. Consequently, it will affect the growth of aquatic plants by inhibiting photosynthesis of plants. Aquatic plants are the important sources of food and oxygen for living creature underwater.

Industry

Water pollution caused by industry is the most common water pollution in developed and developing countries in the world. The industrial sector produces many materials that are easily dissolved in water. Industrial wastewater from every sector has different levels of toxicity. Industrial sector may produce toxic material via mainstream of production line, by-product of the production process or waste. It also occurs that logistic and storage of toxic chemicals are not properly done. Some industrial workers are not concern about environmental issue when they merely dump or bury toxic waste illegally without obeying the regulations. As a result, the toxic waste will contaminate the groundwater and runoff water, and eventually contaminate surface and fresh water. Therefore, the treatments of wastewaters are required for the industry before discharging the wastewater into stream or lake.

Wastewater or waste material treatment needs to fulfil requirement from local authority or Department of Environment (DOE) for every state, city or country. The treatment methods of wastewater or waste material from industries are different and depending on their level of toxicity and content in their wastewater or material. Toxic chemicals such as heavy metals and industrial chemicals are sources of water contamination. Heavy metals such as arsenic, lead and mercury are metals that are detrimental towards human and environment. Thermal pollution is less likely known as a type of contaminant, but it is indeed a critical source of water pollution. The release of heated water from industry to open water will change the ambient temperature. As temperature increases, dissolve oxygen will decrease and thus leads to significant reduction of water quality. The common industries which cause water pollution are agriculture, mining, fishing, nuclear, fuel, plastic, textile manufacturing, cleaning service, auto manufacturing and recreation.

ECONOMIC AND WATER

Water has always played a vital role in human societies, which is labelled as a key driver of viable growth as an input in agriculture, industry, transport, energy and also in healthy ecosystems. Water plays the most important role in agriculture, which equipped over 330 million hectares of irrigated land worldwide. On average, 70 percent of all water withdrawals globally is consumed due to the requirements of crops. Industry accounts for 22 percent of all water consumption which is used for cooling, transportation and washing, and remaining 8 percent is for domestic use. The pattern of water use varies between regions. In low-income and middle-income countries, 82 percent of all water withdrawals is for agricultural, 10 percent for industrial and 8 percent is for domestic use. In high income countries, industrial accounts for 59 percent of water consumption, only 30 percent for agricultural and 11 percent for domestic use. According to Sullivan (2002), higher income countries tend to have higher water consumptions.

Besides crop irrigation, water is also needed for livestock raising and aquaculture. Higher water consumption in agriculture results in a significant increase in the potential yield of the farmed area. Thus, countries with greater irrigated area have the biggest potential in term of their agricultural domestic products. Stability in productions contribute to the price stability which favour investment and global economic growth. In addition, an adequate supply of food is an important condition for economic development which may reduce malnutrition cases around the world. These conditions need sufficient water resources, especially to those countries where agriculture constitutes a high proportion of the gross domestic product (GDP), particularly as a source of employment that contribute to the sustainable economic growth.

In the industrial sector, water is an important production factor in purpose of manufacturing operations, cleaning raw materials and equipment, air conditioning, cooling, and many other activities. In oil producing countries, major amounts of water are used to push the oil out from the deep underground. Without this water pressure, oil and gasoline would be scarce and more expensive which may affects global economy, especially for oil import countries. Another big user of water is the paper industry that needs millions of gallons of water in the various processes that turn a log into a piece of paper. Generally, industries require large supplies of water which enables producers to generate vast amounts of valuable goods that could improve their productivity. Thus, more and cheaper goods can be created, which raises the standard of living by lowering costs and raising wages that stimulate economic growth.

Water for domestic use includes the supply of drinking water and adequate sanitary condition alongside for indoor and outdoor household purposes. Water in households is mainly needed for cleaning and washing, for personal hygiene and also for toilet flushing (Scheele & Malz, 2007). This is directly related to the population’s health conditions which has been a target of economic development. This condition is true since health problems may have a series of adverse impact on economic growth like the reduction of available labour, higher absenteeism rates among worker which contribute to lower productivity due to ailments that affects the families’ potential income (Harris and Melo, 2004). Human capital, as known, being one of important source of economic growth, and living in healthy states will develop maximum potential among workers. Thus, the universal supply of drinking water should be one of the main goals of human development to reach maximum levels of health and income. This is supported by Lawrence *et al* (2002), the lack of appropriate, reliable water supply leads to a poor health status and low gross domestic product (GDP).

Nowadays, water shortage is being a bigger problem, due to the climate change, global warming and high population across regions. Growing water scarcity limiting desirability or potential for investments. The world's population is growing by roughly 80 million per year and freshwater withdrawals have tripled over the last 50 years. According to Onda *et al.* (2012), 1.8 billion people still lack access to freshwater supply and 2.5 billion people need improved sanitation. Due to this problem, there are approximately 1.6 million deaths per year attributed to dirty water and poor sanitation which has killed more children due to the diarrhoea. In general, water scarcity is a major threat to economic growth and stability around the world. The region such as in Middle East and the Sahel in Africa, which are known as the driest continents, could see their growth rate decline by as much as 6% of their GDP due to water-related impacts on agriculture, health and incomes (World Bank, 2017). Due to this fact, nations should take action to better manage water resources since regions with large populations could be living with long periods of negative economic growth.

LIMITATION OF WATER AND WASTEWATER TREATMENT

Water and wastewater are two elements that are very important to human life and all living creature in the world. All organisms need clean water to live and at that same time all living creatures will produce waste from their ecosystem or activity. Those wastes if not properly managed will eventually be discharged and contribute to wastewater. Then, untreated wastewater will affect the surface and ground water. Therefore, it is a task for us human to be responsible to the environment assisted by knowledge and financial.

Financial issue is the main barrier for water and wastewater treatment. Several treatments consume a lot of energy and not economically feasible. Therefore, various treatment methods need to be listed before selecting the best method to be used for water and wastewater treatment. The best example is treatment of small and normal domestic wastewater. In this situation, perhaps biological treatment is more suitable and cost effective rather than modern treatment such as membrane filtration. Additionally, operation and maintenance cost also need to be considered. For example, the coagulation and flocculation process consumes a lot of chemicals which require high operation cost. Mechanical machines, reactors or tanks need to be maintained frequently to be in good condition. Without considering these factors, accident may occur in the treatment plant or the quality of wastewater discharge will not satisfy the standard level.

Another barrier in the water and wastewater treatment is safety aspect. Treatment of hazardous wastewater needs to consider safety element particularly to workers, another living creature and also environment. If the treatment plant needs to use certain microorganism, then it is crucial to investigate the biohazard of that microorganism. With respect to the ecosystem, the treatment should be effective and environmentally friendly. The final barrier is environmental aspect such as weather and natural disaster which may occur in the treatment plant or areas close to it should be taken into account. For example, an open treatment plant in a heavy raining place need to evaluate the amount of raining and design of the treatment plant.

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KEY TERMS AND DEFINITIONS

Crustacean: An invertebrate animal of the large, mainly aquatic group Crustacea, such as a crab, lobster, shrimp, or barnacle.

Eutrophication: Excessive nutrients in any water body, mostly due to run-off from the land, which causes a dense growth of plant life.

Hydrologic Cycle: A natural cyclic processes through which water turned from vapor into the atmosphere through precipitation upon land or water surfaces and ultimately returned into the atmosphere as a result of evaporation and transpiration.

Methaemoglobinaemia: The presence of methaemoglobin in the blood, usually through inheritance or chemicals exposure.

Xenobiotic Compounds: Foreign chemical substance which are not naturally found in biosphere.

Chapter 2

Water Quality Legislation and Regulation

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ABSTRACT

The legal and institutional framework, as well as the challenges and issues in water resources management, serves as the basis for the formulation of a policy framework that seeks to improve water resources management practices in the future. Recently, water resources 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 have reviewed several laws, including the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977, Environmental Quality (Prescribed Premises) (Raw Natural Rubber) Regulations 1978, and Environment Quality (Sewage and Industrial Effluent) Regulation 1979. Legal issues under the constitutional framework water management have also been reviewed. Exploring this topic generates an overview water management implementation in the context of Malaysia.

INTRODUCTION

Environmental pollution is a major concern for a developed country (Arshad et al, 2015). Water is a natural resource that needs to be preserved for future generation to be used without having any problem to get the pure water such as water pollution, higher cost in making water treatment, lack of water preservation and others. The findings indicate that the major problem associated with water pollution is that human heart and kidneys can be adversely affected if polluted water is consumed regularly. Other health problems associated with polluted water are poor blood circulation, skin lesions, vomiting, cholera, gastroenteritis and damage to the nervous system. It also highlighted that residential, agricultural and industrial wastes are three main sources of river pollution in Malaysia (Rafia et al, 2014). All of these problems occurred due to unorganized and badly planning in regards to the discharge of the waste

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water from their premise that will lead to cause the source of natural water to be disturbed. Therefore, the government has taken consideration in the issues and taken out some of the regulation in order to minimize pollution and try to make our natural water free from being polluted.

Wastewater

Waste water includes domestic waste water, consisting of black-water excreta, urine and associated sludge and grey water-kitchen and bathroom waste water or the mixture of domestic waste water from commercial establishments and institutions including hospitals with industrial waste water and run-off rain water (Van et al., 2004).

Appropriate policy decisions and technical interventions are likely to depend on the nature and characteristics of the waste water and the way in which it is being used. Wastewater could be harmful to human beings since it contains a lot of impurities from the previous users and needs to be treated before being safely discharged back to the river or oceans. EPA regulates the discharge and treatment of wastewater under the Clean Water Act (CWA). The National Pollutant Discharge Elimination System (NPDES) issues permits to all wastewater dischargers and treatment facilities. These permits establish specific discharge limits, monitoring and reporting requirements and may also require these facilities to undertake special measures to protect the environment from harmful pollutants.

- Laws and Regulations
    - NPDES Program Basics
    - NPDES Topics: regulatory information by program area, such as animal feeding operations, combined sewer overflows, pesticides and more.
    - Clean Water Act Section 319: the Nonpoint Source Management Program.
- Compliance
    - NPDES Compliance Monitoring
    - NPDES Training Courses and Workshops: for permit writers, dischargers and others.
    - View NPDES Individual and General Permits

The effluent should be pretreated before disposing into the environment. In addition, there is an urgent need to improve their efficiency rate by advanced tertiary treatment processes such as rapid sand filtration, UV disinfection, chlorination, effluent polishing, construction of artificial wetlands etc. That’s why further treatment are necessary for using the studied water as a drinking and aquaculture purposes by implication of modern method and technology (Hassan et al., 2017).

Water Quality

Water quality criteria are developed by aggregating the results of single-species toxicity bioassays. The fundamental premise is that protecting the supposedly most sensitive species from toxicity would enable ecosystems to maintain biological integrity (David et al., 2017). Water quality is referring to the physical, chemical and biological characteristic of water. PH value, colour, dissolved oxygen and turbidity are the tests that be used in measuring water quality. Water quality standard is a provision of state, territorial or federal law approved by Environmental Protection Agency (EPA) to describe the desired condition of a water body or the level of protection on how the desired condition will be expressed or established in the future as stated by United State Environmental Protection Agency. As for Malaysia, Department of Environment used Water Quality Index (WQI) as the basis for environment assessment under National Water Quality Standard for Malaysia (NWQS).

Sewage

Any discharge or release or permit the discharge or release of sewage onto or into any soil, or any inland waters, or Malaysian water are not permitted unless written notification given to Director General as stipulated in the Environmental Quality (Sewage) Regulations, 2009 (P.U.(A) 432/2009)

Leaking sewer systems and illegal cross-connections are implicated in the impairment of the watershed, hence both the sewer and the storm water lines should be routinely inspected (Kirs et al., 2017). The quick growth of the population, land use changed, and the industrial boom has carried huge problems of the environment of Dhaka city, Bangladesh especially on sewage waste water management. Waste treatment in developing countries like Bangladesh is a major anxiety and has become puzzling for various unfavorable conditions. Sewage waste water management has a direct impact on the urban ecosystems, agriculture and river system (Hassan et al., 2017).

CURRENT ISSUES REGARDING WATER QUALITY

River

River is one of the mode of transportation in the previous decade and is still chosen as a medium of transportation nowadays especially at Sabah and Sarawak. Other than that, the river also is a source of daily needs for human beings to drink, cook, washing and is also a source for food. Sadly, some people in their greed for profit and power lacks appreciation for the river and causes pollution to the river in their quest for power.

Domestic sewage, waste from livestock, farming activities especially the usage of inorganic fertilizer, runoff from big city, littering to the river and factories waste are some of the main causes of river pollution (Rizal, 2006). According to Rizal (2006), from 146 numbers of observation of rivers in Malaysia, 80 of it was clean, 59 of it was slightly clean and 7 of it was declared polluted. The remaining polluted rivers were located in the industrial areas which are in Penang, Selangor and Johor.

Groundwater

Groundwater is one of the sources of water that was used in daily activities especially for household needs in the past decade. Groundwater sources are still being practiced by several people in this country nowadays, especially in the rural areas that are using these resources to complete their daily needs besides to lessen their commitment in terms of paying the water bills.

The issue on groundwater pollution is because of high arsenic level that can be harmful to human health in the long term. Areas near radioactive landfill, solid waste landfills, source of water supply and agricultural areas are some areas where high arsenic level could occur (Rizal, 2006). Despite the fact that the dependency on groundwater is not being focused, it also needs to be preserved to maintain the resources for the use of the next generation.

Many communities obtain their drinking water from aquifers. Unfortunately, the ground water can become contaminated by human activity. These chemicals can enter the soil and rock, polluting the aquifer and eventually the well.

Marine

Marine is an adjective that are related to the sea or ocean. In Malaysia, although sea is a natural resource, they are not using seawater in the water supply due to the the cost of treatment process being comparatively higher than the other sources such as river, reservoir, lake and groundwater. Marine functions as the final place for the discharge of wastewater that has been used by consumers and then treated before being released back to the river and lastly diverted to the sea.

According to Rizal (2006), the problem on the marine water is high E. coli, mercury and arsenic level that are very harmful to human health. However, just E. coli was determined that are very common in marine pollution in 7 islands which are resort islands, marine parks and protected islands that are located in Perlis, Kedah, Negeri Sembilan and Penang Island (Rizal, 2006).

CHALLENGES IN MANAGING WATER RESOURCE

Pollution

Environmental contaminants such as water and soil pollution lead to changes in the properties of the components of the environment so that makes their pervious usage impossible and directly or indirectly endanger the benefits of living organisms (Kalhori et al, 2004).

Among all of the challenges, pollution is the most critical part that always can be seen either by the naked eye itself or in the media such as news, newspaper, internet and many more. In Malaysia, the pollution is usually due to poorly manage sewage treatment plant, agro industries, manufacturing industries, discharge of sullage or grey-water from commercial and housing area, pig farming and storm runoff after a downpour (Daud, n.d).

The major cause of pollution is sewage disposal and seweage works. Other than that, the pollution from agro industries is due to wastewater discharge from raw natural rubber factories and palm oil mills, manufacturing is caused due to generating inorganic pollutants, toxic wastes and persistent organic pollutants in the waste water while the sullage or grey-water is due to wastewater from kitchen sink, bathroom, restaurants, wet markets and lastly the pig farming is cause the pollution because content of high organic in the wastewater discharge into the river.

However, according to Rizal (2006), the number of polluted river shows a drastically decreased number from 15 polluted rivers in 2015 to just 7 in the year 2016.

Water pollution is a major concern in country. National Conservation Strategy Report stated that solid and liquid effluents are there as on of water pollution in the country and the cause of extensive water-borne diseases. Only three major sewage treatment plants operate in the country. The sewage without treatment is disposed into irrigation systems. Vegetables cultivated from such wastewater have serious bacterial contamination (Arshad et al.,(2015) The bye products of sugar manufacturing are used in other industries as well. Once the effluents of sugar process are discharged in open water body, water chemistry of the adjacent water channel is changed. Bad odor in the environment is experienced in environment by the residents of attached community due to decomposition of effluents. Plants production and aquatic life is seriously disturbed due to inclusion of high total dissolved salts (TDS) in discharged water. Fish and aquatic life is also disturbed due to waste water with high chemical oxygen demands (COD) and Biological Oxygen Demands (BOD) which diminish oxygen in water channel (Brady and Well, 2002). Local communities are suffering from a variety of health problems including skin, diarrhea, dysentery, respiratory illnesses, anemia and complications in childbirth. Yellow fever, cholera, dengue, malaria and other epidemic diseases are also available in this area. Furthermore, the people are suffering by the odor pollution and respiratory problems (Halder and Islam, 2015)

Public Attitude

Several environmental problems created as a result of urbanization so that the growing population caused to increment of agricultural production and food expanding and provided the expansion of agricultural activities. This has various environmental effects such as greater usage of pesticides and fertilizers which caused to their washing and moving into different layers of soil and ground water and their pollution (Khazaei, 2010). Environmental contaminants such as water and soil pollution lead to changes in the properties of the components of the environment so that makes their pervious usage impossible and directly or indirectly endanger the benefits of living organisms (Kalhori et al, 2004).

Nowadays, the need for awareness of people about the environmental problems of the region seems essential since decision-making at the macro level and in all areas especially on environmental issues is not possible without the participation of the people. Lack of attitude and responsibility are what usually leads to water pollution problems (Rizal, 2006). It is either people or industries, both of these parties are the major contributors to the water pollution problems in Malaysia. People choosing to throw away their rubbish into the river rubbish and industries not treating the wastewater before discharging it back into the river are two common examples of lack in attitude.

Moreover, this habit can cause a big problem such as the plastic waste that has been thrown to the river will flow to the ocean and be eaten by marine life such as turtle or whale mistaking it for jellyfish or food and hence leading toi their death. So, this negative habit should be avoided in order to create a clean environment while also to safe many marine lives. The results of this study show that most of farmers have little knowledge about soil contamination while residents of Khayam and Tabarsi areas have considerable information about status of their water (Mohammadi et al., 2014).

Lack of Enforcement

According to Rizal (2006), lack of enforcement is also one of the biggest challenge in order to preserve the natural resources that are very limited and needs to be well managed. Over exploitation of the logs by irresponsible parties causing the natural forest to keep decreasing in volume whilts giving an impact to the environment such as flooding, landslide, global warming and others is an example of this lack of enforcement.

Based on the Department of Environment (DOE), they already have some of the enforcement strategies in order to control and improving the quality of environment besides to prevent these resources from being polluted. In addition, the enforcement should be effective to ensure the both parties which is public and industries adhere to the law because it is possible to monitor the water source all the time (Rizal, 2006).

Key elements of modern European water management and their contribution to the resilience of the system and conclude that the potential lack of enforcement and adequate feedback of monitoring results does not promote managing for resilience (Green, 2013).

LEGISLATIVE

Introduction

The National Policy on the Environment which integrates the three elements of sustainable development: economic, social and cultural development and environmental conservation was formulated and approved in 2002. The policy aims at continued economic, social and cultural progress and enhancement of the quality of life of Malaysians through environmentally sound and sustainable development. It is based in eight (8) inter-related and mutually supporting principles set to harmonize economic development goals with environmental imperatives:

1. Stewardship of the Environment
2. Conservation of the Nature‟s Vitality and Diversity
3. Continuous Improvement in the Quality of the Environment
4. Sustainable Use of Natural Resources
5. Integrated Decision-making
6. Role of the Private Sector
7. Commitment and Accountability
8. Active Participation in the International Community

In keeping abreast with the country‟s rapid economic development and to meet with the nation‟s aspiration for an improved quality of life, the National Policy on the Environment serves as an important guide to all stakeholders to ensure that the environment is clean, safe, healthy and productive.

Laws and regulations are the sources of the effectiveness to the implementation of the enforcement by the government parties in solving many of the problems such as environmental issues. Mining Enactment 1929, Waters Enactment 1930, Drainage Works Ordinance 1954 and Street, Drainage and Building Act 1974 are the laws that are related to the water quality (Daud, 1977). Then, due to the increment of the environmental issues, the government has replaced the previous laws by introducing Environment Quality Act 1974 that are aimed to control the pollution. Environment Quality (Prescribe Premises) (Crude Palm Oil) Regulations 1977, Environment Quality (Prescribe Premises) (Raw Natural Rubber) Regulations 1978 and Environmental Quality (Sewage and Industrial Effluents) Regulations 1979 are the initial legislative approach in order to manage water quality in Malaysia.

Water Quality Legislation and Regulation

Environmental Quality (Prescribed Premises)(Crude Palm Oil) Regulations 1977

Under regulation 6 on this act, it mentions about the prohibition to making changes that could alter the quality of the effluent such as running, maintain, operating or process that could affect the effluent discharge from the premise. The type of changes to prescribed premise are:

1. Any changes in construction, structure, arrangement of the premise or any building serving in the premise
2. Any changes in the construction, structure, arrangement, alignment, direction or condition of any channeling device, system or facilities serving in the premise.
3. Any changes in any plant, machineries or equipment used or installed at the premise.

Moreover, through regulation 8, the prohibition also highlighted on the dilution of the effluent whether raw or treated at any time and any point that been produce in the prescribed premise. However, the activities will be accepted if a written authorization from Director General based on the term and condition of the authorization is presented.

Other than that, regulation 12 also mentioned about the limitation of the effluent to be discharged into a watercourse which include river, reservoir, lake, stream, canal, drain, spring, well, any part of sea or any source of body or natural surface or subsurface water. The limitation can be referred to in the third, fourth and fifth of the Second Schedule on this act.

In addition, regulation 14 mentioned about the point of discharge of the effluent. The effluent point of discharge is based on the paragraph (1) on this act. According to Third Schedule, Part A: Discharge into a watercourse, after 1st July 1979, the discharge amount shall be $10.00 per metric ton or part of a metric ton of the B.O.D. load of the total amount of effluent to be discharged.

Environmental Quality (Prescribed Premises)(Raw Natural Rubber) Regulations 1978

The act was enforced in two phases which where the first phase Regulation 22, 23 and 24 only be used in the 1st December 1978 while the rest of the Regulations were enforced on 1st April 1979. Based on the regulation 2, prescribed premise is an occupied premise or used for the production of processing of:

1. Raw natural rubber in technically specified form, latex form including prevulcanised or the form of modified and special purpose rubber
2. Coventional sheet, skim, creep or any other form of raw rubber not already describe in quantities of 5 tonnes or more per day or with a production or processing capacity of a simillar quantity

Regulation 6 and regulation 8 are similar with Environment Quality (Prescribe Premises) (Raw Natural Rubber) Regulation 1978 that mentioned about the prohibition of making changes that could alter the quality of effluent and dilution of the effluent. The prohibition is applicable to any type of structure, construction, channelling device, machineries and equipment of prescribed premises.

Besides that, under regulation 10 on this act, every occupier of prescribed is required to submit Form in the First Schedule to the Director General within fourteen days after the ends of each yearly quarter which is in January, April, July and October.

Furthermore, regulation 12 are the acceptable condition for the discharge of effluent from prescribe premises occupied or used for the production of latex or its associated product into a watercourse while regulation 14 are used for production of product others that latex into a watercourse. The requirement of regulation 12 will be used Second or applicable limit according to the Third Schedule while regulation 14 will used second and third column in the Fourth Schedule from this act.

Other than that, regulation 16 mentioned about the prescribed premises or used for production of a combination of products including concentrated latex or its associated products. For the limitation that is not included in either Second, Third or Fourth Schedule, the requirement is as below:

1. The research on effluent disposal or treatment of a kind scale that is likely to benefit that cause of environment protection is being or is to be carried out at the prescribed premisea and that such a concession is necessary for the conduct of such research; or
2. Compliance with the limit according to the Second, Third or Fourth Schedule at the prescribed premises would not be practicable

Under regulation 19, the point of discharge of an effluent is based on the pursuant to Paragraph (1) through this act. Besides, according to regulation 20, an occupier should install, maintain and operate a continuous effluent flow-measuring and recording device for monitoring at the point of the discharge and the quantity of the discharge of effluent during the period of the licence.

Environment Quality (Sewage and Industrial Effluent) Regulation 1979

The Environment Quality (Sewage and Industrial Effluent) was included in the Environment Quality Act 1974 and this act has been used since 1st January 1979. These regulations shall apply to any premises which discharge or release industrial effluent or mixed effluent, onto or into any soil, or into inland waters or Malaysian waters, other than the premises as specified in the First Schedule as according to regulation 3. The lists of premises that are not applicable through this regulation are:

1. Processing of oil-palm fruit or oil-palm fresh fruit bunches into crude palm oil, whether as an intermediate or final product.
2. Processing of natural rubber in technically specified form, latex form including prevulcanised or the form of modified and special purpose rubber, conventional sheet, skim, crepe or scrap rubber.
3. Mining activities.
4. Processing, manufacturing, washing or servicing of any other products or goods that produce industrial effluent or mixed effluent of less than 60 cubic meters per day.
5. Processing, manufacturing, washing or servicing of any other products or goods that produce industrial effluent or mixed effluent of which does not contain oil and grease or those contaminants listed as parameters (v) to (xv) in the first column of the Fifth Schedule.
6. Processing, manufacturing, washing or servicing of any other products or goods where the total load of biochemical oxygen demand (BOD5 at 20ºC) or suspended solids or both, shall not exceed 6 kilogrammes per day (concentration of 100 milligrammes per litre).

Basically, this act explained about the law and regulation to control the discharging of water back into the river by stressing the procedure to be taken before discharging back the water to river, some of the prohibition, restriction and fee for making licence. The prohibition and restriction mentioned in this act were strictly controlled by the responsible parties in order to make sure the environment is free from being polluted.

According to regulation 6 in this act, the substance that are prohibited to be discharged into inland water are inflammables solvent, tar or other liquids immiscible with water and refuse, garbage, sawdust, timber, human or animal waste or solid matters. Besides, the restrictions on discharge of effluents and disposal of any solid waste or sludge in or on any soil or surface of any land are mentioned in regulations 9 and 10 through this act.

Thus, all of the effluents from municipal and industrial wastewater that are to be discharged into inland water must comply with Standard A and Standard B that are stated in the regulation 11 from this act in order to reduce an impact towards human health and especially to the environment.

THE CONSTITUTIONAL FRAMEWORK FOR WATER RESOURCE MANAGEMENT IN MALAYSIA

The power of distribution between Federal and State in the Federal Constitution can be categorized into three parts in Ninth Schedule which are Federal List, List of State and Common List. However, any matters listed under the law of Federal jurisdiction, only central government have power to take an action according to the Federal List. Besides, it is also the same when coming to the State Limit which only the government have the power to control the law.

Moreover, based on the Federal Constitution, it is stated that water is a state responsibility which include rivers, lakes, stream and groundwater. But for some of the water-based project in the state such as hydropower plant, ports navigation, marine fisheries and mining¸ Federal Government still have a power. Other than that, under the Common List, drainage and irrigation has been located under the power of Federal and State Governments jurisdictions. Based on Article 76 of the Constitution, the power to enact the laws under State List is by Federal Government that aims to achieve consistency, follow international standard and follow the direction of parliament. However, the State Legislature needs to approve of it before being used in the regulations.

In 2005, Federal Constitution has amended on the item ‘water supply and services’ from State List to be moved in the Common List. Through the amendment, it has given a way for Federal Government to be involved in the water service sector and to control the water service industry. Before the amendment, the water supply organization has been established by the State Government to run, operate and maintain the water supply service and after the privatization that has been done through concession agreement that are different from state to state it has cause some of the state encounter with high non-revenue water. The amendment need to be done to overcome the problems due to the deterioration of the water quality and also inadequate financial resources from State Government.

In addition, after reshuffling the cabinet in 2004, three ministries on the water-based sector then was divided into three components which are water for environment, water for food and water for people. The Ministry of Natural Resources and Environment is responsible to organize and control water for environment, Ministry of Agriculture and Agro-Based Industry is to take action towards water service requirements for agriculture and food and lastly water for people is a responsibility of the Ministry of

Energy, Water and Communication. Besides, to execute research and development in water industry¸ the Ministry also has established National Hydraulic Research Institute of Malaysia (NAHRIM).

Ministry of Natural Resources & Environment and Ministry of Energy, Green Technology and Water are the two ministries responsible in the water management at the federal. Many departments such as Department of Environment, Department of Irrigation and Drainage, Water Supply Department, Sewerage Service Department, Syabas, Indah Water Consortium and others are under these ministries. All of the departments are responsible to manage water in terms of water service, water supply, sewerage, water treatment, irrigation and drainage, water quality and law enforcement.

The Authorities of Water Resource Pollution Control

There are a few of the authorities that are responsible to control and manage while making sure the source of water is free from pollution. All of the authorities have different functions and jurisdictions. There are three main organizations that are responsible to control and manage the pollution of water which are state government, local authority and federal agencies.

State Government

The state government are responsible to control the forest and its management. Deforestation and sand mining that are out of control are the main causes of river pollution. Based on the National Land Code, state government is an organization who is responsible to manage deforestation and sand mining activities to make sure they have a valid license. Due to its affect on on the storage of water in the forest such as the volume of water decline, high percentage of soil surface runoff and increasing the density of soil bulk, l ogging activities are the main causes of river pollution. The National Forestry Act 1984 was regulated as the law for logging activities and some of the others activities that are related to the forest such as burning, damaging the soil and trees, poisoning and water in the forest area.

Forest management is also related to the water resource management because some of the forest are used as a catchment area. In other words, the main reason for water resource treatment are to maintain the quantity and the quality, diminish, loss or affected the stability for the supply to domestic, commercial and industrial purpose. The two main focus in the resource management are water conservation and protection of water catchment area. In sections 3 and 4 from Land Conservation Act 1960, it is mentioned about the protection of forest areas and hills that are not allow to use for short-term farming or cutting trees and growing in the area. These prohibitions aim to preserve the water catchment area and also to prevent it from pollution.

Other than that, land activities such as farming on privately owned land also gives a good influent towards the conservation of water resources. Based on the section 11 from Land Conservation Act 1960, if the privately owned land is muddy and could pollute the source of water, then the Land Administrator may inform to the landlord to take preventive measures so to avoid from any of the unexpected outcome.

Local Authority

Other than pollution occuring due to forestry and agricultural activities, urban development and development activities also has given an influent especially towards the water pollution. Under Local Government Act 1976 and Road, Drainage and Building Act 1974, some of the prohibition has been mentioned in order for Local Authorities to prevent pollution especially for river water and drainage that are channeling directly to thesource of daily activities of people living. Based on the Section 69 from Local Government Act 1976, it is highlighted that whoever that makes a nuisance or deposits any impurities inside or on the top of the bank of any stream, channel, public drain, or other waterway in the Local Authorities area is one of the offence that a person could be fine not exceeding two thousand ringgit or imprisonment not exceeding one year or both and fine not exceeding five hundred ringgits for every day of continued offence.

Other than that, on the Section 70 from the same act mentioned for the prohibition of an individual person that can cause pollution of the rivers or streams. The list of the prohibition are:

1. Prohibition from put, cause and deliberate to fall or flow to be carried into any stream either alone or combination with other acts or any of the person to interrupt the water flow or to polluted the water, any of the substance solid or liquid from any manufactory, manufacturing process or quarry or any rubbish or other waste.
2. Prohibition that cause the fall or flow or deliberately to fall or flow into any stream any solid or liquid sewage substance.
3. Prohibition to use for the purpose of carrying any laundry business, any stream, channel, public drain or any watercourse or pool, pond or tank.

Shall be guilty that can be fine not exceeding five thousand ringgits or prison not more than two years or both and fine not exceeding five hundred ringgits for every day of continue offence. The law enforcement is good in order to control and avoid from polluting water resources but the penalty for the offences is too low and it has a potential that people could violate the law due to the low penalty.

Under Section 71, the law has mentioned that for the work done through the offences in the section 69 and 70, local authorities have a power to charge the cost to the person who was in offence. In addition, the sum must be deemed as a debt to the local authorities and can be recovered by referring as mentioned in the act for the unpaid rates.

Federal Agencies (Department of Environment)

Department of environment is responsible to observe and maintain the quality of the environment to make sure it is not polluted. Environment Quality Act (EQA) 1976 is the act that are enforced on this department. In section 25 through this act, for the offences of misuse of contaminating substance into the stream can be fined up to RM 100 000 or five years of jail or both. The object of EQA is to control the disposal of pollutants through licensing and not prevent or ban the disposal of the contaminated substance directly. Besides, the premise who has a license may release or dispose discharge into inland water as subjected to the terms and its limitations.

Environment Quality (Sewage and Industrial Effluents) Regulation 1979 was also established in order to control and manage the industrial effluent and sewage effluent. The sewage includes any of the liquid waste or discharge of water that are containing animal or plant and also liquid that containing chemical substance. So, this regulation has regulated people from releasing or causing or permitting the release any of tar or other non-soluble liquid, solvent, human or animal waste or solid material into inland water.

Moreover, Environment Quality (Specific Premises) (Crude Palm Oil) Regulation 1977 and (Raw Natural Rubber) 1978 were enacted in order to control the crude palm oil process and natural rubber activities. According to regulation 6 from both regulations, the owner or occupier of a prescribed premise cannot modify the premise and the operation that can give pollution toward natural environment including alter the effluent and other changes from the premises unless they get a written permission from the Director General of environment. Besides, the discharge of the palm oil and natural rubber effluent into the ditch must comply with the rules and the designated effluent discharge outlet as stated in regulation 12 and 14.

Under Environment Quality (Prescribe Activities) (Environment Impact Assessment) Order 1987, it mentioned about the scope that controls the water pollution. The listed activities that are required to assess environmental impact are as below:

1. Land development such as deforestation to replace with agricultural industry that are covering area of 500 hectares or more.
2. Placement of 100 families or more for agricultural program.
3. Agricultural development such as agricultural conversion that are covering area of 500 hectares or more.
4. Area of 200 hectares or more for dam construction or artificial lake or lake extension.
5. Area of 100 hectares or more for wetland drainage, virgin forests or wild habitat forests.
6. Area of 5000 hectares or more for watering
7. Area of 50 hectares or more for land fishery aquaculture involving purification of mangrove forests.
8. Area of 50 hectares or more for the conversion of hill forest to other land uses.
9. Logging in watersheds
10. Area of logging exceeding 500 hectares.
11. Area more than 50 hectares for the conversion of mangroves to industry, housing and agriculture.
12. Area of mining activities exceeding 250 hectares.
13. Area of taking sand for 50 hectares or more.
14. More than 4500 cubic meter per day for groundwater development for industrial, agricultural or municipal supply.

Under the law from DOE, it has an ability to control the water pollution and only control the pollution form the point of sources while for pollution at non-point sources is a responsible to State and Local Government. Plus, the rain flow into the river is one of the causes of pollution and there is no law governing towards it. In order to control the rivers, various enforcement agencies need to be involved. The overlapping of jurisdictions and inefficient and ineffective result are the cause of the weakness (Ujang, 2009).

Legal Issues Under the Constitutional Framework Water Management

Commonly, in Malaysia there are no uniformity in water management system between one state to another state and there is also complexity in management of water due to the privatization policy and involvement of many stakeholders on water management issues which has caused the environmental issues to become uncontrollable. Besides, every state has its power in the jurisdiction in managing its own water. But, Malaysia Parliament has approved the amendment in Ninth Schedule of the Federal Constitution that has transferred all of the water supply matters and service from State List to the Common List except for Sabah and Sarawak in mid 2005. After the amendment, Federal Government has regulated the water service industry such as for licensing and regulatory service operators that has been enforced on 21 March 2005. However, the power on water resources, water catchment areas and river basins still remain for State Government. Other than that, national Water Service Commission Act 654 and Water Service Industry Act, Act 655 has been changed in terms of managing water services in Malaysia by the Parliament in the mid 2006. Under Act 654, it has outlined the role, function and sphere of SPAN duties and Act 655 has mentioned the regulation about economy, technical and social and protection of consumer. Besides that, in Malaysia, various watersheds systems under the state government management in water supply system has been involved in many of the department because most of the water catchment area are in the forestry that are in the scope of forestry department and after the water flow to the dam it will be managed by the other agencies. Plus, the Department of Irrigation and Drainage are responsible to manage the flood and irrigation, state water board or work department or company that is appointed by the state government will manage water treatment plant, National Water Service Commission (SPAN) will manage after the water treatment to the water storage for consumer, Department of Environment that controls the river water quality and Ministry of Health will be controlled the for water drinking.

Constitutional Conflict

As stated before, State Government have the full power on the water resource management such as water catchment area and ground water, river, land and forest that are remain under the government state jurisdiction. However, Federal Government also have a power in the certain state for the water-based project that will formulate the policies that will be implemented in the state and on Constitutional Amendment 2005 the Federal Government have put an intention to manage water sector in the country. The main objective of the Federal Government is to initiate to the state management to standardize the water service industry but on the other view it is seen as an invasion to the state authority and water resources management in Malaysia.

Duplication of Departmental Authority

Depending on the roles, responsibilities and legislation, there are many department and agencies that are responsible to operate the water resource in Malaysia. It has caused the planning and development of water management fragmented with lack of coordination and consultation. Besides, the impact of the fragmentation also causes the related policies to be uneven and starting from Water Act 1920 (Revised 1989) and nowadays the Federal Government still enacted some of the laws regarding the water. After that, it is being followed by Street, Drainage and Building Act 1974, Town and Country Planning Act 1976, Local Government Act 1976 and Environment Quality Act 1974. In addition, Water Service Industry Act 2005 and National Water Service Commission Act 2005 were approved in the constitutional amendment 2005 and these act were governed by the particular ministry or agency. Gaps are created due to the approved act it has overlaps in term of responsibilities in managing water resources which leads to conflict and competition between the parties that could affect the sustainability of water resources, country development and also security. The main reason of the problem is because there is no clear policy to manage water resources with integrated manner. Therefore, it is need to create a comprehensive and clear policy to guide the role and responsibilities for every parties in managing water resources.

Lack of Manpower

Most of the local authorities produce their own laws that are requires the land developers to construct the connecting drains to discharge to the nearest point in regards to control the flood mitigation. Local authorities also make last minute decision for planning proposals that include layout and drain reserves for storm water drainage. The local authorities also lack the number of staffs that is needed to monitor and enforce the laws. Moreover, the Department of Irrigation and Drainage are always being an advisor to the local authorities in terms or storm and technical matters besides in some case the department also have prepare the plan for drainage master plans or build some of build a network drainage for the local authorities. If they lack the required staff in preparing structural plans and local plans¸ the Town and Country Planning Department also help the local authorities. However, the dependency of the local authorities to other organization could increase the problem and promote unhealthy competition.

Financial Constrain

The design and construction of urban storm drainage is a responsibility of the local authorities but it requires a large funding in order to build effective storm water management facilities. Many of the utilities such as water supply service and transportation has been privatized in order to increase the efficient services due to the lack of fund from the Federal Government. The lack of income is faced by the local authorities due to the privatization. However, the local authorities could obtain the fund from financial institutions that the Federal Government act as a guarantor for or use federal grants and loans. The lack of fund also becomes an obstruction to the local authorities from implementing or giving subsidies or rebates or provide water saving equipment to the consumer as is done by the local authorities in Australia and Japan.

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 water management laws in the country. The most important challenges is on the change the mindset of the Malaysia community to reduce the water at 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. Partnerships and the continued cooperation of various stakeholders in water management efforts should be enhanced in the provision of resources for the effective implementation of water management.

It is important to determine how we will protect our water resources so that both human and environmental services are maintained as competition for freshwater resources increases. Demands on fresh water will inevitably increase as a result of increasing urban, industrial, and agricultural use in support of population and economic growth.

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Chapter 3

Advanced Oxidation Processes for Water and Wastewater Treatment:

An Introduction

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ABSTRACT

Advanced oxidation processes (AOPs) have recently received attraction for treatment of different wastewaters. AOPs have an ability to oxidize a high quantity of refractory organic matters, traceable organic, or to increase wastewater biodegradability as a pre-treatment prior to an ensuing biological treatment. In this chapter, the fundamental mechanisms of different AOPs such as ozonation, hydrogen peroxide, UV, persulfate, and Fenton oxidation are summarized. The combination of different oxidation processes such as O3/H2O2, O3/UV, O3/Fenton+, O3/persulfate are evaluated. Several persulfate activation techniques are also summarized.

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INTRODUCTION

The advanced oxidation processes (AOPs) have been widely studied for the treatment of drinking water and industrial effluents. Generally, most AOPs are based on the generation of the highly reactive oxidizing species, such as hydroxyl radicals (Buxton et al., 1999), which could degrade a variety of organic pollutants. Table 1 shows the oxidation potential of some of common and strong oxidizing radicals.

Advanced oxidation processes (AOPs) are currently popular in effluent treatment to degrade recalcitrant compounds, which are difficult to remove by biological processes. Despite being highly efficient, when applied in an isolated way in leachate treatment, AOP do not reach effluent discharge standards established by the existing legislation, requiring post-treatment techniques to also be applied (Moravia et al., 2013).

They are also characterised by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for radicals production. Thus allowing a better compliance with the specific treatment requirements (Andreozzi et al., 1999).

A suitable application of AOP to solid waste leachate treatments must consider that they make use of expensive reactants as H_2O_2, and/or O_3. Therefore it is obvious that their application should not replace, whenever possible, the more economic treatments as the biological degradation (Andreozzi et al., 1999). A list of some of different possibilities offered by AOPs is given in Table 2.

Table 1. Oxidation Potential for some common oxidants (Huling & Pivetz, 2006)

No.	Oxidant Radical	Oxidation Potential (E_h)
1	Hydroxyl radical $OH^\bullet$	2.8V
2	Sulfate radical $SO4^{\bullet -}$	2.6V
3	Ozone O_3	2.1V
4	Persulfate anion $S_2O_8^{-2}$	2.1V
5	Hydrogen peroxide H_2O_2	1.8V
6	Permanganate ion MnO_4^-	1.7V
7	Peroxymonosulfate anion HSO_5^-	1.4V

Table 2. Advanced oxidation processes (Andreozzi et al., 1999)

H_2O_2/Fe^{2+}	(Fenton)
H_2O_2/Fe^{3+}	(Fenton-like)
H_2O_2/Fe^{2+} (Fe^{3+})/UV	(Photo assisted Fenton)
H_2O_2/Fe^{3+} - Oxalate	
Mn^{2+}/Oxalic acid/Ozone	
TiO_2/hv/O_2	(Photocatalysis)
O_3/ H_2O_2	
O_3/ UV	
H_2O_2/ UV	

The potentialities offered by AOP can be exploited to integrate biological treatments by an oxidative degradation of toxic or refractory substances entering or leaving the biological stage. Another aspect concerning the opportunity of AOP application is that referring to the polluting load of wastes normally expressed as COD. Only wastes with relatively small COD contents ($\leq$5.0 g/l) can be suitably treated by means of these techniques since higher COD contents would require the consumption of too large amounts of expensive reactants. Wastes with more massive pollutants contents can be more conveniently treated by means of wet oxidation or incineration (Mishra et al., 1995).

FENTON PROCESSES

The Fenton process has been widely studied in recent years, and analyses indicate Fenton process to be one of the most cost-effective alternatives among potential physicochemical technologies for leachate treatment (Deng, 2007). Fenton's oxidation is one of these advanced oxidation processes (AOPs) with high efficiency and low capital costs. It is a mixture of H_2O_2 and ferrous salts, capable to generate aggressive hydroxyl radicals at ambient temperature. The shaped radicals are able to oxidise a wide range of chemicals in aquatic medium, theoretically all organic compounds containing hydrogen (RH). The Fenton's procedure could be effective to achieve not only good oxidation of organics, but also their removal due to the coagulation run in the presence of ferrous salts (Gotvajn et al., 2011).

Fenton process can achieve two alternative goals exploiting the strong oxidation potential of hydroxyl radicals (•OH) as one of advanced oxidation processes (AOPs): first is the reduction of the COD content of wastewater up to the chosen maximum allowable concentration value through the mineralization of recalcitrant contaminants. The second is the development of the biodegradability of treated effluents with the aim of making their subsequent biological treatment possible (Mojiri et al., 2013).

The renewed interest of researchers for this classic, old reactive system, discovered by Fenton the last century (Fenton, 1894), is today underlined by a significant number of investigations devoted to its applications in wastewater treatments.

It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in wastewater such as phenols and herbicides. Production of hydroxyl radicals by Fenton reagent (Haber & Weiss, 1934) occurs by means of addition of H_2O_2 to Fe^{2+} salts:

$$Fe^{2} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + \bullet OH \quad (1)$$

This is a very simple way of producing hydroxyl radicals (•OH) neither special reactants nor special apparatus being required.

This reactant is an attractive oxidative system for wastewater treatment due to the fact that iron is very abundant and non-toxic element and hydrogen peroxide is easy to handle and environmentally safe. It must be stressed that the behaviour of the system cannot be completely explained on the basis of the sole reaction (Eq. 2.2). In fact, as it has been pointed out in many recent studies (Pignatello, 1992). The adoption of a proper value of pH (2.7–2.8) can result into the reduction of Fe^{3+} to Fe^{2+} (Fenton-like):

$$Fe^{3+} + H_2O_2 \leftrightarrow H^{+} + FeOOH^{2+} \quad (2)$$

$$FeOOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \quad (3)$$

proceeding at an appreciable rate. In these conditions, iron can be considered as a real catalyst.

PHOTO- AND ELECTRO-FENTON PROCESSES

The rate of degradation of organic pollutant with Fenton–Fenton like reagents is strongly accelerated by irradiation with UV-VIS light (Kiwi et al., 1993 and Pulgarin and Kiwi, 1996). This is an extension of Fenton process which takes advantage from UV-VIS light irradiation at wavelength values higher than 300 nm (Eq. 2.5). In these conditions, the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and the occurrence of Fenton reactions due to the presence of H_2O_2 as it appear in Eq. 4.

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + OH\bullet \quad (4)$$

Despite of the great deal of work devoted by researchers to these processes scanty indications have been found about their industrial applications. This is not surprising since Fenton processes application requires strict pH control and sludges can be formed with related disposal problems (Andreozzi et al., 1999).

UV/ Fe^{3+} – Oxalate/H_2O_2

An improvement of photoassisted Fenton processes is the UV-VIS /Ferrioxalate/ H_2O_2 system which has been very recently demonstrated (Safarzadehet et al., 1996) to be more efficient than photo-Fenton for the abatement of organic pollutants:

$$[Fe^{III}(C_2O_4)_3]^{3-} + hv \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + C_2O_4^{\cdot-} \quad (5)$$

$$C_2O_4^{\cdot-} + [Fe^{III}(C_2O_4)_3]^{3-} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2 \quad (6)$$

$$C_2O_4^{\cdot-} + O_2 \rightarrow O_2^{\cdot-} + 2CO_2 \quad (7)$$

Ferrioxalate is the oldest and best known photo-active example of Fe^{3+}-polycarboxylate complexes (Andreozzi et al., 1999). Irradiation of ferrioxalate in acidic solution generates carbon dioxide and ferrous ions Fe^{2+} free or complexed with oxalate which in combination with H_2O_2 provides a continuous source of Fenton's reagent. Safarzadehet et al. (1997) reports that the energy required for treating the same volume of selected wastewater (toluene, xylenes, mek) is about 20% of the energy required by photo-Fenton system. The high efficiency of this process as compared to other UV processes is attributed to the fact that:

- Ferrioxalate absorbs over a broad range of wavelengths (200–400 nm) thus utilising more efficiently the UV-VIS radiation;
- The quantum yield of Fe^{2+} formation is 1.0–1.2 over the range of irradiation whereas that of Fe^{2+} with photo-Fenton process decreases from 0.14 at 313 nm to 0.017 at 360 nm;
- A great difference in the efficiency is observed with wastewaters containing aromatic pollutants whose hydroxyderivatives produced in first oxidation stage strongly absorb in the same UV range as H_2O_2 and Fe^{3+} leading to a very slow rate of destruction of the parent molecules.

Electro-Fenton Method

Electro-Fenton method for treatment of landfill leachate was used in the studies performed by Zang et al. (2006) and Lin and Chang (2000). In a study performed by Lin and Chang (2000), they found that electro-Fenton process achieved 67.3% COD removal. In the study conducted by Zang et al. (2006), COD removal was 87.2% in case of using a pair of Ti/RuO_2 and IrO_2 type electrodes.

In the electro-Fenton process, formation rate of the hydroxyl radical is controlled by the applied current electricity. Mohajeri et al. (2010) improved the removal efficiency of COD and colour from stabilized leachate by increases the current density. As well as its effectiveness in removing organics and colour; advanced oxidation process can also be used to improve biodegradability of landfill leachate.

PHOTOCATALYSIS

Photocatalytic processes make use of a semiconductor metal oxide as catalyst and of oxygen as oxidizing agent (Ollis and Al-Ekabi, 1993). Many catalysts have been so far tested, although only TiO_2 in the anatase (one of the three mineral forms of titanium dioxide) form seems to have the most interesting attributes such as high stability, good performance and low cost (Zhang et al., 1994). The initiating event in the photocatalytic process is the absorption of the radiation with the formation of electron-hole pairs:

$$TiO_2 \xrightarrow{hv} e^- + h^+ \tag{8}$$

The considerable reducing power of formed electrons allows them to reduce some metals and dissolved oxygen with the formation of the superoxide radical ion $O_2^{\cdot -}$ whereas remaining holes are capable of oxidizing adsorbed H_2O or HO^- to reactive HO radicals:

$$TiO_2\,(h^+) + H_2O_{ad} \rightarrow TiO_2 + HO_{ad}^{\cdot} + H^+ \tag{9}$$

$$TiO_2\,(h^+) + HO_{ad}^{-} \rightarrow TiO_2 + HO_{ad}^{\cdot} \tag{10}$$

These reactions are of great importance in oxidative degradation processes due to the high concentration of H_2O and HO^- adsorbed on the particle surface (Andreozzi et al., 1999).

Some adsorbed substrate can be directly oxidized by electron transfer:

$$TiO_2(h^+) + RX_{ad} \rightarrow TiO_2 + RX_{ad}^{\bullet +} \tag{11}$$

Unfortunately a significant part of electron-hole pairs recombine thus reducing the quantum yield.

In the most part of the works devoted to the photocatalysis the possible exploitation of the wavelengths of the solar spectrum is stressed. However, this is only partially true since the overlapping between the absorption spectrum of TiO_2 and that of the sun at ground is rather poor (Andreozzi et al., 1999).

OZONE OXIDATION SYSTEMS

Ozone has recently received much attention in landfill leachate treatment technology due to its powerful chemical oxidant and high capacity for oxidation (SEPA 2003; Wu et al. 2004). Several applications of ozone on landfill leachate treatment have been conducted and with several catalysing technologies (Cong et al., 2015; Sun et al., 2014; Zhu et al., 2014). Tizaoui et al. (2007) obtaining 27% and 87% removal for chemical oxygen demand (COD) and colour, respectively, during the ozonation of leachate. Hagman et al. (2008) obtained 22% COD reduction. Rivas et al. (2003) conducted 30% depletion of COD. Since, there is no single method which could effectively remove all the pollutants simultaneously, several methods were applied to catalyze ozone in order to enhance the oxidation process (Chen and Wang, 2014), some of important catalyzing techniques are discussed in the coming texts:

Ozone/Hydrogen Peroxide

To illustrate the fundamental chemistry upon which O_3/H_2O_2 processes are based, a reference to the ozone chemistry in aqueous alkaline solutions is required. This argument has been extensively and successfully studied by Hoignè et al. (1998) in the attempt of giving a chemical explanation to the short life time of ozone in alkaline solutions. Hoigné showed that the ozone decomposition in aqueous solution develops through the formation of OH radicals. In the reaction mechanism OH^- ion has the role of initiator:

$$HO^- + O_3 \rightarrow O_2 + HO_2^- \overset{H+}{\leftrightarrow} H_2O_2 \tag{12}$$

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{\bullet -} \tag{13}$$

$$HO_2^\bullet \leftrightarrow H^+ + O_2^{\bullet -} \tag{14}$$

$$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -} \tag{15}$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^\bullet \tag{16}$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \quad (17)$$

$$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2 \quad (18)$$

The mechanism also elucidates the role exerted by H_2O_2 since it is formed during the ozone decomposition in aqueous solution. It is clear therefore that the addition of hydrogen peroxide to the ozone aqueous solution will enhance the O_3 decomposition with formation of OH radicals (Hoignè et al., 1998).

The influence of pH is also evident, since in the ozone decomposition mechanism the active species is the conjugate base HO_2^- whose concentration is strictly dependent upon pH. The increase of pH and the addition of H_2O_2 to the aqueous O_3 solution will thus result into higher rates of OH radicals production and the attainment of higher steady-state concentrations of OH radicals in the radical chain decomposition process (Glaze and Kang, 1989). It must be remarked that the adoption of the H_2O_2/O_3 process does not involve significant changes to the apparatus adopted when only O_3 is used, since it is only necessary to add an H_2O_2 dosing system (Andreozzi et al., 1999).

MN^{+2}/OXALIC ACID/OZONE

The system Mn^{+2}/oxalic acid can be conveniently used to enhance ozone decomposition to produce HO radicals. Mn^{+2} catalysed ozonation of oxalic acid has been shown to develop according to a radical mechanism at pH >4.0 at which Mn(III)-dioxalate and Mn(III)-trioxalate are formed (Andreozzi et al., 1992). In these conditions, the oxidation process proceeds presumably through the formation of OH radicals as a result of a reaction between manganese complexes and ozone. The system has been demonstrated to be effective for the abatement of refractory pollutants such as pyrazine and pyridine (Andreozzi et al., 1995).

H_2O_2 PHOTOLYSIS

This process is effected by irradiating the pollutant solution containing H_2O_2 with UV light having wavelengths smaller than 280 nm. This causes the homolytic cleavage of H_2O_2 (Baxendale and Wilson, 1957).

$$H_2O_2 \xrightarrow{hv} 2OH\bullet \quad (19)$$

In aqueous solution, the cage effect of water molecules lowers the primary quantum yield to 0.5. Since H_2O_2 itself is attacked by OH radicals the overall quantum yield becomes one.

The major drawback of this process is due to the small molar extinction coefficient of H_2O_2 which is only $18.6M^{-1}\ cm^{-1}$ at 254 nm, only a relative small fraction of incident light is therefore exploited in particular in the cases where organic substrates will act as inner filters. The rate of photolysis of aqueous H_2O_2 has been found to be pH dependent and to increase when more alkaline conditions are used (Legrini et al., 1993). This may be primarily due to the higher molar absorption coefficient of the peroxide anion HO_2^- which at 254 nm is $240M^{-1}\ cm^{-1}$.

PHOTOCATALYTIC OZONATION AND O_3/UV

A modern study conducted by Mehrjouei et al., (2015) aims to describe photocatalytic ozonation as a combination of two different techniques for hydroxyl radical generation; photocatalysis and ozonation, and to highlight its advantages for water and wastewater treatment compared to these two technologies. An extensive review on the mechanisms, kinetics and economic aspects of photocatalytic ozonation has been performed to explore the synergistic effects produced by applying this oxidation method to the degradation, mineralisation and detoxification of different organic pollutants in aqueous media. As far as the oxidation and mineralisation of recalcitrant organic contaminants in water and wastewater are concerned, the combination of ozone, appropriate photocatalyst(s), optimum design and optimised conditions will lead to higher degradation, removal rates and efficiencies compared to using ozonation and photocatalysis separately (Mehrjouei et al., 2015).

O_3/UV process is used to improve the oxidation of ozone against organics. The combined O_3/UV process is more efficient at generating hydroxyl radicals. When ozone is used together with UV, ozone decomposition is enhanced to yield hydroxyl radicals. Ozone readily absorbs UV radiation in solution at 254 nm wavelength producing H_2O_2 as an intermediate, which then decomposes and release hydroxyl radical (Munter 2001), (Equation 20 – 21).

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \text{ (In the presence of UV)} \tag{20}$$

$$2O_3 + H_2O_2 \rightarrow 2OH^{\cdot} + 2O_2 \tag{21}$$

O_3/UV process is an advanced water treatment method for the effective oxidation and destruction of toxic and refractory organics in water. Basically, aqueous systems saturated with ozone are irradiated with UV light of 254 nm in a reactor convenient for such heterogeneous media. The extinction coefficient of O_3 at 254 nm is $3600 M^{-1} cm^{-1}$ much higher than that of H_2O_2. O_3/UV oxidation process is more complex than the other ones, since $OH^{\bullet -}$ radicals are produced through different reaction pathways (Peyton & Glaze, 1988).

It is clear that under these conditions the system has the chemical behaviour of both O_3/H_2O_2 and H_2O_2/UV systems (Legrini et al., 1993 and Glaze et al., 1987). From the photochemical point of view, the absorption spectrum of ozone provides a much higher absorption cross section than H_2O_2, and inner filter effects by e.g. aromatics are less problematic (Legrini et al., 1993).

O_3/H_2O_2 PROCESS

O_3/H_2O_2 process is classified within the group of chemical AOPs and produces hydroxyl radicals through a sequence of reactions initiated by hydroperoxide anion, the conjugate base of hydrogen peroxide (Equation 22).

$$O_3 + H_2O_2 \rightarrow OH^{\cdot} + HO_2^{\cdot} + O_2 \tag{22}$$

The use of O_3/H_2O_2 system is to increase the power of the ozone by producing more hydroxyl radicals. This type of advanced oxidative process (O_3/H_2O_2), uses hydrogen peroxide activated ozone to create the hydroxyl and perhydroxyl radicals which can be mineralize organics in wastewater. Different studies have been conducted using O_3/H_2O_2 process for improving oxidation potential in treatment of landfill leachate (Tizaoui et al., 2007; Cortez et al., 2010; Wang et al., 2004; Naumczyk et al., 2012).

pH variance can be used in AOPs during ozonation. The use of ozone at high pH is favorable for the release of hydroxyl radicals with higher oxidation potential under indirect oxidation effects of hydroxyl radicals, and is more efficient than the direct reaction of ozone molecule under an acidic condition (Tizaoui et al., 2007; Lucas et al., 2007).

O_3/FENTON

The performance of ozone/Fenton in advanced oxidation process (AOPs) in treating stabilized leachate was well investigated in recent studies. The study curried out by Aziz and Abu Amr (2015) revealed that the use of ozone/Fenton ($O_3/H_2O_2/Fe_2^+$) in AOPs is more efficient in removing COD and colour in low concentrations of semi-aerobic stabilized leachate and in improving biodegradability. In this study the initial COD varied between 250 and 2360 mg/L, colour varied between 470 Pt. Co. to 4530 Pt. Co., and NH_3-N varied between 150 mg/l to 1170 mg/l. Accordingly, the removal efficiencies varied between 60% and 87% for COD, 95% to 100% for colour, and 12% to 22% for NH_3–N. Ozone consumption for COD removal was calculated, and the lowest amount of consumed ozone (1.3 KgO_3/ Kg COD) corresponded to the highest initial concentration of COD (2360 mg/L), with 60% removal of COD during 1 h ozonation. Moreover, the biodegradability (BOD_5/COD) ratio improved from 0.09 in raw leachate to 0.27 at 500 mg/L initial COD. The study concluded that Ozone/Fenton is an efficient method for stabilized leachate treatment and for improving biodegradability at natural pH, which suggests enhancement of the availability of applying biological treatment of leachate without pH adjustment of the effluent after ozonation (Aziz & Abu Amr, 2015a).

O_3/PERSULFATE

Ozone with persulfate in advanced oxidation processes was investigated in several studies (Abu Amr et al., 2014). A comparison study was carried out by Aziz et al., (2015b), the study investigated the performance of the three ozonation techniques in AOPs, namely, ozone alone, ozone/Fenton, and ozone/persulfate in treating stabilized leachate. According to the results, the performance of ozone alone was poor, and utilizing new advanced oxidation material during ozonation of such leachate was required to improve leachate treatability. Ozone/Fenton in AOP is a viable choice for degrading and decolourizing stabilized leachate. However, the performance of the ozone/persulfate process to improving biodegradable and soluble organic fractions in stabilized leachate was better than that of other processes. It can be concluded that ozone/persulfate process is the best choice for improving biodegradable and soluble fractions in stabilized leachate (Aziz et al., 2015b).

Performance of the combined use of persulfate and ozone for the treatment of a Malaysian stabilized solid waste leachate, was investigated (Abu Amr et al., 2013b). The maximum removal efficiency for COD, color, and NH_3-N were 72%, 93%, and 55%, respectively, at optimal operational conditions of

80 g/m^3 O_3 dosage, 35 g $Na_2S_2O_8$ (1 g/7 g COD=$S_2O_8^{2-}$) persulfate dosage, pH 10, and a reaction time of 210 min. Moreover, the biodegradability of the stabilized leachate was enhanced, suggesting a biological treatment process after O_3/persulfate. The combination of persulfate and ozone performed more efficiently in stabilizing leachate treatment compared with using ozone only and persulfate only (Abu Amr et al., 2013b).

EFFECTS OF CHEMICAL OXIDATION ON COD FRACTIONS AND BIODEGRADABILITY OF THE LEACHATE

It is well acknowledged by the fact that landfill leachate contains large quantities of nonbiodegradable and toxic constituents including organic substances and that several treatment steps must be adopted to achieve a satisfactory removal of hazardous pollutants (Wu et al. 2004). Recently, the combination of biological and physical-chemical processes is being considered as the most appropriate technology for manipulation and management of high-strength effluents (Rivas et al. 2003).

Advanced Oxidation Processes (AOPs) are physical-chemical processes that involve the generation of highly reactive hydroxyl radicals in quantities that can destroy or detoxify even refractory organics, while enhancing the biodegrability of leachate by cleavage of aromatic structures, and dissociating the carbon-halogen, carbon-carbon single and carbon-carbon double bonds (Ince 1998). A partial or complete destruction of the high-molecular contaminants can be achieved (Kim and Huh 1997). As a consequence, expensive polishing of the effluents and production of unwanted residuals can be avoided (Dichtl et al. 1997; Geenens et al. 1999).

When AOPs are used as a pre-treatment method the oxidant doses are chosen in such a way that they cause only partial mineralization (Dichtl et al. 1997) resulting in an increase of the biodegradable fraction, which could thereafter be followed by a biological treatment process. This should involve much lower ozone doses than the complete treatment of leachates, and would, therefore lower the capital costs, as well as the operating costs of the process (Beaman et al. 1997).

Sardinia et al. (2007) found in their study that ozonation of the leachate slightly accelerated their biodegradation in the solid state anaerobic digestion when implemented at the beginning of the methanogenic phase. In the acidogenic as well as in the stabilized methanogenic phase the ozonation did not cause any improvement in the leachate biodegradation. Repeatable AOPs (hydrogen peroxide combined plus low pressure UV lamp) implementation in the acidogenic phase led to the inhibition of anaerobic processes. There was no consequent influence of the AOPs treatment on the leachate biodegradation in the methanogenic phase (Sardinia et al., 2007).

Selçuk et al. (2006) achieved a 30% to 39% rate for the removal of soluble COD from wastewater by using pre-ozonation. Dogruel et al. (2011) evaluated the biodegradation and treatability of COD fractions based on the particle size of organics in leachate. Erden et al. (2011) obtained a 60% increase in soluble COD by using the Fenton process in pre-treating stabilized activated sludge. Recent studies conducted on COD fractions of the stabilized leachate and by applying a number of oxidation techniques and treatment methods (Abu Amr et al., 2014 and Abu Amr et al., 2013a).

PERSULFATE

Persulfate Chemistry and Physical Properties

Persulfate, known also as peroxydisulfate or peroxodisulfate, is a sulfate peroxide with the chemical structure $[O_3S\text{-}O\text{-}O\text{-}SO_3]^{2-}$ (Ahmad, 2008; Liang et al., 2004). Persulfate can degrade a wider range of environmental contaminants at faster rates, and it has been used as an agent in a number of industrial applications such as an initiator for olefin polymerization in aqueous systems, as a micro-etchant for printed circuit boards, for leaching of textiles, and in studies related to industrial wastewater treatment (Killian et al., 2007).

Persulfate is the newest form of oxidant currently being used for *In Situ* Chemical Oxidation (ISCO) (Huling & Pivetz, 2006). There are three possible salts of persulfate: potassium, ammonia and sodium. The solubility of potassium persulfate is very low for environmental applications, and the reaction of ammonium persulfate results in an ammonia residual, which is an undesirable reaction product (Ocampo, 2009). Therefore, sodium persulfate ($Na_2S_2O_8$) is the most common and feasible form used to date in *in situ* chemical oxidation (ISCO) (Behrman and Dean, 1999; EPA, 2006; Huling & Pivetz, 2006).

Sodium persulfate costs approximately $1.20/lb (Brown and Robinson, 2004). The solubility of $Na_2S_2O_8$ is high (73g/100g H_2O at 25°C) and the density of a 20 g/L solution (1.0104 g/mL) (FMC, 2006) at 25 °C is greater than water. Therefore, the density-driven transport of a high concentration solution of $Na_2S_2O_8$ would occur in the subsurface. Persulfate is more stable in the subsurface as compared to H_2O_2 and O_3 (Huang et al., 2002), and can persist in the subsurface for weeks, suggesting that the natural oxidant demand for persulfate is low.

The persulfate anion ($S_2O_8^{2-}$) is not significantly involved in sorption reactions. These characteristics make persulfate an attractive oxidant because it persists in the subsurface, can be injected at high concentrations, can be transported in porous media, and will undergo density-driven and diffusive transport into low-permeability materials (Huling & Pivetz, 2006).

Persulfate salts are dissociated in water to the persulfate anion ($S_2O_8^{-2}$) which, despite having a strong oxidation potential ($E^o = 2.1$ V) Table 2, is kinetically slow to react with many organic compounds. Studies have indicated that persulfate anions can be activated to generate sulfate radicals ($SO_4^{\bullet-}$) (Eqs 2.21 to 2.28), which are stronger oxidants compared to the persulfate anion ($E^o = 2.6$ V) as it shown in Table 3 (Liang et al., 2007; Watts & Teel, 2006).

Conventional oxidants can accept electrons from persulfate ions to form the sulfate anion radical, but the reaction rate is extremely slow. Therefore, the oxidation of target contaminants by this oxidant has to be accelerated by activation of persulfate, thus increasing the rate persulfate decomposition and the rate of sulfate free radical formation (Liang et al., 2007; Todres, 2003).

Several methods that have been extensively used for the activation of persulfate such as heat, light, gamma radiation, and transition metals (Eqs 2.21 to 2.28) (Anipsitakis and Dionysiou, 2004a; Liang et al., 2007; Waldemer et al., 2007). Alos catalysis of $S_2O_8^{2-}$ to $SO_4^{\bullet-}$can be achieved at elevated temperatures (35 to 40°C), with ferrous iron (Fe (II)), by photo (UV) activation (Eqs. 2.21 to 2.23) or with base (i.e., elevated pH). In addition to Fe, other general activators include the ions of copper, silver, manganese, cerium, and cobalt (Liang et al., 2004a, and references therein). Their initiation reactions, which result in the formation of sulfate radicals, are illustrated in details within the coming sections.

Another common approach to activate the generation of sulfate radicals is the use of base (Liang et al., 2007). Recent studies have demonstrated the influence of pH on the generation of reactive oxygen species in base-activated persulfate systems (Corbin, 2008). Under these conditions most sulfate radicals are converted to hydroxyl radicals ($OH^{\bullet}$), which can proceed through propagation reactions to give the same reactive species (hydroxyl radicals, hydroperoxide, superoxide, and hydrogen peroxide) as those that are found in catalyzed hydrogen peroxide propagations (CHP) systems (Gonzalez and Martire, 1997; Liang et al., 2007).

Persulfate Oxidation Reactions

Oxidation of organic compounds by persulfate is very complex and is the topic of a considerable amount of recent research. A range of oxidation reactions are known to be involved and each of these is influenced by various factors in the subsurface including site specific geochemistry, pH, temperature, contaminant type, native organic matter, etc. Known oxidation reactions related to persulfate include both direct oxidation reactions and radical oxidations (Wilson et al., 2013).

Direct Oxidation

Persulfate reacts directly with many organic materials, exchanging electrons in a process known as direct oxidation. The strong oxidizing potential of persulfate makes oxidation of many organic contaminants thermodynamically favourable (ITRC, 2005). It should be noted, however, that a thermodynamically favourable reaction means only that the energy of the products is lower than the energy of the reactants. The reaction may or may not proceed at rates that are favourable. In fact the direct oxidation of organic pollutants by persulfate, where the two electrons are transferred simultaneously as above, has long been shown to proceed at kinetically slow rates (House, 1962).

Radical Oxidation

In addition to the direct oxidation pathway, persulfate has the propensity to generate radicals as it mentioned recently. Radicals are generated when the persulfate anion reacts with another compound to form atoms with unpaired electrons (radicals). Radicals generally are very reactive, rapidly oxidizing other compounds (increased kinetic rates compared to direct oxidation) and often forming a series of radicals in a chain reaction referred to as "propagation". Radical species within a propagation series can be inorganic species or organic radicals generated by electron exchange (Wilson et al., 2013). It should be noted, however, that radicals by their very nature are highly reactive and ephemeral. As a consequence, they are notoriously difficult to detect. Much of the understanding of radical formation, propagation and behaviour throughout the ISCO field remains theoretical and inferred through a combination of thermodynamic probability and the nature of transitional oxidation intermediates formed (Wilson et al., 2013).

The most common radicals generated by persulfate under conditions employed in ISCO are thought to be the sulfate radical and the hydroxyl radical as it shown in Eqs. 23 and 24, respectively (Peyton, 1988; Furman et al., 2012).

$$S_2O_8^{2-} + 2e^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} \tag{23}$$

$$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \qquad (24)$$

Both the sulfate radical and hydroxyl radical are very strong oxidizers with standard oxidation potentials of 2.6V and 2.8V, respectively as it shown in Table 2 (Huling and Pivetz, 2006). These primary radicals react with other compounds very rapidly through what is thought to be a variety of reaction mechanisms including direct electron transfer, addition to double bonds and hydrogen abstraction (removal of hydrogen atom, often generating another radical). Most of the research conducted to date on persulfate radicals generated during persulfate ISCO has focused upon the impact of these two species. Other radical species, however, are also thought to play an important role including the perhydroxl radical ($HO_2^{\bullet}$) and superoxide anion ($O_2^{\bullet -}$) (Watts, 2012).

Formation of $SO_4^{\bullet -}$ may initiate the formation of $OH^{\bullet}$ (Eq. 27) and a series of radical propagation and termination chain reactions where organic compounds can be transformed (Huang et al., 2002, and references therein).

$$S_2O_8^{2-} + Fe^{+2} \rightarrow Fe^{+3} + SO_4^{\bullet -} + SO_4^{2-} \qquad (25)$$

$$S_2O_8^{2-} \xrightarrow{UV} 2\ SO_4^{\bullet -} \qquad (26)$$

$$SO_4^{\bullet -} + H_2O \rightarrow OH^{\bullet} + HSO_4^{-} \qquad (27)$$

$$SO_4^{\bullet -} + Fe^{+2} \rightarrow Fe^{+3} + SO_4^{\bullet -} + SO_4^{2-} \qquad (28)$$

Using of Persulfate in Advanced Oxidation Processes

The activated persulfate oxidation, in recent years, is an emerging approach for the removal of organic compounds in water and soil (Xu and Li, 2010). This technology is based on the production of sulfate radicals ($SO_4^{\bullet -}$), and has attracted great scientific and technological interest in the area of water treatment and in situ chemical oxidation in the remediation of soil and groundwater (Anipsitakis & Dionysiou, 2004b; Anipsitakis et al., 2006; Fang & Lo, 2011).

Persulfate is the most recent oxidant used for ISCO treatment and has advantages over other oxidants. Based on bench-scale tests conducted with persulfate, it is known to degrade a wide variety of organic contaminants (Siegrist et al., 2011), have a low natural oxidant interaction (NOI) (Sra et al., 2010), and have a higher standard reduction potential compared to other oxidants (Yen et al., 2011). Additionally, once activated, persulfate generates free radicals, further increasing its oxidation potential (Angela, 2013).

Persulfate ($S_2O_8^{2-}$) offers some advantages over other oxidants as a solid chemical at ambient temperature with the ease of storage and transport, high stability, high aqueous solubility and relatively low cost. These features let it to be a promising choice for cleanup applications. Reactions of persulfate with organic pollutants, however, are generally slow at ambient temperature, and activation of persulfate is necessary to accelerate the process (Xu et al., 2012; Anipsitakis & Dionysiou, 2004b).

Since persulfate oxidation at ambient temperature is usually not effective, it is commonly used with UV light or under high temperature to initiate its radical oxidation mechanisms. Sulfate free radicals, generated from photolytic or heat decomposition of persulfate (Eq. 26), may initiate a series of radical chain reactions (Eqs. 29 -39) (Berlin, 1986), where organic compounds (i.e., M in Eq. 2.28) are usually degraded.

$$S_2O_8^{2-} \xrightarrow{heat} 2SO_4^{\bullet} \tag{29}$$

$$S_2O_8^{2-} + M \rightarrow 2SO_4^{\bullet -} + M^{\bullet} \tag{30}$$

$$SO_4^{\bullet -} + M \rightarrow M^{\bullet} + \text{products} \tag{31}$$

$$HO^{\bullet} + M \rightarrow M^{\bullet} + \text{products} \tag{32}$$

$$M^{\bullet} + S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} + \text{products} \tag{33}$$

$$SO_4^{\bullet -} + HO^{\bullet} \rightarrow \text{chain termination} \tag{34}$$

$$SO_4^{\bullet -} + M^{\bullet} \rightarrow \text{chain termination} \tag{35}$$

$$2SO_4^{\bullet} \rightarrow \text{chain termination} \tag{36}$$

$$HO^{\bullet} + M^{\bullet} \rightarrow \text{chain termination} \tag{37}$$

$$2HO^{\bullet} \rightarrow \text{chain termination} \tag{38}$$

$$2M^{\bullet} \rightarrow \text{chain termination} \tag{39}$$

Since other used oxidants, such as hydrogen peroxide and ozone, have relatively short lifetimes in the subsurface as compared with persulfate, persulfate are being studied as a potential alternative oxidant for the remediation of groundwater and soil contaminated with toxic organic contaminants. In addition, persulfate has been widely studied for the treatment of water and wastewater (Xu et al., 2012). In the coming sections, we reviewed the activation methods of persulfate and its environmental application.

Persulfate Activation

As stated above, sodium persulfate has the ability to transfer electrons directly in the process of direct oxidation. It is generally accepted, however, that the kinetics of contaminant destruction through direct oxidation alone is far less suitable for ISCO than the kinetics achieved by activating the formation of radicals (Petri et al., 2011).

The radical oxidation of organic compounds with persulfate can be viewed as having three distinct phases. Activation is generally defined as the initiation of radical formation. This is followed by a period of Propagation, where the first radicals oxidize the target contaminant, but may also produce other inorganic radicals and perhaps radicals of organic compounds (including target pollutant fragments). This, in turn, is followed by Termination, where sequential electron exchange is no longer active (Wilson et al., 2013).

Mechanisms employed to achieve activation of persulfate for ISCO have historically included use of iron, heat, hydrogen peroxide, and alkaline activation (base).

Transition Metal Activation of Persulfate

Ferrous Ion or Chelated Ferrous Ion Activation of Persulfate

It has been recognized for decades that certain transition metals can stimulate the formation of radicals when combined with persulfate. Among these, the use of dissolved iron has been the most practiced transition metal activator for ISCO, primarily due to its low environmental toxicity (Wilson et al., 2013).

Ferrous iron (Fe II), when mixed with persulfate is known to donate electrons initiating the generation of the sulfate radical (Crimi & Taylor, 2007) which in turn oxidizes target compounds or produces other radicals. It is believed that ferrous iron offers superior degradation kinetics compared to other valence states, although ferric iron (Fe III) has been shown in certain circumstances to increase degradation kinetics of certain relevant groundwater contaminants when compared to inactivated persulfate (Block et al., 2004).

In practice, the use of dissolved ferrous iron as an activator comes with limitations. Ferrous iron (Fe II), while soluble upon application to the subsurface, is quickly oxidized to ferric iron (Fe III) as it donates electrons to initiate the formation of the sulfate radical. Ferric iron rapidly precipitates from solution as iron hydroxide rendering it less effective in activation (Petri et al., 2011). To maintain ferrous iron activation of a persulfate ISCO system, one must maintain the pH <3 in the aquifer or apply the iron with chelation agents to ensure dissolution (Liang et al., 2004).

The use of chelation agents to maintain dissolved iron concentrations for persulfate activation has been studied (Liang et al., 2004). The research generally indicates favorable results for such ligands as citric acid, trisodium phosphate, and EDTA. The practical application of these chelating agents shows limitations with regard to the environmental acceptability of these compounds for use in aquifers and the cost of applying large amounts of chelated metals. Lastly, the use of organic chelation agents itself presents a certain demand upon the oxidant as the oxidant will, to some extent, attack the ligands themselves. The extent of this demand and the impact on overall ISCO efficiency is unknown and would certainly be site specific (Sperry et al., 2002).

Liang et al. (2004) used ferrous ion Fe^{2+} to activate persulfate to produce $SO_4^{\bullet-}$ for the degradation of TCE (trichloroethylene). The experiments under various molar ratios of $S_2O_8^{2-}/Fe^{2+}/TCE$ in an aqueous system indicated that partial TCE degradation occurred almost instantaneously and then the reaction stalled. Either destruction of $SO_4^{\bullet -}$ in the presence of excess Fe^{2+} or the rapid conversion of all Fe^{2+} to Fe^{3+} limited the ultimate oxidizing capability of the system. Sequential addition of Fe^{2+} in small increments resulted in an increased removal efficiency of TCE. Therefore, Fe^{2+} played an important role in generating $SO_4^{\bullet -}$.

Chen et al. (2009) evaluated the feasibility of using ferrous ion-activated persulfate oxidation to remediate groundwater contaminated with methyl tert-butyl ether (MTBE). In this study, batch experiments were conducted to evaluate the effects of various factors on the efficiency of MTBE degradation, including persulfate concentration, ferrous ion concentration, and persulfate. The results showed that ferrous ion-activated persulfate oxidation was capable of degrading MTBE efficiently. Persulfate and ferrous ion concentrations correlated with MTBE degradation rate. However, excess addition of ferrous ion resulted in the decreased MTBE degradation rate most likely because of competition for sulfate free radicals between ferrous ion and MTBE.

Zero-Valent Iron (ZVI) Activation of Persulfate

In the literature, another efficient advanced oxidation process, which is based on the zero-valent iron-mediated composition of persulfate that results in the generation of strong oxidizing species (sulfate free radicals) in aqueous solution, was also reported (Zhao et al. 2010). The results showed that ZVI significantly improved the degradation efficiencies of 4-chlorophenol in the presence of persulfate at ambient temperature. The optimum loading of ZVI was 0.20 g L^{-1}, and 88% removal of 4-chlorophenol was observed in 1 h. The addition of methanol and tert-butyl alcohol as hydroxyl free radical and sulfate free radical scavengers proved the presence of sulfate free radicals in the ZVI-persulfate reaction system. The degradation of 4-chlorophenol was accompanied by the formation of hydroquinone, 1,4-benzoquinone, and small molecule compounds such as oxalic acid and succinic acid, and the hydroquinone pathway was regarded as the main step in the oxidation of 4-chlorophenol. Chloride ion release and formation of oxidation intermediates were evidence of 4-chlorophenol degradation involving sulfate free radicals.

Mineral Activation of Persulfate

Liang et al. (2010) investigated the feasibility of activated persulfate oxidation of methyl ertbutyl ether (MTBE), using pyrite (FeS_2) as the source of ferrous ion activator. Under the FeS_2-activated $S_2O_8^{2-}$ condition, the sulfate free radical $SO_4^{\bullet -}$ is the predominant reactive species generated. The oxidation reactions were able to completely degrade MTBE when given sufficient doses of FeS_2 and $S_2O_8^{2-}$ and sufficient reaction time (e.g., 3 g L^{-1} FeS_2 and 5 g L^{-1} $Na_2S_2O_8$ within 4 h). The generation and subsequent degradation of the primary MTBE degradation intermediate products, including tert-butyl formate, tert-butyl alcohol, methyl acetate and acetone, were observed. The detailed reaction mechanism proposed for a $SO_4^{\bullet -}$ driven oxidation process indicated that the destruction of MTBE most likely happened through a hydrogen abstraction via attack of the $SO_4^{\bullet -}$ at the intermediate methoxy group. In another study, Ahmad et al. (2010) investigated persulfate dynamics in the presence of subsurface minerals as a basis for understanding persulfate activation for *in situ* chemical oxidation (ISCO). The mineral-mediated decomposition of persulfate was investigated with four iron and manganese oxides and two clay minerals at both low pH (< 7) and high pH (>12). The manganese oxide birnessite was the most effective initiator of persulfate for degradation of nitrobenzene, and the iron oxide goethite was the most effective mineral for degradation of hexachloroethane. A natural soil and two soil fractions were used to confirm persulfate activation by synthetic minerals. The results demonstrated that synthetic iron and manganese oxides could activate persulfate, but iron and manganese oxides in the natural soil did not show the same reactivity, most likely due to the lower masses of the metal oxides in the soil relative to the masses in isolated mineral systems.

Thermal Activation of Persulfate

Persulfate activation can be stimulated by exposing a solution of sodium persulfate to elevated temperatures. It has generally been found that the rate of persulfate activation increases with the temperature of persulfate solutions (Liang et al., 2003). Thermal activation is thought to proceed according to Eq. 2.27 where heat decomposes persulfate into two sulfate radicals.

The efficiency of thermal activation for use in persulfate ISCO systems is not as intuitive as one might expect. While activation appears to increase with temperature, so do the rates of reactions that compete with the degradation of the target contaminant. Thus, depending upon site conditions, temperature and contaminant characteristics, thermal activation may increase the persulfate oxidant demand relative to other activation technologies as the oxidant is consumed in side reactions (Wilson et al., 2013).

Probably the greatest limitation to the commercial use of thermal activation for ISCO is the considerable cost of heating soil and groundwater or other contaminated open environment. Thermal activation of persulfate for ISCO is rarely practiced other than in association with thermal extraction technologies such as subsurface heating/vapour extraction (Wilson et al., 2013).

Alkaline Activation of Persulfate

In the presence of high pH, persulfate is known to activate and undergo the formation of sulfate radicals. It is a direct result of the requirement for base in the chemical reaction to form sulfate radicals. This activation technique is widely practiced in ISCO remediation generally by applying solutions of either sodium hydroxide or potassium hydroxide. Once activated, propagation continues through the formation of hydroxyl radicals, etc. At high pH conditions ($\text{pH} > 11$), alkaline activation is very productive in generating the primary sulfate and hydroxyl radicals (Wilson et al., 2013). This, in turn, propagates the formation of ancillary inorganic radicals as well as organic radicals from native organic materials and from the target contaminants themselves. It should be noted also that at pH ranges above pH 11 simple alkaline hydrolysis plays a significant role in the breakdown of some organic compounds. Here the presence of hydroxide ion in high concentration can decompose organics independent of any radical oxidation (Wilson et al., 2013).

The main limitation with alkaline activation of persulfate for ISCO remediation is the cost and logistics associated with injecting of large volumes of caustic solutions multiple times in order to maintain the alkaline conditions in the targeted environments. This requirement is driven by both the natural buffering capacity of most targeted environments (such as subsurface) and the acidic conditions created as persulfate decomposes. It is common for alkaline activated persulfate applications to rapidly drop below the effective pH range well before the persulfate oxidizer has decomposed, requiring the practitioner to remobilize to the site and reinject the alkaline activation solution multiple times (Wilson et al., 2013).

Photochemical Activation of Persulfate

Salari et al. (2009) investigated the photooxidative decolorization of C.I. Basic Yellow 2 (BY2) using UV radiation in the presence of persulfate in a rectangular photoreactor. $S_2O_8^{2-}$ and UV-light showed negligible effect when they were used independently. The removal efficiency of BY2 was sensitive to the operational parameters such as initial concentrations of $S_2O_8^{2-}$ and BY2, light intensity, flow rate and pH. The conversion ratios of BY2 at the volumetric flow rates of 330, 500 and 650 mL min^{-1} were 84%, 79% and 51% in 30 min, respectively. The results showed that light intensity was a beneficial parameter for dye removal. In the presence of $S_2O_8^{2-}$, the photo-oxidation quantum yield obtained was higher than direct photolysis quantum yield, suggesting that photo-decay of BY2 was dominated by photo-oxidation. The results also showed that applying a desired persulfate concentration could reduce the electrical energy.

In addition, Criquet and Leitner (2009) studied the photolysis of $S_2O_8^{2-}$ for the removal of acetic acid in aqueous solution and compared with the H_2O_2/UV system. The $SO_4^{\bullet-}$ radicals generated from the UV irradiation of $S_2O_8^{2-}$ yielded a greater mineralization of acetic acid than the OH radicals. Acetic acid was oxidized by $SO_4^{\bullet-}$ radicals without significant formation of intermediate by-products. Increasing system pH resulted in the formation of OH radicals from $SO_4^{\bullet-}$ radicals.

Recently, Lin et al. (2011) investigated both the feasibility of using a UV/sodium persulfate process to treat phenol in aqueous phase and the effect of pH on degradation efficiency and TOC removal. The results revealed that a high initial persulfate concentration (i.e., 84 mM) and a lower initial phenol concentration (i.e., 0.5 mM) resulted in rapid and complete phenol degradation within 20 min. For all three pHs evaluated (i.e., 3, 7 and 11), complete phenol degradation was also achieved after 30 min of treatment by UV/sodium persulfate oxidation processes (i.e. under an sodium persulfate/phenol molar ratio of 84/0.5) with pseudo-first-order rate constants $k_{\text{obs, phenol}}$ of 0.14-0.16 min^{-1} (average half-life $t_{1/2}$ = 4.5 min). The UV-Vis spectrum scanning of the aqueous solution during treatment identified the development of brown colour in the wavelength range of 400-460 nm. The colored intermediate compounds formed were suspiciously similar to those observed during Fenton treatment. However, a more aggressive oxidation at pH 11 showed a rapid and more complete removal of TOC in aqueous phase. Therefore, it was recommended that UV photolytic persulfate activation under basic pH was a preferred condition for the treatment of phenol (Xu et al., 2012).

Activated Carbon

For remediation of trichloroethylene (TCE) contaminated groundwater, activated carbon (AC) has been used to adsorb and reduce the TCE concentration and to manage contaminant migration. Additionally, AC might also act as an activator of persulfate to generate sulfate free radical for contaminant destruction (Xu et al., 2012). The combined use of AC and persulfate to treat TCE was examined (Liang et al., 2009). The degradation of persulfate in the presence of AC followed a first-order kinetic behaviour, and the faster persulfate degradation was observed when elevated AC dosage was used. Higher initial persulfate concentration resulted in a decrease of the persulfate degradation rate. Upon persulfate oxidation, the AC surface properties were altered. The adsorption behaviour for the original AC fitted the pseudo second-order kinetic model while the pseudo-first-order kinetic model was suitable for predicting oxidized AC performance. During the persulfate oxidation of TCE with AC as an activator, the results showed that TCE removal could be a net result of adsorption and oxidation, in which a partial mineralization of TCE to release chloride occurred (Xu et al., 2012).

Microwave-Assisted

Microwave (MW)-activated persulfate oxidation with or without active carbon (AC) has been reported for the degradation of an azo dye acid orange 7 (Yang et al., 2009). It was found that (up to 1000 mg L^{-1}) was completely decolorized within 5~7 min under an 800 W MW furnace. The presence of chloride ion will delay the decolorization rate while activated carbon will enhance the decolorization rate. Subsequently, Lee et al. (2009) used microwave-induced to activate persulfate to decompose persistent and bio-accumulative perfluorooctanoic acid (PFOA) in water at 60, 90, and 130°C.. Microwave–hydrothermal treatment was carried out in a microwave digestion system, which provided 800 W of microwave energy with a frequency of 2450 MHz at full power. Persulfate was an efficient oxidant for degradation of PFOA even at the room temperature of 27 °C. Higher temperature accelerated the PFOA decomposition rate, but an extremely high temperature (130 °C) would lead to the formation of significant amounts of radical oxidants thus causing lower mineralization efficiency. The solution pH value was another important factor to influence the degradation rate. The decomposition rate in acidic condition was 1.1–7.4 times faster than in alkaline condition (Xu et al., 2012).

CONCLUSION

In the chapter, the trend and performance of different chemical applications for advanced oxidation processes on wastewater treatment were evaluated. The effectiveness and applicability of the recent and different updated processes were introduced. In general, the variations in treatment efficiency can be attributed to the different types of wastewater. Some types of wastewater with high organic and inorganic concentration may require additional or combination treatment process enhance their oxidation potential. AOPs are recently used ozonation combined with persulfate, Fenton, hydrogen peroxide and UV to improve the oxidation potential during a one-stage ozonation process and to reduce treatment time consumed when applying a combination treatment process. AOPs are an efficient method in treating industrial wastewater.

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Chapter 4

Application of Persulfate in Textile Wastewater Treatment

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ABSTRACT

As textile and dyeing industries increase, pollution due to effluent discharges from the same industries also increase and become of great concern to a healthy environment. In an attempt to understand the generation and treatment of textile wastewater, this chapter discusses the processes from which textiles are made, items of importance that are used in the production process which may account for the characteristics of the wastewater and persulfate, applied in the treatment of textile wastewater. Although these wastewaters are generally characterized by color, fluctuating pH, heat, salts, suspended solids (SS), the presence of metal ions, biological oxidation demand (BOD), and chemical oxygen demand (COD), color is the most obvious. The presence of color in the effluents from textile dyeing and finishing is due to the inefficient dyeing processes, resulting in unfixed forms of the dyestuff. To achieve the primary objective of obtaining a clean environment, there is a need for continuous monitoring of textile wastewater discharges, of which major concern is color.

INTRODUCTION

The desire to achieve and maintain a green environment continue to increase. The Environmental Engineer and other Environmentalists make every effort towards its sustainability and indeed everyone should join in these efforts as the benefit is to be enjoyed by all. These necessitates the clean-up of coloured, unsightful, non-biodegradable and often toxic, textile wastewater discharges that is able to endanger every specie that is exposed. Health and the general wellbeing within the environment suffers a great

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setback from the exposure to water pollution, aquatic habitat is particularly affected. Water pollution, involves contamination by particulate matter, chemicals and bacteria that deteriorate its purity. One of the most common source of water pollution is the industrial wastewater which could pose serious environmental threat if not properly treated prior its discharge either directly into any surface water or via sewers. Similarly, textile wastewater may degenerate the environment due to the high content of chemical substances, suspended solids and intense colour among other characteristics. Several point source water pollution have been traced to the disposal of textile wastewater which have worked against the wellbeing of both human and aquatic lives. Downstream waters have also been negatively affected aesthetically, (Yadav & Verma, 2014) Also, contamination of both surface and ground waters have made them unfit for irrigation and drinking, (Marwari and Khan, 2012).

To this end, it is very important that definite steps should be taking to treat pollution of water at source, and to the required standard before an eventual discharge into either sewers or surface waters.

While the most obvious characteristic of any polluted water is colour, it may not necessarily be the most detrimental of them all. Colours and dyes have a long history and are important components of our daily lives. In the beginning, natural plants and insect sources were used by the dye industry for their generation and then rapidly turned to synthetic manufacturing processes. But now, the Synthetic dyes are considered a major part of our lives, (Rauf & Ashraf, 2009; Divya et al., 2013). Many synthetic dyes, particularly azo dyes, were found to be toxic, carcinogenic and mutagenic and were therefore banned throughout the world, (Ashraf et al. 2012; Shah et al., 2013). However, their manufacture and use have continued because of their ease of synthesis, low cost and other desirable properties (Bafana et al., 2011; Shah et al., 2013). Azo dyes have been considered the largest group of dyes and/or industrial colourants which are currently representing 60-70% share in the worlds dye market (Singh & Arora, 2011; Mahne, 2012; Wu et al., 2012). One of its basic properties is the ability of the bonds to resist breakdown, and thus exhibit the capacity for persistence and accumulation in the environment, (Shah et al., 2013).

Textile Production

Similar to paper, food, tannery, cosmetic and related industries, textile industries use dyes as colourants in their production. About 15% of the over 0.7million tons of artificial dyes that are manufactured annually worldwide are lost during the production processes, (Mahmoodi et al., 2011).

The application of dyes by the textile industry has grown steadily because they react well with fibers and the colour is stable. Dyes have been discussed more in literatures because of their high solubility in water and also as effluents containing environmentally problematic compounds (Papić et al., 2009) in (Guimarães et al., 2012) which are visible even in small quantities because of their brilliance, (Robinson et al., 2001).

Dyeing and finishing in textile production generates the largest quantity of wastewater. The raw materials are cleaned with water and the latter is also used in many flushing stages in the wet production (Mahamuni and Adewuyi, 2010; Oller et al., 2011). Generally, the traditional textile finishing industry use about 100 liters of water to process about 1 Kg of textile material but the new closed-loop technologies such as the reuse of microbial or enzymatic treatment of dye effluents may help to reduce the enormous water pollution (Shah et al., 2013).

Textiles

The textile industry is considered as an important sector in the economy and environmental indicators of any concerned nations. The global market for it consists of 60% clothing, 35% home and furnishing and 5% of technical and nonconventional textiles, namely; sports, medical and military textiles (Ngô & Van de Voorde, 2014).

The relevance of textile industries to the manufacture of clothes and clothing materials cannot be over emphasized. According to (Sultana et al., 2013), the textile industry is very important because its materials are used in varying ways including clothes for wearing. Although their products are affected by the styles in clothing wears, changes with the season and the trends in fashion. But despite their importance, their existence also increases a very crucial environmental issue that is bordered on wastewater discharges.

Stages of Textile Production

Textile industries are usually fragmented and consists of a complex production system which includes but not limited to the making of fiber, yarns, fabrics for apparel and home furnishing among other products. These processes involves the use of large amounts of chemicals and water as the basic raw materials, the resultant of which poses a risk to the environment (Alkaya and Demirer, 2014). Textile and apparel industries are characterized by unpredictable demands and a huge product variety which causes the textile wastewater variation in characteristics and the resultant difficulty to be treated by the commonly used biological processes (Ngai et al., 2014).

A general concern in the textile production is with the dyeing process, where an average of ten times more water is used for the preparation, dye washing, and rinsing stages, (Agustina and Ang, 2012). The most common processes applied in textile fabric productions including dyeing and other finishing procedures involves the combination of the processes shown in Table 1.

Characterization of Textile Wastewater

For the dyeing and printing processes, the textile industries greatly use synthetic dyes, (Shah et al., 2013) thereby generating very large quantities of complex chemical substances which remains as unspent materials in the wastewater resulting from various textile processing stages (Yonar et al., 2005; Cheung et al., 2009; Verma et al., 2012; Divya et al., 2013). It is considered that 10-15% dyes are lost to the wastewater during the dyeing process (Shah et al., 2013).

These wastewaters are therefore highly toxic, mutagenic and characterized by high suspended solids (SS), Colour, pH, COD, BOD and heavy metals, resulting from unspent dye baths, (Ahmad et al., 2002; Fibbi et al., 2012; Marwari and Khan 2012; Salazar et al., 2012).

For the resultant effects of the textile wastewater characteristics, suspended solids may block the penetration of sunlight that is required by submerged aquatic vegetation, and they may also cause low levels of dissolved oxygen DO. Firstly, visible colour in wastewater constitutes an eye sore, then it affects aesthetics, it does not allow the transparency of water and also obstructs gas solubility of the receiving water bodies, (Fu and Viraraghavan 2001). Oil and grease negatively affects aquatic lives. They hinder the normal penetration of sunlight, oxygen diffusion, and hence the respiration of all of micro and macro organisms and plants. Similar effects can be felt for the pH and temperature, hence the need for monitor-

Table 1. Processes in textile production

Sizing;	Starch, modified starch, carboxymethyl cellose, polyvinyl acetate, and gums are applied to transform cotton yarns to woven fabrics.
Weaving;	Yarns from the earlier process are converted into fabrics in a dry operation. However, looms that use water jets may also be used instead.
Desizing;	In this process, the substances previously applied to the yarn during the sizing procedure are removed.
Scouring;	Generally, the process involves the removal of both natural and applied substances to synthetic and natural materials. Pectins, spinning oils, natural waxes, and other non-cellulosic components are removed using hot alkaline solution, commonly of caustic soda or soda ash in the scouring process. However, scouring intensity depends on the material type.
Bleaching;	Bleaching involves the removal of the natural yellowish colouring to increase the whiteness of cotton and other fibers.
Mercerizing;	This process is applicable to pure cotton fabrics that are treated with concentrated caustic soda bath and neutralized by a final acid wash.
Fulling/milling;	The process mates and shrinks woolen fabrics and certain worsted fabrics to make denser.
Dyeing/Printing;	Colour is added to fabrics in this process.
Finishing;	To improve the specific properties of finished fabrics, this process applies finishing agents for softening, cross-linking and waterproofing of both natural and synthetic textiles.

(Correia et al., 1994; Babu et al., 1995; Dos Santos et al., 2007; Kalra et al., 2011; Ngai et al., 2014, Fagbenro and Aziz, 2014).

ing wastewater characteristics so as not to exceed the standard. Typical textile wastewater characteristics are as shown in Table 2.

High concentration of additional parameters can be found in textile wastewater such as Chromium, Copper, Iron, Led and Manganese. Hussain et al., (1970) evaluated the composition of textile wastewater from six major textile industries in India. Table 3 summarizes the average values of 23 parameters determined in these wastewaters.

Generally, it can be concluded that the wastewater of the textile industry is highly viscous with high-suspended solids and high total dissolved solids. The total dissolved solids are high due to the use of chemical of high solubility and the suspended solids are due to the precipitation of salts and undissolved impurity separated from gray cloth. Textile wastewater is rich in chloride, sodium and bicarbonate. The overall heavy metal concentration is quite low. Chromium is high due to the use of chromium salts and chromium based dyes.

The Advanced Oxidation Technology`

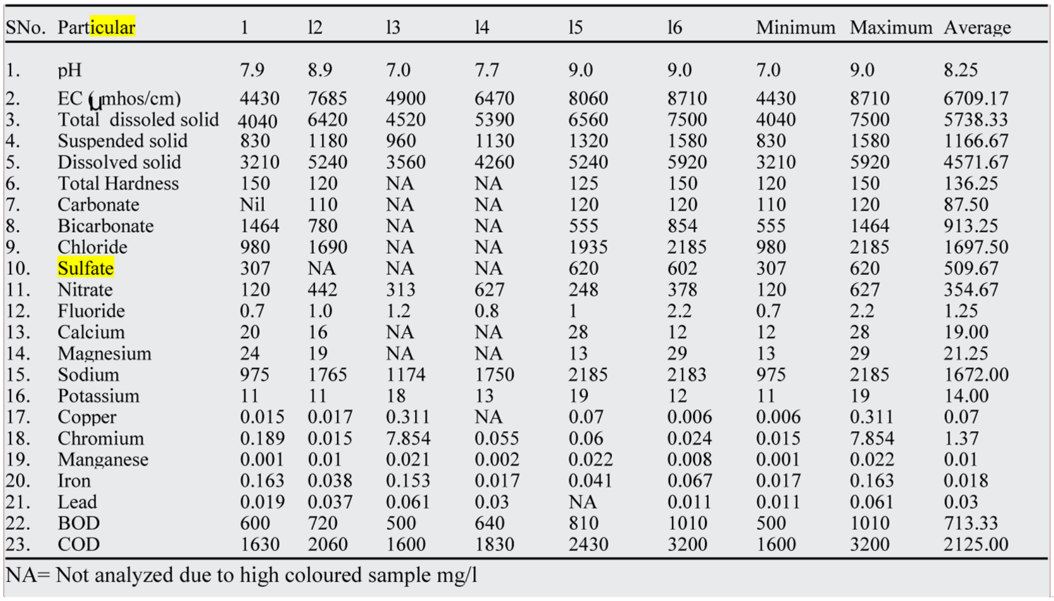
The advanced oxidation technology is not entirely new, hence, the continuous study of the processes as there is yet room for further development of the processes and a need to achieve greater efficiency, (Vilhunen and Sillanpää, 2010). There has been various understanding and several definitions of the advanced oxidation processes (AOPs) but more commonly, and in a more practical sense, AOP refers to the treatment processes involving hydrogen peroxide (H_2O_2), UV light, Ozone (O_3) and Ultrasound, acting either singly, in combination or serially and with or without catalysts, such as semiconductors or metal ions (de Abreu et al., 2012; Chitra et al., 2012). AOPs were also considered as the set of chemical processes applied in the treatment of water and wastewater by the reactions with hydroxyl radicals ($OH^{\cdot}$) especially, in oxidation. These processes are based on the generation and utilization of reactive species

Table 2. Textile wastewater characteristics

Characteristics	Units	Value
Colour	Pt.Co./ADMI	(50-2,500)
Temperature (T)	^{o}C	(21-62)
pH	-	(6.95-11.8)
Biological oxygen demand (BOD)	mgl^{-1}	(80-6,000)
Chemical oxygen demand (COD)	mgl^{-1}	(150-30,000)
Total Solids (TS)	mgl^{-1}	(6000-000)
Total suspended solids (TSS)	mgl^{-1}	(15-8,000)
Total Dissolved solids (TDS)	mgl^{-1}	(2,900-3,100)
Total Kjeldahl Nitrogen	mgl^{-1}	(70-80)
Oil and Grease	mgl^{-1}	(5-5,500)
Total alkalinity (as $CaCO_3$)	mgl^{-1}	(17-22)

(Correia et al., 1994; Babu et al., 1995; Al-Kdasi et al., 2004; Kalra et al., 2011; Sarayu and Sandhya 2012; Franco and Azevedo 2013; Fagbenro and Aziz, 2014).

Table 3. Composite textile wastewater (Hussain et al., 1970)



SNo.	Particular	1	l2	l3	l4	l5	l6	Minimum	Maximum	Average
1.	pH	7.9	8.9	7.0	7.7	9.0	9.0	7.0	9.0	8.25
2.	EC (umhos/cm)	4430	7685	4900	6470	8060	8710	4430	8710	6709.17
3.	Total dissoled solid	4040	6420	4520	5390	6560	7500	4040	7500	5738.33
4.	Suspended solid	830	1180	960	1130	1320	1580	830	1580	1166.67
5.	Dissolved solid	3210	5240	3560	4260	5240	5920	3210	5920	4571.67
6.	Total Hardness	150	120	NA	NA	125	150	120	150	136.25
7.	Carbonate	Nil	110	NA	NA	120	120	110	120	87.50
8.	Bicarbonate	1464	780	NA	NA	555	854	555	1464	913.25
9.	Chloride	980	1690	NA	NA	1935	2185	980	2185	1697.50
10.	Sulfate	307	NA	NA	NA	620	602	307	620	509.67
11.	Nitrate	120	442	313	627	248	378	120	627	354.67
12.	Fluoride	0.7	1.0	1.2	0.8	1	2.2	0.7	2.2	1.25
13.	Calcium	20	16	NA	NA	28	12	12	28	19.00
14.	Magnesium	24	19	NA	NA	13	29	13	29	21.25
15.	Sodium	975	1765	1174	1750	2185	2183	975	2185	1672.00
16.	Potassium	11	11	18	13	19	12	11	19	14.00
17.	Copper	0.015	0.017	0.311	NA	0.07	0.006	0.006	0.311	0.07
18.	Chromium	0.189	0.015	7.854	0.055	0.06	0.024	0.015	7.854	1.37
19.	Manganese	0.001	0.01	0.021	0.002	0.022	0.008	0.001	0.022	0.01
20.	Iron	0.163	0.038	0.153	0.017	0.041	0.067	0.017	0.163	0.018
21.	Lead	0.019	0.037	0.061	0.03	NA	0.011	0.011	0.061	0.03
22.	BOD	600	720	500	640	810	1010	500	1010	713.33
23.	COD	1630	2060	1600	1830	2430	3200	1600	3200	2125.00

NA= Not analyzed due to high coloured sample mg/l such as radicals. The hydroxyl radical ($OH^{\cdot}$) is one of the strongest inorganic oxidants and has a potential of $E^0=8V$. They are very unstable and highly reactive because of their oxidation potential, (Mahamuni and Adewuyi, 2010). The hydroxyl radicals and indeed radicals in general are able to oxidize a broad range of organic pollutants rapidly and non- selectively, (Chakrabarti and Dutta, 2004; Dokuzoğlu and Alkan 2010; Chitra et al. 2012; Ashraf et al., 2012).

Textile wastewater contain many pollutants, making it high in organic and inorganic chemical content, chemical oxygen demand (COD), total organic carbon (TOC), and colour. Therefore, it is difficult to be degraded by the conventional methods; hence the use of the advanced oxidation processes.

AOPs also include both photocatalytic (i.e. involving Ultra violet light or Ultra Sound) and non-photocatalytic (i.e. dark) processes. AOPs have emerged as an important destructive method for removing most of the organic and inorganic pollutants such as reactive dyes. They have been effective in the complete mineralization of pollutants such as dyes to CO_2, water, and inorganic compounds, although they may be very expensive when used solely since they are primarily chemical based (Poyatos et al., 2010; Oller et al., 2011; Verma et al., 2012; Fagbenro and Aziz, 2014). Therefore, researches on AOPs have continued in a desire and an effort to improve on the treatment of effluents and the hope to achieve complete mineralization of dyes by its use at a minimized cost. AOPs also serve as pre-treatment methods as they have been used to enhance the biotreatability of wastewaters which contain various organic compounds that are non-biodegradable and/or toxic to common microorganisms, (Wu et al. 2012; Rizzo 2011; Divya et al., 2013).

Persulfate

Persulfate (PS) also sometimes called Peroxydisulfate has a chemical formula of S_2O_8 and it is from Sodium Persulfate. The latter with a chemical formula of ($Na_2S_2O_8$) has been recently introduced in the insitu chemical oxidation (ISCO). Sodium persulfate salts are dissolved in water to form a strong oxidant; the persulfate anion ($S_2O_8^{2-}$) which has a potential of $E^0=2.01$. The persulfate anion is further activated by one or a combination of thermal and chemical means which includes pH adjustment to generate intermediate sulfate free radicals with a chemical formula of ($SO_4^{\cdot-}$). However, the sulphate free radicals are stronger oxidants, (Liang et al., 2007; Rodriguez et al., 2014). Although the free radicals are stronger, the persulfate oxidation is however considered not very reactive at atmospheric temperatures (Huang et al., 2002).

While in aqueous solutions the half-cell Persulfate reaction and the equations of heat activation are given in equation 1 and 2. When in contact with organic compounds the sulfate radical generated in equation 2 may initiate a series of chain reactions in contact with organic compounds, equation 3 – 8, (Huang et al., 2002; Liang et al., 2007).

$$S_2O8_2^- + 2e^- \rightarrow 2SO_4^- \ (E0=2.01) \tag{1}$$

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^- \tag{2}$$

$$S_2O_8^{2-} + X \rightarrow 2SO_4^{\cdot -} + X. \tag{3}$$

Where X represents organic compounds.

$$SO_4^{\cdot -} + H_2O \rightarrow SO_4^{\cdot -} + OH^{\cdot} + HSO_4^{\cdot -} \quad (4)$$

$$SO_4^{\cdot -} + X \rightarrow X^{\cdot} + \text{Products} \quad (5)$$

$$OH^{\cdot} + X \rightarrow X^{\cdot} + \text{Products} \quad (6)$$

$$X^{\cdot} + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + \text{Products} \quad (7)$$

$$SO_4^{\cdot -} + OH^{\cdot} \rightarrow \text{Chain termination with free radicals} \quad (8)$$

Persulfate Chemistry

The chemistry of persulfate involves the kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. Persulfate oxidation include both direct oxidation reactions and radical oxidations. In the direct oxidation, persulfate directly reacts with organic compounds and release electrons. The standard oxidation potential of persulfate is 2.0V which is similar to ozone (2.1V) and higher than hydrogen peroxide (1.8V), sodium percarbonate (1.8V), and permanganate (1.7V) (ITRC, 2005). The high oxidizing potential of persulfate makes oxidation of organics thermodynamically applicable. The direct oxidation of organics by persulfate, where the two electrons are transferred simultaneously has long been shown to proceed at slow rates (House, 1962).

For radical oxidation, in addition to the direct oxidation way, persulfate has the ability to generate sulphate radicals. Sulphate radicals are generated when the persulfate anion reacts with another compound to form atoms with unpaired electrons.

Persulfate Activation

Persulfate oxidation reactions with organic contaminants especially, are catalyzed to speed up its' kinetics, increase its rate of decomposition and enhance the destruction of contaminants in soil, water and wastewaters. Activation is necessary due to the rather slow nature of the persulfate oxidation at ambient temperature. Techniques used to assist persulfate oxidation in the treatment of water and wastewater include; thermal activation (Huang et al., 2002; Liang et al., 2003; Johnson et al., 2008), photochemical activation (Criquet & Leitner, 2009; Lin et al., 2011; Frontistis et al., 2014), ferrous ion activation (Liang et al., 2004; Xu and Li, 2010), chelated ferrous ion activation (Liang et al., 2004), zero-valent iron activation (Oh et al., 2009; Deng et al., 2014), mineral activation (Ahmad et al., 2010; Teel et al., 2011), activated carbon/PS activation (Tsai et al., 2009; Yang et al., 2011; Tsai et al., 2011), microwave activation (Shiying et al., 2009), and integrated activation (Anipsitakis & Dionysiou, 2004; Saien et al., 2011). The latter, integrated activation involves the integration of two or more techniques and or media of treatment. However, among the activation techniques in current use, thermal activation is the least studied (Johnson et al., 2008). More recently however, clinoptilolite has been applied with persulfate to treat textile wastewater (Fagbenro and Aziz, 2015b).

Also, a 99% degradation of azo dye orange G in aqueous solutions was obtained within 30 minutes, (Xu and Li, 2010). Degradation of azo dye Orange G in aqueous solutions by persulfate with ferrous ion The investigation of azo dye Acid Orange 7 (AO7) degradation by PS, peroxymonosulphate (PMS) and H_2O_2 under activations by heat (25-80^{o}C), UV light (254nm) and different anions showed that heat (>50^{o}C) activated PS is an effective degradation technology with a PS >> PMS > H_2O_2 degradation order for heat activation, (Yang et al., 2010). Persulfate can also be activated by iron and other minerals, such as silver, copper, zinc, cobalt and manganese forming the sulfate radical, as shown in Table 4. (Matzek and Carter, 2016).

Table 4. Iron, heat and UV light activated persulfate degradation of various organics (Matzek & Carter, 2016).

Iron-Activated degradation	**Analyte Conc. (mmol L^1)**	**Persulfate Conc. (mmol L^1)**		**Maximum analyte removal**	**Rxn time (min)**	**Optimal Molar ratio**	**Form of iron**
Aniline	0.05	2.5		100%	10	1:50:100	Fe0
	0.05	2.5		73%	240	1:125:25	Fe2þ
Bisphenol A	80	2		100%	45	1:5:4	Fe0
	80	2		100%	30	1:5:4	Fe2þ Continuous addition
	80	2		97%	30	1:5:4	Fe2þ Sequential addition
p-Nitroaniline	0.2	8		100%	270	1:40:115	nano-Fe3O4
2,4-Dichlorophenol	0.184	12		93%	60	1:65:197	nano-Fe0
Orange G	0.1	1		100%	30	1:10:10	Fe2þ or Fe3þ
Trichloroethene	0.1	1		100%	120	1:10:10	Fe0
	0.15	4.5		>99%	5	1:30:30:150	Fe0, biochar support
	0.15	2.25		>99%	30	1:15:2:10	Fe2þ, hydroxylamine
Heat-Activated Degradation					Optimal Temp. (C)	Synergistic Effects	
Aniline Atrazine	0.05 0.05	2.5 1		100% 100%	60 90	80 60	þ5 mM Fe0 none
2,4-Dichlorophenol Dimethyl Phthalate	0.184 0.0515	12 10.8		100% 100%	60 1080	50 40	þ36 mM Fe0 none
1,4-Dioxane	1.135	26		100%	180	60	none
Monochlorobenzene	1.136 0.00179	26 179		100% 100%	240 120	60 60	þ18 mM Fe2þ none
UV Light-Activated degradat	ion				Fluence rate (mW cm2)	Synergistic effects	Wavelength/Power (nm/W)
Acid Blue 113	0.073	6.3	97.70%	120	e	no pH effect	254/14
Atrazine 2-Methylisoborneol	0.00464 0.238	1 0.01	50% 86%	e 10	e 1.29	pH ¼ 7.4 no pH effect	254/- 254/60
Phenol Tetramethyl ammoniahydroxide	0.1 1.1	0.5 50	95% 100%	900 130	0.18 4.5	þ0.2 g/L Fe3O4 pH ¼ 2.0	295-400/20 254/15

WASTEWATER TREATMENT

There are various techniques for the treatment of industrial effluents including textile wastewater. They are broadly categorized into physical, chemical and biological methods (Anjaneyulu et al., 2005). A combination of two or more of the primary treatment techniques may also be used. Physico-chemical, bio-physical and electro-chemical technologies are simple examples of the combination of the treatment methods. Table 5 highlights the basic categories of methods.

As color is a major issue with textile wastewater, a review of previous techniques successfully used for its treatment is summarized in Table 6.

Both physical and chemical methods have been considered as the traditional methods for treating textile wastewater, (Palamthodi et al., 2013). Textile wastewaters are difficult to treat by regular biological methods because of the non-biodegradable nature of dyes (most commonly Azo dyes) that are used, (Karthikeyan et al., 2011; Maghri et al., 2012).

The biological treatment methods have not been very successful when applied in isolation for treating textile wastewater; therefore, they are used as either pre-treatment, post-treatment or applied in combination with other methods. Among the methods being used for the treatment of textile wastewater are; the electrochemical method (El-Ashtoukhy and Amin, 2010; El-Desoky et al., 2010; Ge et al., 2012),

Table 5. Summary of different treatment processes for textile wastewater

Categories	Treatment Method	References
Physical Method	Adsorption	(Bhatnagar and Sillanpää 2010; Lim et al., 2010; Gupta et al., 2011; Mahmoodi et al., 2011)
	Ion exchange	(Ahmad et al., 2012; Syafalni et al., 2012)
	Membrane filtration	(Ciardelli et al., 2001; Robinson et al., 2001; Ahmads et al., 2002; Liu et al., 2012)
Chemical method	Coagulation/Flocculation	(Tatsi et al., 2003; Golob et al., 2005; Harrelkas et al., 2009)
	Advanced Oxidative processes (AOP): UV (Photochemical), H_2O_2, Ozonation based processes.	(Arslan-Alaton et al., 2012; Hammami et al., 2012; Franco and Azevedo, 2013; Garcia et al., 2013; Soares et al., 2013; Bahmani et al., 2014)
Biological Methods	Aerobic, Anaerobic, Biofilm-based, Fungal Metabolic activities.	(Işık and Sponza, 2008; Ahmad et al., 2012; Khouni et al., 2012; Lotito et al., 2012; Kim et al., 2013)

Fagbenro and Aziz (2014).

Table 6. Color Removal from various Wastewater types

Technique	Type of wastewater	Color removal (%)	Reference
Bamboo based-AC	Cotton textile mill	91.84	(Ahmad and Hameed, 2009)
Electrochemical treatment	Textile wastewater	98.6	(Bhatnagar et al., 2014)
Photo-oxidation	Textile industry effluent	86	(Deshannavar et al., 2012)
$O_3/H_2O_2/UV$	Polyester & acetate fiber dyeing	96	(Azbar et al., 2004)
Heat activated persulfate	Cotton textile wastewater	99.4	(Fagbenro and Aziz, 2015a).

coagulation/flocculation (Moghaddam et al., 2010; Verma et al., 2012; Rodrigues et al., 2013), membrane, (Barredo-Damas et al., 2010; Amini et al. 2011; Aouni et al., 2012).

Dyeing effluents are of varying composition and are problematic in nature (Bisschops and Spanjers, 2003). Also, the sole application of the conventional biological, physical and chemical treatment methods are either entirely unsuccessful or difficult, resulting in the transfer of pollutant from one phase to another, rather than their destruction. The transfer of phases consequently leads to secondary pollution (Dongfang and Feng, 2012). There's therefore a need for an effective treatment method for the textile wastewater. In this regard, the advanced oxidative process (AOP) has fared well as an advanced chemical treatment technique. However, AOPs are expected to be carefully monitored during its operation, to avoid a partial oxidation of organic contaminants that may result in the formation of intermediates which are more toxic than the parent compounds as may happen with the conventional treatment methods, (Poyatos et al., 2010; Rizzo, 2011).

One of the major environmental concern regarding the clothing and textile industries is the quantity and quality of the wastewater discharges. Characteristically, textile wastewater are strong coloured from the use of dyes, and the resultant effects include esthetic problems and ecological disadvantage to the aquatic ecosystem, (Hao et al., 2000; Al-Ghouti et al., 2003; Mittal et al., 2014), therefore, it is imperative that the wastewater be treated to remove colour. Also, the processes involved in the production of textile materials require the use of very many types of chemical based products which consists of organic and complex structured compounds (Al-Kdasi et al., 2004). The complexity and non-biodegradable nature of the wastewater generated thereof has necessitated the use of relatively newer, advanced, effective and economical techniques for its treatment. A high organic load, toxic compounds as well as COD in textile wastewater are bio recalcitrant, therefore a chemical pre-treatment which can adequately reduce the loadings before an eventual biological treatment may be applied (Martınez et al., 2003). Textile wastewaters are difficult to treat by regular biological methods because of the non-biodegradable nature of dyes (most commonly Azo dyes) that are used, (Karthikeyan et al., 2011; Maghri et al., 2012). Reisner (2016) summarized the degradation of several components in wastewater by activated persulfate (Table 7).

Treatment of Textile Wastewater Using Persulfate at Ambient Temperature

Persulfate oxidation has been considered not very reactive at ambient temperature, (Huang et al., 2002). A review of previous studies, particularly Fagbenro and Aziz, (2015d) showed a similarity of findings. At ambient temperature, the influence of persulfate (S_2O_8) oxidation of real textile wastewater was investigated for the removal of colour, suspended solids (SS) and chemical oxygen demand (COD). The effect of oxidant dosage, initial solution pH and contact time were studied in a series of batch experiments using Persulfate (PS) in Sodium Persulfate as the oxidant. Oxidant dose was considered as PS/COD molar ratio, varied from 1/1-10/1. An increase in parameter removal against increased oxidant dose was observed, especially for colour and suspended solids as shown in Figure 1. The findings were similar to those of Yang et al., (2010). Although removals continue to increase with an increase in oxidant dose, it would be uneconomical to use a higher oxidant dosage, therefore a dosage of 4/1, (i.e. PS/COD) molar ratio was adopted in a bid to use less chemical. However, a particularly low COD removals was observed for the various oxidant dosages investigated and only a maximum of 14% removal was observed at an oxidant dose of 9/1.

Table 7. Degradation of various compounds by activated persulfate in wastewater (Reisner, 2016)

Compound	Initial value	Persulfate	Activator	Optimal performance
Acid orange 7 (AOS 7)	0.1 mM	Sodium sulfate 12 mM	Electrochemically activated Anode $Ti/RuO_2/IrO_2$ Cathode stainless steel	95.7% AOS 7 removal occurred in 60 minutes adding 1 mM Fe (II) at pH = 3 and current density 16.8 mA cm^{-2}. The degradation efficiency was not significantly affected by pH value and increased with the increase of persulfate and Fe(II) concentration. 57.6% COD removal was achieved after 60 minutes and 90.2% after 600 minutes. Solution's acute toxicity increased during the first stage of the reaction and afterwards decreased with the progress of the oxidation.
Acid orange 7 (AO7)	0.057 mM	Sodium persulfate 5.7 mM	Activated carbon (adsorbent and catalyst, 5 g/L)	More than 97% AOS 7 removal occurred in 5 hours at pH = 5.1 and 25 °C. The pH had a significant role in organic degradation, optimal initial pH was nearneutral. Higher persulfate or activated carbon dosages resulted in higher AO7 degradation rates to certain amount. The course of AO7 degradation by the activated carbon/persulfate system occurred in the porous bulk or the boundary layer on the external surface of activated carbon granules.
Aniline	0.05 mM	Sodium persulfate 2.5 mM	Iron-activated Fe (0) 0.4 g/L	Complete aniline removal occurred in 10 minutes at 25 °C at pH = 4 or in 60 minutes at 80 °C at pH = 7. The process was affected by radical scavengers
Aniline	0.05 mM	Sodium persulfate 2.5 mM	Iron activated Fe (II) 0.12 mM	72.8% aniline removal occurred in 4 hours, at pH = 7 and 22.5 °C, where the persulfate/Fe(II)/aniline molar ratio was 125/25/1. Excess ferrous ions were scavengers for free sulfate radicals. It could be controlled with chelating agent as citric acid, EDTA and oxalic acid. Citric acid was the most effective.
Azo dye Acid Blue 113 (AB113)	50 mg/L	Sodium persulfate 6.3 mM	UV irradiation 14W λ = 254 nm	97.7% AB113 removal occurred in 120 minutes. The colour removal efficiency and degradation rate decreased with increase of AB113 concentration. pH had no significant effect on removal efficiency. UV intensity affected AB113 removal efficiency significantly.
Azo dye Orange G (OG)	0.1 mM	Sodium persulfate 4mM	Fe (II) 0.1 mM	Optimum conditions for OG degradation were at pH = 3.5, with persulfate/ferrous ion/(OG) concentrations 4 mM, 4 mM and 0.1 mM, respectively in 30 minutes. The presence of inorganic ions had inhibitory effects on the OG degradation in the following order of NO_3^- $<Cl^- <H_2PO_4^- <HCO_3^-$.

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Table 7. Continued

Compound	Initial value	Persulfate	Activator	Optimal performance
Azo dye Orange II	100 mg/L	Persulfate 2.0 g/L	Combination of electrochemical method and heterogeneous activation of persulfate Fe-Co/SBA-15 catalyst 1.0 g/L	95.6% Orange II removal occurred at pH = 6 in 60 minutes when anodic oxidation was combined with the Fe-Co/SBA-15 catalyst. Oxidant was activated by the continuously regenerated Fe(II) and Co(II). At pH 9 to 3, the degradation rate increased from 0.056 to 0.069 mM/min, while the efficiency increased only from 93.7% to 99.8%, because during the process pH dropped almost at the same level (pH = 3). Due to the side reaction between persulfate and free sulfate radical, insignificant increase of persulfate dosages led just to higher consumption of persulfate. Increasing the catalyst dosage accelerated Orange II degradation. Increasing Orange II concentration led to increase of degradation only to certain amount. Dye molecules competed with persulfate to adsorb onto the catalyst surface, and the loading dye molecules on the catalyst surface would decrease the active surface sites available for the activation of persulfate.
Azo dye C.I. Reactive Red 45 (RR45)	80 mg/L	Potassium persulfate 84.87 mM and 138.43 mM	Iron-activated Fe (II) 1.64 mM or Fe (0) 4.27 mM	> 92% RR45 removal occurred regardless of initial pH, iron activator type and concentration, or oxidant concentration within investigated ranges. The use of Fe (0) avoided loading the wastewater with unnecessary contour anions and enabled a wider pH range of application, having higher mineralization rate of 53% compared to Fe (II) 35%.
Beta-lactam antibiotics (penicillins – AMP and cephalosporin – CEP)	25 - 50 µg	Sodium persulfate 1 mM	Ultraviolet (UV) light-activated $\lambda = 254$ nm UV fluence 0 - 320 mJcm^{-2}	75.6% AMP and 90.7% CEP removal occurred at UV fluence 320 and 240 mJcm^{-2}, respectively at 25°C. It was found that chloride ion had a slight positive impact on degradation rate, but inorganic anions such as nitrate and sulfate did not have any impact. Hydrogen peroxide addition also did not have a synergistic effect.
Bisphenol A (BPA)	80 µM	Potassium persulfate 2 mM	Iron-activated Fe (0) 8 mg	Complete BPA degradation occurred in 45 minutes at pH = 5. Adding 7mg Fe (0) fastened the degradation to 30 minutes.
Bisphenol A (BPA)	80 µM	Potassium persulfate 2 mM	Iron-activated Fe (II), continuous addition 8 mg	Complete BPA degradation occurred in 30 minutes at pH = 5.
Bisphenol A (BPA)	80 µM	Potassium persulfate 2 mM	Iron-activated Fe (II), sequential addition 8 mg	97% degradation occurred in 30 minutes at pH = 5.

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Table 7. Continued

Compound	Initial value	Persulfate	Activator	Optimal performance
Ciprofloxacin (CIP)	10 mg/L	Sodium persulfate 1.92 g/L	Ultraviolet (UV) irradiation λ = 254 nm intensity 1 mW cm^{-2}	95% CIP was degraded in 30 minutes at pH = 7 and 25°C. Efficiency of degradation was increased with higher persulfate concentration. However, excessive persulfate inhibited the degradation. EtOH and TBA were scavengers and reduced the degradation rate significantly.
Ciprofloxacin (CIP)	30 µg	Potassium persulfate 600 µg	Fe (II) 600 µg	95.8% degradation rate was achieved at pH = 6, in 240 minutes. Adding chelated agents (CA, EDTA or EDDS), the degradation rate decreased. At pH = 6, in 240 minutes the degradation rate decreased from 71.2% to 68.6% using CA, to 60.4% using EDTA and to 42.1% using EDDS, whereas 300 µg potassium persulfate was used.
Cyanide	50 mg/L	Sodium persulfate 0,8 g/L	UV (h_V= 254 nm)	79% cyanide removal occurred at pH = 11, in 30 minutes and at air flow rate 0.4 L/min. Increasing persulfate concentration slightly increased the removal of cyanide (at 1.5 g/L 86%). It was explained with persulfate being itself scavenger of sulfate radical.
2,4-Dichlorophenol (DCP)	30 mg/L	Sodium persulfate 12.5 mM	Iron-activated nano-Fe (0) 2.0 g/L	92.5% DCP removal occurred within 150 minutes at pH = 3
Dimethyl phthalate (DMP)	0.0515 mmol/L	Sodium persulfate 10.3 mmol/L	Thermally activated (20 – 40°C)	Complete DMP removal occurred at 40°C within 18 hours at pH = 3.1.
p-Hydroxybenzoic acid (HBA)	100 µM	Sodium persulfate 2 mM	Electron beam 3 MeV vertical scan beam, 600 Gy dose	More than 80% HBA was degraded. Addition of persulfate induced a change in the reaction pathway. In the absence of persulfate, the main by-product formed was 3,4-dihydroxybenzoic acid, while in presence of persulfate, 1,4-benzoquinone was detected and the hydroxylated by-products were not present. High pH and dissolved oxygen decreased the HBA degradation.
Ibuprofen (IBU)	20.36 µM	Sodium persulfate 1.0 mM	Thermally activated (40 – 70°C)	Complete IBU degradation occurred at pH = 7 after 20 and 40 minutes of reaction at 70 and 65°C respectively. Both, increasing and decreasing pH lowered IBU degradation rate. Increase in sodium persulfate concentration for fixed IBU concentration resulted in faster IBU degradation rate.
Ibuprofen (IBU)	1 mM	Potassium persulfate 20 mM	Gamma irradiation 60-Co radiation chamber, 80 kGy dose	97% IBU removal efficiency occurred at pH = 7. Due to the fact that free sulfate radical reacts directly with the benzene ring forming of benzene radical cation followed by the benzyl type radical, the decay was much faster compared to hydroxyl radical.

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Table 7. Continued

Compound	Initial value	Persulfate	Activator	Optimal performance
Landfill leachate	COD 1254 mg/L Ammonia nitrogen 500 - 2000 mg/L	Sodium persulfate 156.75 mM	Thermally activated (27 – 50 ºC)	pH = 3-4, higher temperature, and higher dose of persulfate favoured the removal of COD and ammonia. At $S_2O_8^{2-}$:12 COD = 2 and 50°C, the COD removal rates were 79% and 91% at pH = 8.3 and 4, respectively; and the ammonia nitrogen removal reached 100% at both pH values.
Landfill leachate	COD 1900 mg/L	Sodium persulfate 62.5 mM	Electrochemical: anode Ti/ IrO_2RuO_2-TiO_2, cathode Ti Fe (II) 15.6 mM	62.2% COD removal occurred at pH = 3 in 60 minutes, current density was 13.89 mA/cm². At higher pH the degradation rate was lower, e.g. at pH = 9, the removal was only 22%. COD removal efficiency increased with persulfate concentration. However, it led to the side reaction between persulfate and free sulfate radical. Fe (II) dosages were effective until 15.6 mM, in case of higher dosages the Fe (II) acted as a scavenger. Higher densities (>13.89 mA/cm²) caused side reactions.
Landfill leachate	Total organic arbon (TOC) 55 ± 19 mg/L Colour (UV254)	Sodium persulfate 4762 mg/L	Microwave irradiation	TOC removal of 79.4%, colour removal of 88.4%, and UV_{254} removal of 77.1% were reached at power 550W, 85°C and within 30 minutes. Reaction rates increased with microwave power, although at 775W the effect was opposite. Larger persulfate doses had a scavenging effect.
Landfill leachate (stabilized)	COD 1780 – 2530 mg/L NH_3-N 780 – 1090 mg/L	Sodium persulfate 35 g	Ozone 80 g/m³	72% COD and 55% NH_3-N removal occurred at pH = 10, in 210 minutes. Increasing the pH, the removal efficiencies for COD and ammonia were also increased. Although the removal of compounds increased with time, the optimal time was 210 minutes. It was found that persulfate and ozone act as oxidants better together than separately.
Landfill leachate (stabilized)	COD 19180 - 20448 mg/L NH_3-N 2450 - 3400 mg/L	Sodium persulfate 5.88 g	H_2O_2 8.63 g	81% COD and 83% NH_3-N removal occurred at pH = 11, in 120 minutes. Elevating pH the removal of compounds was increased, although significant removal efficiency was obtained also at neutral pH. Although the removal of compounds increased with time, the optimal time was 120 minutes. It was found that persulfate and hydrogen peroxide act as oxidants better together than separately.
Phenol	0.1 mM	Sodium persulfate 50 mM	Ultraviolet (UV) irradiation 20W λ = 295-400 nm UV fluence 0.18 mWcm⁻²	95% removal occurred in 900 minutes, adding 0.2 g/L magnetite (Fe_3O_4) at pH = 5.
Phenol	20 ppm	Potassium persulfate 1.48 g/L	Carbon nanotubes, 0.2 g/L catalyst	Complete phenol removal occurred in 45 minutes and at 45ºC. Increase of temperature increased the degradation speed (at 25 ºC complete removal was achieved in 90 minutes).

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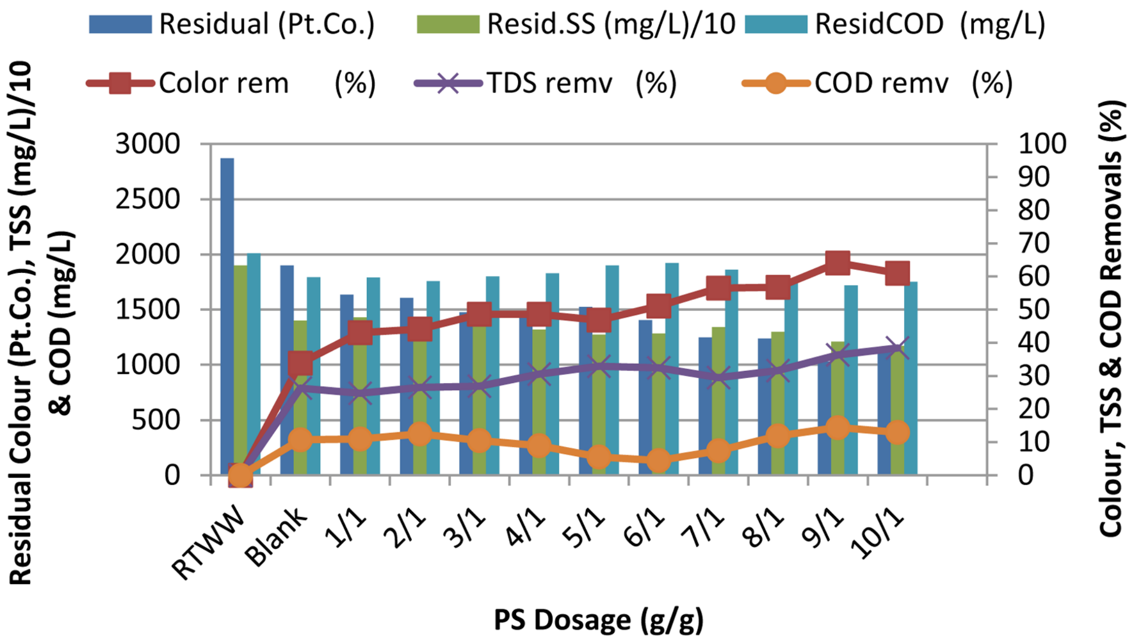
Table 7. Continued

Compound	Initial value	Persulfate	Activator	Optimal performance
p-Nitroaniline (PNA)	0.2 mM	Sodium persulfate 8 mM	Iron oxide magnetic nanoparticles Fe3O4 5.32 g/L	Complete removal occurred at 270 minutes, at 25 ºC, at pH = 7. The mineralization rate was 67%. Increasing persulfate or Fe$_3$O$_4$ concentrations, the degradation rate increased until certain amount -16 mmol/L and 7.98 g/L, respectively. Increasing temperature or decreasing pH, increased PNA degradation rate. The higher was initial concentration of PNA, the lower was the degradation rate.
Sulfamethoxazole (SMX)	30 µg	Potassium persulfate 2400 µg	Fe (II) 2400 µg	µg potassium persulfate was used, the degradation rate increased from 29.8% to 35.5% and 49.7%, respectively in 240 minutes. Adding EDDS at the same conditions did not have almost any effect (degradation rate was 29.5%).
Tetramethylammonium hydroxide (TMAH)	1.1 mM	Sodium persulfate 50 mM	Ultraviolet (UV) irradiation 15 W λ = 254 nm UV fluence 4.5 mWcm^{-2}	Complete TMAH removal occurred in 130 minutes, at 20°C and at pH = 2. TMAH degradation increased with increasing persulfate dosage till persulfate concentration was 50 mM. Higher reaction temperature and stronger UV irradiation increased also the degradation of TMAH.

Figure 1. Effect of Persulfate dosage based on the PS/COD molar ratio
(Fagbenro and Aziz, 2015d)



Similarly, since initial pH of solution plays a significant role in the persulfate oxidation of textile wastewater, it was also studied in the work under review for the removal of colour, suspended solids and COD. The pH of the sample wastewater was 11.49, prior the treatment with persulfate. The addition of persulfate into the system lowered the pH, making it acidic according to the oxidant dose applied. At an oxidant dose of 4/1 (PS/COD molar ratio), a variation of initial pH from 2-11, were conducted. It was observed that the parameter removals were most favoured by an acidic medium, achieving an optimum at pH of between 2, 2.5, and 3, after a 60 minutes reaction time as shown in Figure 2. Although persulfates are known to be very reactive at pH below 3, but pH above 10 is also favourable, (Block et al., 2004; Liang et al., 2007). Some optimum parameters removals of 68% colour, 61% suspended solids were observed at pH of 2 while 32% COD removals were observed at pH 3 after a 60 minutes reaction time.

The responses of the same parameters removals to a variation in reaction time were equally monitored over a 420 minutes reaction time. At ambient temperature, oxidant dose of 4/1 (PS/COD molar ratio), and pH of 2, colour and suspended solids removals were observed to have a gradual increase up to 85% and 71% respectively within a 360 minutes reaction time as shown in Figure 3. While COD removal was rapid, yet very low (32% maximum), even after the initial 60 minutes reaction time and without any further significant increase beyond this period. Although relatively effective, the reviews of the results of PS oxidation of textile wastewater indicates the relatively slow reactions at ambient temperatures. Hence, the persulfate anion is said to be kinetically slow in its reaction with oxidizable organics, (Liang et al., 2007).

Figure 2. Effect of Solution pH, using a PS/COD of 4/1
(Fagbenro and Aziz, 2015d)

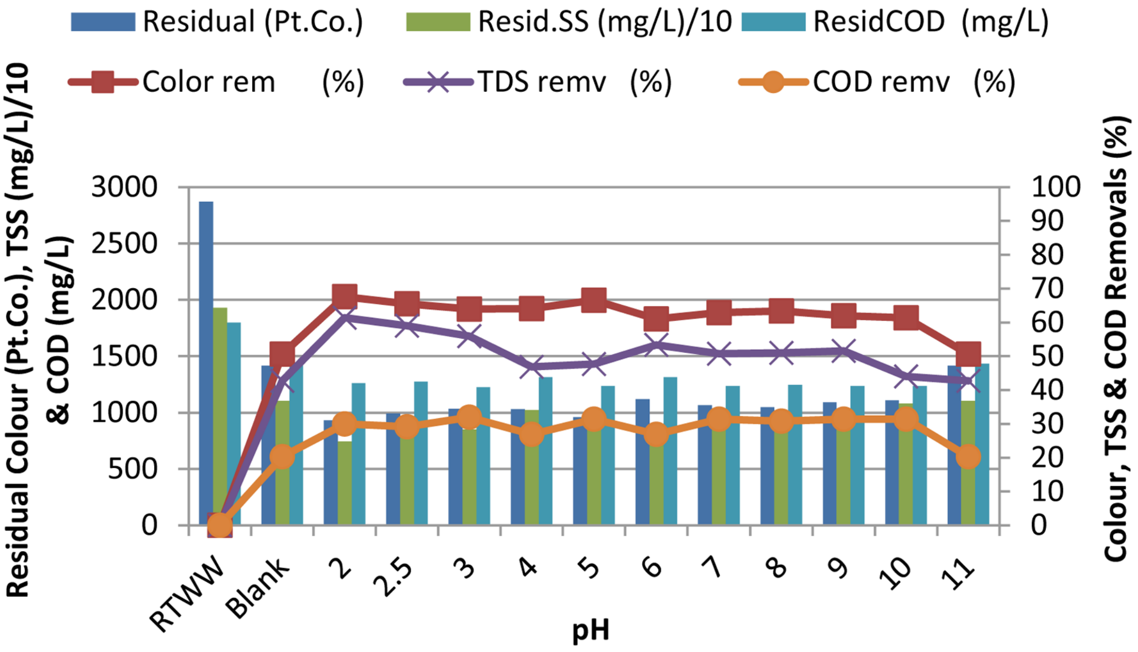
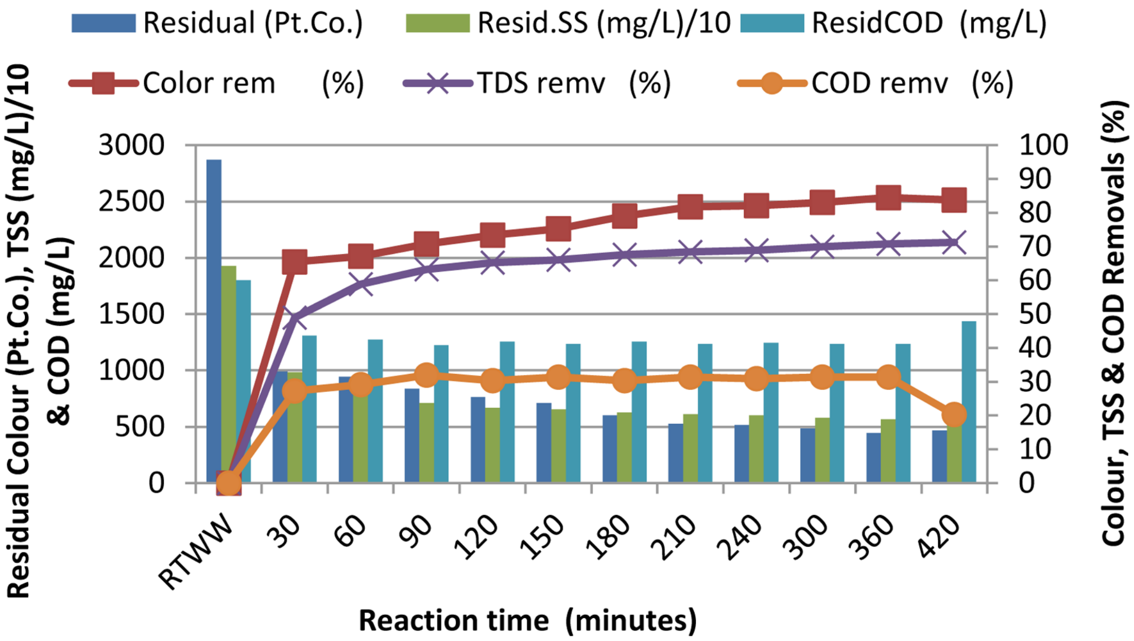


Figure 3. Effect of Contact Time (minutes), using a PS/COD molar ratio of 4/1
(Fagbenro and Aziz, 2015d)



Treatment of Textile Wastewater Using Persulfate at Elevated Temperatures

The relative slow capacity of persulfate to oxidize contaminants in water and wastewater at ambient temperatures has necessitated its activation by various means. In an attempt at investigating the influence of Persulfate activation by thermal means, for the removal of colour in raw textile wastewater, Fagbenro and Aziz, (2015a), also considered the efficiency of the technique in relation to time dependent influence of temperature variance, PS dosages and pH variance. They applied different dosages of persulfate at temperatures of 25°C, 40°C, 50°C and 60°C and at the initial pH of the wastewater prior the experiments. A much lower removal of colour was observed for the experiments which were not thermally activated i.e. at 25°C. Parameter removals continue to increase with persulfate dose and elevation of temperature as shown in the review presented in Figure 4. The increase in colour removal with an increase in oxidant dosage shows the relative importance and the influence of PS dosing on the system. Similar findings were made by (Gu et al., 2011), where a dosage of 100/1 were used for the complete removal of the contaminant in a thermally activated PS oxidation. Also, the wide variation in removals at 25°C and other temperatures investigated showed the positive influence of thermal activation and hence, elevation of temperature on the PS oxidation of contaminants in textile wastewater. Although conventional oxidation of dyestuffs and organic compounds has been reported to be difficult at low concentration (Al-Kdasi et al., 2004), however, it would be highly uneconomical to use very high dosages of oxidants. Hence, a 4/1 dosage of PS was applied for the subsequent experiments in the study under review.

Figure 4. Influence of persulfate dosage on colour removal at 25°C, 40°C, 50°C and 60°C
(Fagbenro and Aziz, 2015a)

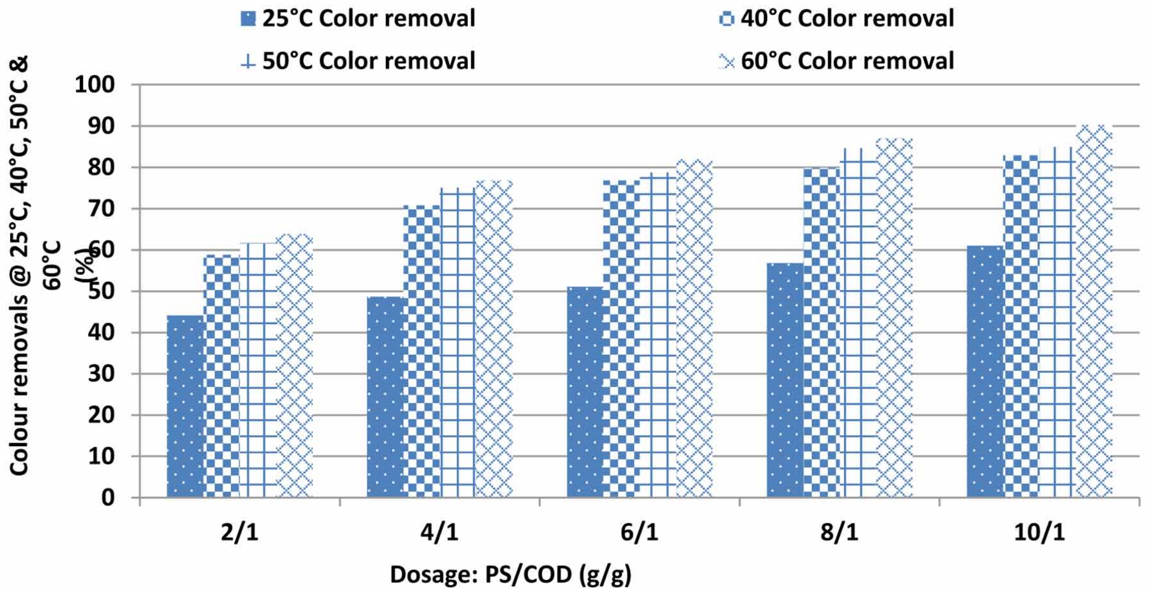
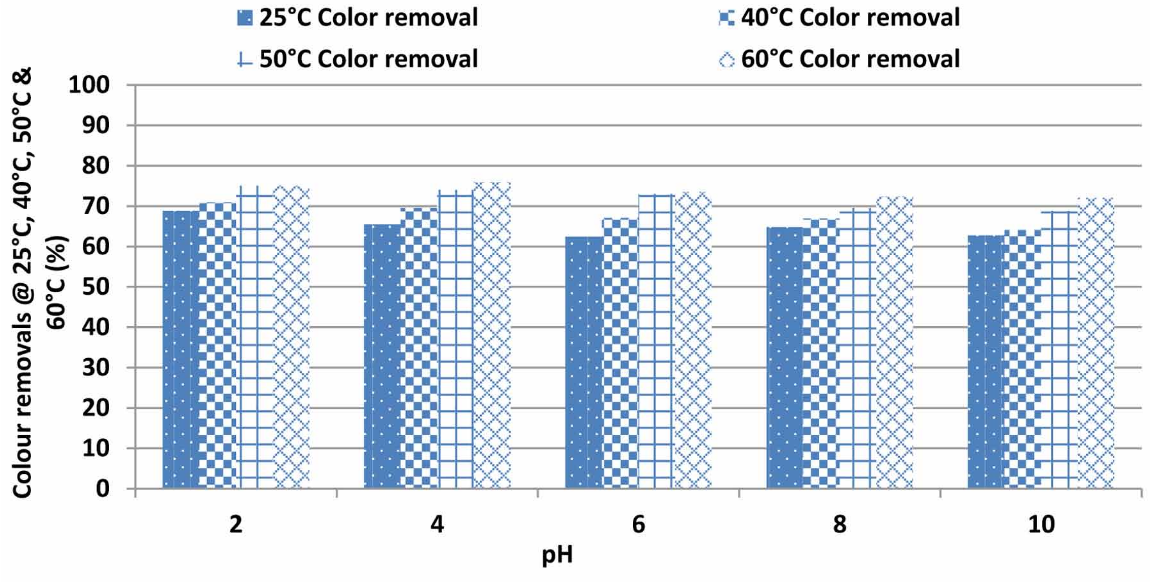


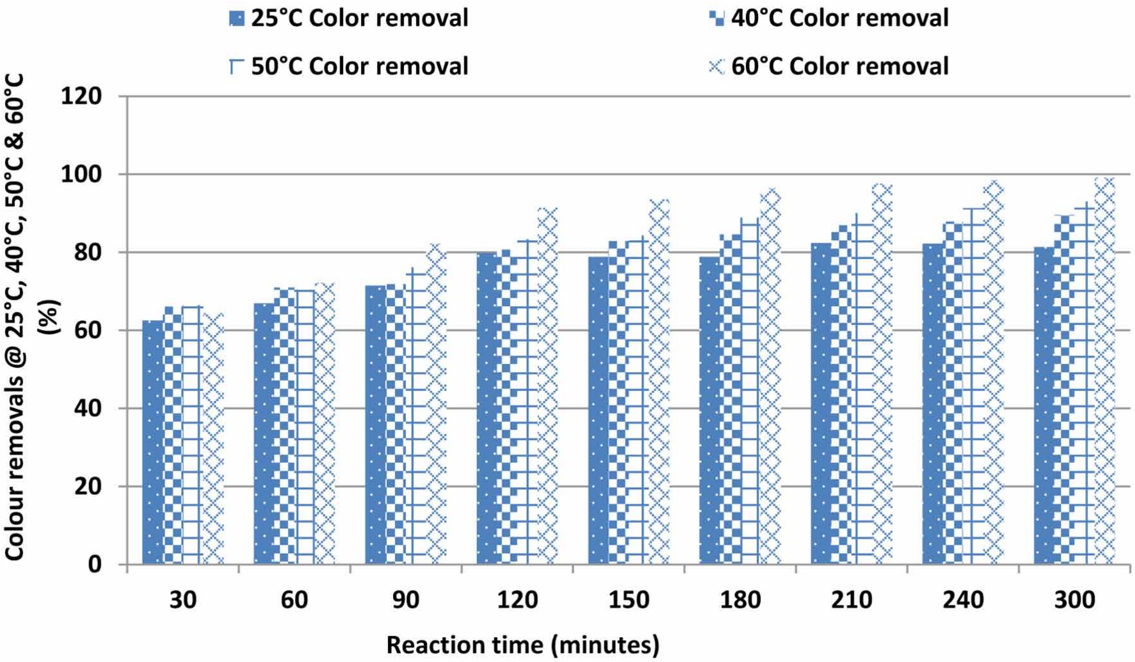
Figure 5. Effect of initial pH of solution on colour removal at 25°C, 40°C, 50°C and 60°C
(Fagbenro and Aziz, 2015a)



The initial pH of solution has been reported as a significant factor in many aqueous systems (Andreozzi et al., 1999; Zhao et al., 2014), hence its influence was also determined in the main study under review. The study revealed that all the reactions were favoured by an acidic medium, especially between pH 2 - 4, irrespective of the temperatures considered. Likewise, (Liang et al., 2007) in his research and review of earlier works reported a similarity of findings which is also supported by the report of experimental results of (Gu et al., 2011) and their conclusion that acidic conditions were most favourable.

Reaction time was very significant in the removal of colour, as there was a wide variation between different temperatures that were investigated when the reaction time was increased as shown in Figure 6. The margin of decolourization was particularly obvious at temperatures of between 40ºC and 60ºC but not far different between 25ºC and 40ºC showing that increases in temperature i.e. thermal activation was also very significant in the decolourization reactions. Almost complete i.e. 99% decolourization of the sample textile wastewater was achieved at 60ºC and 240 minutes reaction time. This is in line with the previous findings that thermal activation assists the persulfate oxidation kinetics to achieve an improved performance in the oxidation of organic pollutants in water and wastewaters (Huang et al., 2002).

Figure 6. Effect of initial pH of solution on colour removal at 25°C, 40°C, 50°C and 60°C
(Fagbenro and Aziz, 2015a)



CONCLUSION

The current chapter examined the application of persulfate as an advanced oxidation process to the treatment of wastewater generated from the production of textile materials. It discussed the textile industry, highlighting the characteristics of the wastewater generated and the problems associated. Athough colour has been identified as the most obvious parameter of the textile wastewater, other problematic parameters include a high total suspended solids, certain heavy metals and trace elements which required specific and efficient treatment processes. In this chapter, several treatment techniques and their applications to textile wastewater have been summarized. The chapter focused on persulfate applications in textile wastewater treatment because it has higher oxidation potential for the removal of organic and inorganic pollutants.

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Chapter 5

Advanced Oxidation Processes (AOPs) to Treat the Petroleum Wastewater

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ABSTRACT

Petroleum wastewater generation is one of the main pollutants associated with oil refineries processes. The petroleum wastewater usually contains a complex variety of materials and organic compounds. Dedicated treatment facilities are required before the petroleum wastewater can be discharged to the environment. Researchers worldwide are still searching for a total solution to solve petroleum wastewater problem. In this chapter, different chemical treatment methods for the petroleum wastewater including coagulation-flocculation, Fenton and electro-Fenton oxidation, photocatalyst oxidation, and advanced oxidation processes are reviewed and discussed. Nevertheless, the efficiency of each process was also evaluated. It can be concluded that the performance of these processes is mainly attributed to petroleum wastewater type and initial organic concentrations whereas treatment performance weakens reported at higher initial concentrations of pollutants.

INTRODUCTION

The petroleum wastewater is a complex organic liquid and can have enormously adverse environmental impacts, depending on the characteristics of the materials, which exist in them. In general, the pollutants in wastewater can be divided into organic matters and inorganic matters, which included nitrogen, phosphorus, ammonia and iron chlorides as well as heavy metals (Tengrui et al., 2007). A large amount

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of water is used during the petroleum refinery activity. Consequently, significant volumes of wastewater are generated.

Advanced oxidation processes (AOPs) have a capability of rapid degradation of recalcitrant pollutants in the aquatic environment. They have shown high efficiency to remove the organic compounds from effluents even when they are present in low concentrations (Silva et al., 2015; Masomboon et al., 2010; Paz et al., 2013; Philippopoulos & Poulopoulos, 2003) and did not form environmentally dangerous byproducts (Giri & Golder, 2014). A remediation of hazardous substances is attributed to hydroxyl radical ($^{\cdot}OH$), which exhibits reactivity toward organic compounds and has the potential to destroy and degrade them (Hermosilla et al., 2009). Many techniques are used to enhance the production rate of hydroxyl radicals by chemical additives (such as hydrogen peroxide (H_2O_2)), external energy (such as sunlight), catalysts (such as titanium dioxide (TiO_2)) and the integration of two or more AOPs (such as TiO_2/Fenton/sunlight) (Kim et al., 2012). Using solar energy in the AOPs could reduce processing costs and make the AOPs more affordable for commercial use (Amor et al., 2015). AOPs might be used in wastewater treatment for reduction of chemical oxygen demand (COD), color, odor and specific pollutant or sludge treatment (Amor et al., 2015; Tony et al., 2012).

The photocatalyst is a promising technique for the treatment of contaminated water, which has been widely studied during recent years because it is fast, effective, eco-friendly, economically viable, and able to completely oxidize organic molecules at a low energy (Kwon et al., 2008). When TiO_2 is exposed to sunlight, a hole in the valence band and an electron in the conduction band are generated by light induction. This hole causes the oxidation of hydroxyl ions and produces the hydroxyl radicals at the TiO_2 surface while in the solar photo-Fenton process, the formation of hydroxyl radicals bases on the reaction between Fe^{+2} and H_2O_2 under sunlight irradiation. The photocatalyst processes have shown promising results in the treatment of non-biodegradable and toxic compounds (Boundjou et al. 2012). The major drawbacks of Fenton process are iron complexation by carboxylic intermediates. However, these complexes could be photoactivated by the photo-Fenton process and additional hydroxyl radicals ($HO^{\bullet}$) generation (Amor et al., 2015). The solar photo-Fenton is based on using solar radiation to increase production of hydroxyl radicals ($HO^{\bullet}$) and photoactive complexes through the Fenton process (Amor et al., 2015; Fernandes et al., 2014; Lucas et al., 2012; Pignatello et al., 2006).

Petroleum Wastewater Characteristics

The typical characteristics of the petroleum wastewater are shown in Table 2.1. Oil, grease, phenolic compounds, nitrogen, and sulphur components are mainly the compounds that are present in petroleum wastewater (Abdelwahab et al., 2009; Kavitha & Palanivelu, 2004; Lathasree et al., 2004; Pardeshi & Patil, 2008; Yang, 2008).

The oil and grease in the petroleum wastewater are sticky and can clog drain pipes. They also cause unpleasant odors and capable of corroding drain pipes (Xu & Zhu, 2004). The phenolic compounds is a threat to the environment due to their extreme toxicity and ability to remain for long periods in the environment (Abdelwahab et al., 2009; Kavitha & Palanivelu, 2004; Lathasree et al., 2004; Pardeshi & Patil, 2008; Yang, 2008). The nitrogen and sulphur components in the petroleum wastewater are represented in the form of ammonia and hydrogen sulphide (H_2S), respectively (Altaş & Büyükgüngör, 2008). In addition, Naphthenic acids (NAs) are one class of compounds in wastewaters from petroleum industries that are known to cause toxic effects, and their removal from oilfield wastewater is an important challenge for remediation of large volumes of petrochemical effluents (Wang et al., 2015). Due to the petroleum wastewater content high polycyclic aromatics, which are very toxic, it was considered hazardous pollutants on the environment (Mrayyan & Battikhi, 2005; Wake, 2005). The identification of the organic pollutants in petroleum refinery wastewater in some refineries showed that the major compounds were different fractions of petroleum aliphatic hydrocarbons (up to C_{10}) and the well-known aromatic compounds such as benzene, toluene, and ethyl-benzene (Saien & Nejati, 2007). Seif (2001) showed that the maximum removal for COD and BOD were around 1400-1500 mg L^{-1} and 25-30 mg L^{-1}, respectively, from different sources of petrochemical wastewater by using physical treatment and concluded that separation and individual treatment for each source was a good alternative to treatment full quantity after mixing of different sources. (Wang et al., 2015) reported that the percentage of aromatic naphthenic acids (NAs) in total naphthenic acids (NAs) was estimated to be 2.1-8.8% in a refinery wastewater treatment plant. These effluents were composed of grease and petroleum compounds, which consist of three main hydrocarbon groups; Paraffin [very few carbon atoms (C_1 to C_4) such as Methane (CH_4), Ethane (C_2H_6) and Propane (C_3H_8)], Naphthene [such as Cyclohexane (C_6H_{12}) and Dimethyl Cyclopentane (C_7H_{14})], and Aromatics [The more carbon atoms a hydrocarbon molecule such as Benzene (C_6H_6), Toluene (C_7H_8) and Xylene (C_8H_{10})]. When a crude oil contained appreciable quantities of sulphur, it was called sour crude. Thus, sour water was a specific stream of petroleum refineries, which contain slowly biodegradable compounds and toxic substances (Coelho et al., 2006). The petroleum wastewaters could vary greatly in their specifications, depending on the plant configuration, operation procedures, and type of oil being processed (Saien & Nejati, 2007).

The following general conclusions can be drawn from these characteristics of petroleum wastewater reported by various researchers as shown in Table 1; the composition of effluent in petroleum wastewater depended on the crude quality, the operating conditions, and the sources of wastewater pollutants. Thus, the big difference was shown in the specification of wastewater among the investigated studies and a wide variety of pollutants at varying concentrations.

The average sulphide concentration was about 20 mg L^{-1}, but it was a high concentration in sour water stream, which has complex chemical compositions such as oil, phenols, sulphides, mercaptans, ammonia, cyanides and other micro-pollutants. Thus, (El-Naas et al., 2009) reported that the sulphide concentration was 1222 mg/L.

Various environmental protection agencies set maximum limits of discharge for each component of the petroleum wastewater as shown in Table 1 to protect the environment from the hazardous composition in petroleum wastewater. The fuel additives, which are carcinogenic such as dichloroethane (DCE), Dichloromethane (DCM) and *t*-butyl methyl ether (tBME), are considered the most of the undegraded total petroleum hydrocarbon (Diya'uddeen et al., 2011).

Chemical Treatment Technologies for Petroleum Wastewater

Chemical treatment consists of using some chemical reaction or reactions to improve the water quality. A previous work by Sun et al. (2008) reported that using a microwave-assisted catalytic wet air oxidation process achieved more than 90% of COD removal and increase BOD_5/COD ratio from 0.04 to 0.47 at 30 min to treat petroleum wastewater at 150 °C with 0.8 MPa pressure. Although high efficiency was reached, a 150 °C is not promising due to the high energy cost.

Table 1. Summary of characteristics of petroleum wastewater and standard discharge limits for petroleum wastewater effluents

The reference		pH	COD (ppm)	BOD (ppm)	TSS (ppm)	NH_3 (ppm)	Ph. (ppm)	S^{-2} (ppm)	Tur. (NTU)	Oil (ppm)	TDS (ppm)	TOC (ppm)
Vendramel, 2015		8.3	1250	-	150	-	-	-	-	-	-	-
(Aljoubory & Senthilkumar 2014)		6.5-9.5	550-1600	-	-	-	-	-	-	-	1200-1500	220-265
(Saber et al. 2014)		6.7	450	174	150	-	-	-	-	870	-	119
(Gasim et al. 2013)		8.5	7896	3378	-	13.5	-	-	-	-	-	-
(Tony et al. 2012)		7.6	364	-	105	-	-	-	42	946	-	-
(Hasan et al. 2012)		7	1343	846	74	-	-	-	83	240	-	398
(Farajnezhad & Gharbani 2012)		7.5	1120	-	110	-	-	-	-	-	-	-
(Abdelwahab et al. 2009)		8	80-120	40.3	22.8	-	13	-	-	-	-	-
(El-Naas et al. 2009)		9.5	4050	-	80	-	-	1222	-	-	-	-
(Altaş & Büyükgüngör 2008)		7.2-9.2	220	-	-	-	-	20	-	-	-	-
(Dincer et al. 2008)		2.5	21000	8000	2580	69	-	-	-	1140	37000	-
(Zeng et al. 2007)		6.5-6.8	500-1000		90-300		20	15-30	150-350	400-1000	3000-5000	-
(Demırcı et al. 1998)		6.5-8.5	800	350	100	-	8	17	-	3000	-	-
Standard Discharge Limits (S.D.L)	(Ma et al. 2009)[a]	6-9	< 100	< 15	< 70	< 15	-	-	-	-	-	-
	(Diya'uddeen et al. 2011)[b]	6-9	< 150	< 30	< 30	-	-	< 1.0	-	-	-	-
	(Aljoubory & Senthilkumar 2014)[c]	6-9	< 200	< 20	< 30	< 10	< 0.1	< 1.0	-	-	<2000	< 75

[a] wastewater discharge standard of China (State Environmental Protection Administration of China, 1996).

[b] Environmental Health Safety Guidelines (2009).

c wastewater discharge standard of Oman (2005).

Advanced Oxidation Processes (AOPs)

AOPs may be used in petroleum wastewater treatment for overall organic content reduction, specific pollutant destruction, sludge treatment, increasing the bioavailability of recalcitrant organics and color reduction (Silva et al. 2015). AOPs depended on the generation and increasing the concentration of hydroxyl radicals (Brillas & Casado, 2002). Kim et al. (2012) indicated that hydroxyl radical exhibits reactivity toward organic compounds and also an environmentally friendly oxidant because of its ability to dissociate into nontoxic and harmless products. Hydroxyl radical has high oxidation potential (1.80-0.87 V) at pH (0-14) and considers one of the most powerful oxidizers. In addition, hydroxyl radical is stronger than chlorine and chlorine dioxide (Neyens & Baeyens, 2003).

Hydrogen Peroxide Oxidation

The hydroxy1 radical has a high standard oxidation potential (2.80V) and considers the second strongest oxidant after fluorine (Hermosilla et al. 2009). In addition, it exhibits high reaction rates compared with other conventional oxidants such as hydrogen peroxide and O_3. Hydroxy1 radicals are the main reactive species which have the potential to degrade organic pollutants, the toxic chemicals, bio-refractory compounds and react with many inorganic solutes with high-rate constants (Diya'uddeen et al. 2011).

They also react rapidly with most alkenes and aromatic compounds, which are unreactive with hydroxy1 radicals. Many oxidation processes or combinations of processes to generate hydroxy1 radicals have been attempted such as Fenton and electro-Fenton process or use a combination of strong oxidants like hydrogen peroxide with catalysts (Gogate & Pandit, 2004). Hydrogen peroxide (H_2O_2) considers not only as a relatively cheap, efficient and safe oxidant and easy to degradation of various inorganic and organic pollutants (Gogate & Pandit, 2004). The effectiveness of hydrogen peroxide (H_2O_2) to degrade recalcitrant pollutants depends on an intermediate associate to produce hydroxyl radicals (Gogate & Pandit, 2004). However, H_2O_2 has very low rates of direct oxidation for complex materials if it is used alone in petroleum wastewater. So, it should be combined with other conventional oxidants such as UV light and O_3 (Diya'uddeen et al. 2011). Due to its slow self-decomposition rate, Hydrogen peroxide (H_2O_2) oxidation alone may not be effective enough to degrade high concentration of recalcitrant pollutants in petroleum wastewater. Therefore, the use of hydrogen peroxide (H_2O_2) alone considers not economically favorable and requires to be used with other advanced oxidation techniques such as Fenton reagent (using activation of H_2O_2 by iron salts) to synergistically enhance its oxidizing capability. The use of H_2O_2 as an oxidant has been investigated in several of the works, for example, Bustillo-Lecompte et al. (2015) showed that the treatment of petroleum refinery wastewater by using a bench scale UV/H_2O_2 photo-reactor in batch mode achieved the highest removal of TOC of 78.38% at 45 min and a pH of 5. Saien & Nejati (2007) obtained the highest level of COD degradation, which was 90% COD reduction, by a relatively low catalyst concentration of 100 mg L^{-1} in a pre-treated effluent while Coelho et al. (2006) revealed that using the H_2O_2, H_2O_2/UV, UV, photocatalysis and ozonation processes did not lead to satisfactory results, reducing at most 35% of dissolved organic carbon (DOC) in the sour water stream (SWS) and they reported a 21% DOC removal in the sour water stream (SWS) at a high catalyst loading of 200 mg L^{-1} (in comparison with 100 mg L^{-1} reported by (Saien & Nejati 2007)) within 1h of irradiation time. These results might be due to the adverse effect of excess H_2O_2 on the reaction.

Hydroxyl Radical (•OH)

The mechanism of photocatalyst and Fenton processes depended on the generation and increasing the concentration of hydroxyl radicals. The hydroxyl radical has a very high oxidation potential, high efficiencies and less generation of sludge (Al-Rasheed 2005). In addition, it operated within a wide pH range. Under high light incident intensity, The higher catalyst activity occurs because the photons are present in excessive amounts leading to more reactive species generation and more destruction of organic compounds (Laoufi et al. 2008). The intensity of UV irradiation increases the formation of hydroxyl radicals (Stepnowski et al. 2002). The photons enhance photocatalytic degradation by causing favorable collusion chances between photons and activatable centers (Wang et al. 1999).

Understanding the roles of TiO_2 and ZnO in the removal of organic compounds by photocatalyst treatment and photocatalytic mechanism helps to determine the optimal dosages for them because they are used to produce the hydroxyl radicals necessary to oxidize organic matter. These types of reactions are activated by absorption of a photon with sufficient energy (equal or higher than the band-gap energy of the catalyst). The absorption leads to a charge separation due to a promotion of an electron (e^-) from the valence band of the semiconductor catalyst such as TiO_2 or ZnO to the conduction band. Thus, a hole (h^+) generates in the valence band (Eydivand & Nikazar 2015; Gaya & Abdullah 2008). Mostly, an increase in the removal efficiency is related to a rise in intensity of light due to a rise in the photon flux of electrons in the conduction band (Vohra & Tanaka, 2002).

The relevant reactions in the semiconductor surface (such as TiO_2) governing the degradation of pollutants can be expressed as follows (Equation (1-8)) (Eydivand & Nikazar 2015):

$$TiO_2 + hv(UV) \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$TiO_2(h^+_{VB}) + H_2O \rightarrow TiO_2 + H^+ + {}^{\cdot}OH \quad (2)$$

$$TiO_2(h^+_{VB}) + OH^- \rightarrow TiO_2 + {}^{\cdot}OH \quad (3)$$

$$TiO_2(e^-_{CB}) + O_2 \rightarrow TiO_2 + {}^{\cdot}O_2^- \quad (4)$$

$${}^{\cdot}O_2^- + H^+ \rightarrow HO_2^{\cdot} \quad (5)$$

$$M + {}^{\cdot}OH \rightarrow \text{degradation products} \quad (6)$$

$$M + h^+_{VB} \rightarrow \text{oxidation products} \quad (7)$$

$$M + e^-_{CB} \rightarrow \text{reduction products} \quad (8)$$

Where:

M is the molecule of pollutant
hv is the photon energy required to excite the semiconductor electron from the valence band (VB) region to the conduction band (CB) region.

Generally, an increase in degradation is associated with an increase in light intensity due to an increase in the photon flux of electrons in the conduction band (Vohra & Tanaka 2002). The natural solar radiation activate more electrons to jump to the conduction band from the valence band (Feroz et al. 2011). The success of the photo-Fenton treatment depends on the formation of hydroxyl radicals, which are successfully produced in the presence of both iron and H_2O_2. In Fenton process, hydrogen peroxide and iron are two major chemicals.

The mechanism of Fenton process has three major steps (Equations (9-12)) (Silva et al., 2015; Krutzler & Bauer, 1999):

1. Production of hydroxyl radicals ($^{\bullet}OH$).

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + {}^{\bullet}OH \quad (9)$$

2. Reproduction of Fe^{+2} ions by energy.

$$[Fe(OH)]^{+2} \xrightarrow{hv} Fe^{+2} + {}^{\bullet}OH \tag{10}$$

$$[Fe(COOCR)]^{+2} \xrightarrow{hv} Fe^{+2} + CO_2 + R^{\cdot} \tag{11}$$

3. 3. Degradation of the organic compounds by hydroxyl radicals ($^{\bullet}OH$).

$$^{\bullet}OH + RH \rightarrow \text{Oxidation products} \rightarrow CO_2 + H_2O \tag{12}$$

The complexity of intermediate compounds during the reaction and the high initial reaction rate made the study of Fenton process very difficult in industrial wastewater (Lucas & Peres, 2009).

COMPARISON FOR FENTON AND THE PHOTOCATALYTIC APPLICATIONS

Fenton, Photo-Fenton, and Fenton-Like Processes

The AOPs have the capability of rapid degradation of recalcitrant pollutants in the aquatic environment. They have shown high efficiency to remove the organic compounds from effluents even when they were present at low concentrations (Silva et al., 2015; Masomboon et al., 2010; Paz et al., 2013; Philippopoulos & Poulopoulos, 2003). Remediation of hazardous substances was attributed to hydroxyl radical, which exhibit reactivity toward organic (Hermosilla et al., 2009).

There are two Fenton reactions; the standard Fenton reaction between Fe^{+2} ions and hydrogen peroxide (H_2O_2) and the Fenton-like reaction between Fe^{+3} ions and hydrogen peroxide (H_2O_2) (Yeh et al., 2008). Fenton reaction under light such as sunlight or UV is the so-called photo-Fenton and more hydroxyl radicals (●OH) are generated (Torrades et al., 2004).

The organic materials in petroleum wastewater can be successfully removed by heterogeneous photocatalytic processes such as Fenton, photo-Fenton, and electro-Fenton. Due to their potential for destroying a wide range of organic chemical materials, these processes continue to receive attention.

Solar photo-Fenton is based on using solar radiation to increase production of hydroxyl radicals ($^{\cdot}OH$) and photoactive complexes through the Fenton (Amor et al., 2015; Fernandes et al., 2014; Lucas et al., 2012; Pignatello et al., 2006). Using solar energy in AOPs could reduce processing costs and make it more affordable for commercial use (Amor et al., 2015).

Several excellent reviews have been written on these processes (Akpan & Hameed, 2009; Diya'uddeen et al., 2011; Fujishima et al., 2008; Rajeshwar et al., 2008) in wastewater treatment particularly, Fenton, photo-Fenton, and electro-Fenton oxidation to remove the dissolved organic content of petroleum refinery sourwater. They showed that a combination of the Fenton and photo-Fenton processes was the oxidation method that led to the best results (Coelho et al., 2006), for example, (Tony et al., 2012) obtained 50% COD removal after using (H_2O_2/ Fe^{2+}/UV) method under pH 3 and H_2O_2/Fe^{2+} ratio 10. In a study performed by Silva et al. (2015), the highest oil removal achieved was 84% after 45 min of reaction by using 0.44 mM and 10 mM of ferrous ions and hydrogen peroxide, respectively. (Yavuz et al., 2010) showed that the most efficient method was the electro-Fenton process followed by the electrochemical oxidation using born doped diamond (BDD) anode while the electrocoagulation was found to be ineffective for the treatment of petroleum refinery wastewater (PRW). Ramteke and Gogate (2015) reported that using combined Fenton and ultrasound achieved 95% COD removal from petroleum wastewater at pH 3.

Dincer et al. (2008) evaluated the applications of the Fenton and photo-Fenton processes for the treatment of oil recovery industry wastewater. Under the most favorable conditions for the Fenton process (pH 3, Fe^{2+}: 23.16 g L^{-1} and H_2O_2: 200.52 g L^{-1}, a mass ratio of 8.658 for H_2O_2: Fe^{2+}), 86% of the initial COD was removed (from 21000 to 2980 mg L^{-1}) from the petroleum wastewater. In the photo-Fenton process, the optimal ratio H_2O_2/Fe^{2+} was 168 and the optimum operating conditions was 8400 mg L-1 H_2O_2, 50 mg L-1 Fe^{2+}, 39 ^{o}C, and pH 3. Under these conditions, the photo-Fenton process achieved a COD removal of 81%.

In another petroleum refinery effluent treatment study by Hasan et al. (2012), the maximal TOC and COD reduction achieved within 30 min of oxidation reaction were 70% and 98.1%, respectively using Fenton-like oxidation at optimized conditions of H_2O_2 dosage of 1008.0 mM, Fe^{2+} dosage of 686.0 mg, pH 3, a mass ratio of 5 for H_2O_2:Fe^{2+} dosage and a molar ratio of hydrogen peroxide to the organic wastewater [H_2O_2]:[PRE] of 12 while for Fenton oxidation, they reported petroleum refinery effluent treatment was low. Saber et al. (2014) reported that a COD removal of more than 83% was achieved under optimal conditions (pH 3, a mass ratio of 2.66 for H_2O_2: Fe^{2+} and ratio of 10.03 for H_2O_2/COD) within 90 min. Davarnejad et al. (2015) showed that maximum COD removal was around 82.55% at H_2O_2/PRW (Ratio of a mole of H_2O_2 per petroleum refinery wastewater volume) of 0.04, H_2O_2/Fe^{2+} molar ratio of 2.75, pH of 3.5 and reaction time of 90 min. Da Rocha et al. (2013) showed that the 53% COD removal was achieved by the solar photo-Fenton process from petroleum wastewater.

Parilti (2010) carried out the investigation on a treatment of a petrochemical industry wastewater by the solar photo-Fenton (Fe^{3+}/H_2O_2/solar) process using the box-Wilson experimental design method. The solar photo-Fenton (Fe^{3+}/H_2O_2/solar) process was applied to a petrochemical refinery wastewater in Izmir, Turkey. BOD to COD ratio obtained was 0.5 by them. About 49 percent degradation of the petrochemical industry wastewater was possible. Although the Fenton process has high degradation efficiency of COD and environmental friendliness, it is limited by the iron sludge, which needs final disposal (Pignatello et al., 2006) . In order to solve this issue, the Fenton process could be improved by the combined application of photocatalyst TiO_2.

The summary of the maximum percentage COD removal (%) and the optimum pH by photo-Fenton and Fenton-like applications to treat the petroleum wastewater reported by various researchers are shown in Figure 1 and Figure 2, respectively. In Fenton oxidation, organic pollutants are oxidized into CO_2 and water to avoid a problem of contaminants shifting from one phase to another. Also, the operation at room temperature and atmospheric pressure prevents volatilization and discharge of unreacted wastes. Rubio-Clemente et al. (2015) revealed that photo-Fenton processes were highlighted due to their fast and removal efficient for pollutants.

The following important points should be noted from the discussion in Table 2; According to several studies, treatment with Fenton and photo-Fenton appeared to be an appropriate method for oxidizing recalcitrant compounds from petroleum wastewater at acidic conditions. Use of the solar photo-Fenton in the case of commercial applications would be significantly cheaper and was also suitable to treat the petroleum wastewater. The majority of the studies reported that the optimal pH for the Fenton and photo-

Figure 1. Summary of the maximum percentage COD removal (%) by Fenton and Photo-Fenton process in the petroleum wastewater

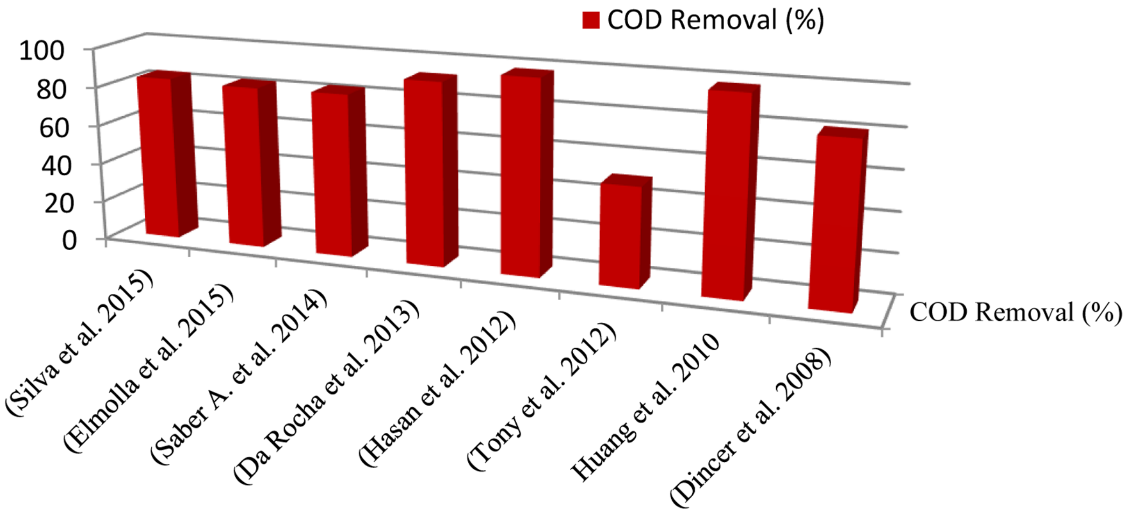
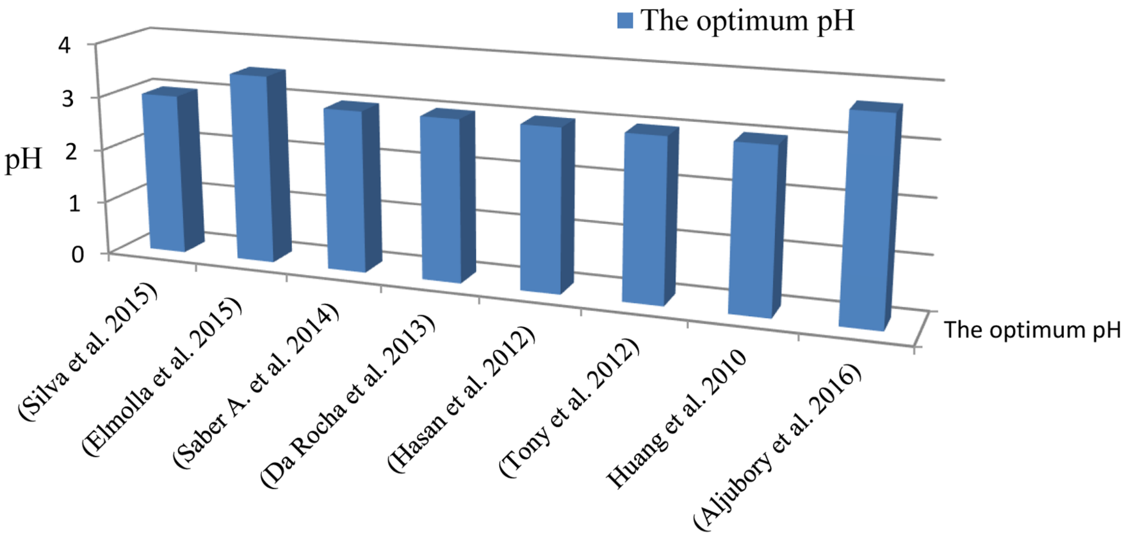


Figure 2. Summary of the optimum pH for Fenton and Photo-Fenton process in the petroleum wastewater



Fenton processes was strongly acidic conditions (pH 3). The oxidative ability of the photo-Fenton process was greater than that of the Fenton process to treat the petroleum wastewater in the studies. Many authors showed that the optimal mass ratio of Fenton's reagent (H_2O_2/Fe^{2+}) was from 2 to 10, but it sometimes was more than 200 due to the complex matrices of organic pollutants in petroleum wastewater. Most of the previous studies did not assess the effect of a long reaction time on a stability of these methods during the treatment. Some important sides of these processes required more study such as solar intensity quantification during the solar photo-Fenton.

Table 2. Summary of the treatment efficiencies of Fenton and Photo-Fenton process in the petroleum wastewater

	The process	**parameter**	**Max. Removal efficiency (%)**	**The optimum conditions**							**Ref.**
				pH	**H_2O_2**		**Fe^{2+}**		**H_2O_2/ Fe^{2+} ratio**	**Time reaction (min)**	
					ppm	**mM**	**ppm**	**mM**			
1	H_2O_2/Fe^{2+}/ UV	TOG	84	3	-	10	-	0.44	22.7	45	(Da Silva et al., 2015)
2	H_2O_2/Fe^{2+}	COD	82.7	3.5	800	-	267	-	3	150	(Elmolla, 2015)
3	H_2O_2/Fe^{2+}	COD	83	3	4510		1700	-	2.7	90	(Saber et al., 2014)
4	H_2O_2/Fe^{2+}/ solar	COD	92.7	3	-	485	0.93	-	521	420	(Da Rocha et al., 2013)
5	H_2O_2/Fe^{3+}	COD	98.1	3	-	1008	686	-	5	30	(Hasan et al. 2012)
		TOC	70								
6	H_2O_2/Fe^{2+}	COD	35	3	400		40	-	10	90	(Tony et al., 2012)
	H_2O_2/Fe^{2+}/ UV	COD	50								
7	H_2O_2/Fe^{3+}	COD	63	3	1080		5	-	216	60	(Huang et al., 2010)
	H_2O_2/Fe^{3+}/ UV		98								
8	H_2O_2/Fe^{2+}	COD	86	3	200		23		8.7	60	(Dincer et al. 2008)
	H_2O_2/Fe^{2+}/ UV		81	3	8400		50		168	210	
9	H_2O_2/Fe^{2+}/ solar	COD	78	3	1000	-	80	-	12.5	180	(Aljubory et al. 2017)
		TOC	64								

Photocatalyst of TiO_2/Fenton and ZnO/Fenton

Many technics enhanced the production rate of hydroxyl radical by chemical additives (H_2O_2), external energy (UV, sunlight), catalysts (TiO_2) and the integration of two or more AOPs such as (TiO_2/Fenton/ sunlight) and TiO_2 photocatalysis (UV)/Fenton (Kim et al., 2012). The photocatalyst of TiO_2 with Fenton was applied by several previous studies to enhance oxidation of contaminants. Tony et al. (2009) reported that a 71% and 84% COD removal were achieved at the natural pH by using Fenton/TiO_2/ UV and Fenton/TiO_2/UV/air, respectively to treat the diesel oil-water emulsion while only 18% COD removal under same conditions was observed by the using Fenton/ZnO/UV. This result was attributed to the surface area of TiO_2 was more than that for ZnO (Tony et al., 2009). Moreover, a recent study by Kim et al. (2012) obtained 78% benzoic acid removal at circum-neutral pH (6.5-7.5) by using the / TiO_2/Fe^{+3}/ H_2O_2/ UV system, which is very efficient in increasing production of reactive oxidants and improve the reactivity of the oxidant. However, the addition of Fe $^{+3}$ and H_2O_2 to the UV/TiO_2 system at higher pH values (pH>7) caused the negative effects. The same results were also observed in another study by Zarei et al. (2012), which they revealed that using the electro-Fenton /TiO_2 with Mn^{2+} under UV achieved about 70% phenol removal from aqueous solutions at 150 min under an acidic condition. They found that the pH and TiO_2 concentration were the main factors while Nogueira et al. (2004) showed that TiO_2 concentration was less important than the roles of iron and H_2O_2 in the photodegradation of 4-chlorophenol. Comparing this work with the previous works is summarized in Table 3.

SUMMARY OF ADVANCED OXIDATION PROCESSES (AOPS)

The objective of this study is to summarize investigations and studies and shows brief details of advanced oxidation processes (AOPs).

The big difference was shown in the specification of wastewater among the investigated studies and a wide variety of pollutants at varying concentrations. The most compounds in petroleum wastewater were the mixture of hydrocarbons and inorganic compounds. Advanced oxidation processes (AOPs) have the capability of rapid degradation of recalcitrant pollutants in the aquatic environment. However, the literature regarding petroleum wastewater treatment is very little and advanced oxidation processes (AOPs) are still not being used on an industrial scale in oil refineries. Most studies were focused on the degradation of some pollutants found in the petroleum wastewater such as sulphides, ammonia, phenols and organic materials.

Table 3. Summary of Fenton/TiO_2 application in the petroleum wastewater

	The method						**Wastewater type**	**Removal material**	**Ref.**
	TiO_2	*Zn***O**	Fe^{+2}	H_2O_2	*solar*	*UV*			
1	✓	■	✓	✓	✓		Milli-Q water	DNPH	(Kim et al. 2012)
2	✓	✓	■	■	■	✓	aqueous solutions	Phenol	(Anju et al. 2012)
3	✓	■	✓	✓	■	✓	aqueous solutions	Phenol	(Zarei et al. 2012)
4	■	✓	✓	✓	■	✓	oil-water emulsion	COD	(Tony et al. 2009)
	✓	■	✓	✓	■	✓			
5	✓	■	✓	✓	■	✓	dye polluted water	Azo dye	(Bouras & Lianos 2008)
6	✓	■	✓	✓	✓		aqueous medium	4CP	(Nogueira et al. 2004)
								DCA	
								TOC	
7	✓	■	■	■	✓		aqueous imidacloprid	Imidacloprid	(Malato et al. 2001)
	■	■	✓	✓	✓				
8	✓	■	✓	✓	✓		Pesticide wastewater	Chloropyrif	(Alalm & Tawfik 2013)
								COD	
9	✓	■	✓	✓	✓		Petroleum wastewater	COD	(Aljubory et al. 2015a)
								TOC	
								RI	
	✓	✓	✓	✓	✓		Petroleum wastewater	COD	(Aljubory et al. 2015b)
								TOC	
								RI	

This study focused on works that investigated advanced oxidation processes (AOPs) by monitoring general petroleum wastewater parameters such as TOC, COD, BOD, oil, and phenols. It presented an overview of photocatalytic degradation of pollutants in petroleum wastewater and highlighted the basics of these processes including the optimum parameters.

Comparison Based on pH

This parameter has a significant effect on removal the organic compounds (Alhakimi et al., 2003). The pH of petroleum wastewater effects on the surface of TiO_2 and forms three different species namely TiOH, $TiOH_2^+$ and TiO^- to account for variations in the behavior of the catalyst with pH (Yang et al., 2007).

In an acidic condition, the TiOH and $TiOH_2^+$ are the predominant species with a positively charged catalyst surface in the petroleum wastewater because the isoelectric point of TiO_2 varieties between pH 4 and 6 due to the surface of the catalyst has various ionization states and influence the amount of adsorption of the substrate on the catalyst surface (Akpan & Hameed, 2009; Li et al., 2006; Silva et al., 2007; Yang et al., 2007).

Higher degradation was obtained under acidic conditions due to strong adsorption from electrostatic attraction, for example, Topare et al. (2015) showed that the maximum reduction in chemical oxygen demand (COD) of 60% from petroleum industry wastewater was observed in acidic medium at pH 3, 50 ºC and 1 g L^{-1} catalyst concentration by employing heterogeneous photocatalytic of TiO_2 process. An acidic medium can also favor organic degradation as shown by the degradation of acid brown 14 (Shahrezaei et al., 2012). Shahrezaei et al., (2012) reported that a maximum reduction in COD of more than 83% was achieved from petroleum refinery wastewater by using a batch circulating photocatalytic reactor in aqueous catalyst suspensions of titanium dioxide (TiO_2) at the acidic conditions (pH 4). The hydroxyl radicals (●OH) are abundant in wastewater at high and neutral pH while positive holes are the predominant oxidation species at low pH (Akpan & Hameed, 2009). The surface under alkaline conditions becomes negatively charged. Thus, resulting in repulsion between the organic compounds and catalyst and reducing the removal efficiency due to decrease the adsorption rate (Li et al., 2006). The organic compounds can be better degraded by various pH values, for example, (Habibi & Vosooghian, 2005) indicated that methyl benzimidazole sulphide degradation was favored by a neutral pH while methyl phenyl sulphide was better degraded at an alkaline condition.

Pera-Titu et al. (2004) explained that pH was an important parameter for the Fenton process because pH of the solution controlled the production of the hydroxyl radical and the concentration of ferrous ions. (Chu et al., 2012) found that the oxidation potential of hydroxyl radicals decreased with increasing pH. Removal of COD and phenol compounds depended on the initial solution pH. (Oliveira et al., 2014) revealed the H^+ in excess reacts with the H_2O_2 producing $H_3O_2^+$, which was stable and does not react with the Fe^{2+}, and thus there was a decreased formation of hydroxyl radicals. Furthermore, the hydroxyl radicals could be consumed by parallel reactions in the presence of an excess of H^+. (Chu et al., 2012) found that at pH below 3, degradation efficiency decreased. The degradation was much slower under an initial pH of 2.0. At very low pH values, iron complex species $[Fe(H_2O)_6]^{2+}$ exist, which reacts more slowly with hydrogen peroxide than other species (Pera-Titus et al., 2004).

At initial pH values (4.0-5.0), the activity of Fenton reagent was reduced due to the presence of relatively inactive iron oxyhydroxides and formation of ferric hydroxide precipitated (Rubio-Clemente et al., 2015). The degradation was also slower, which was due to the formation of iron species capable of inhibiting the reaction between Fe^{2+} and H_2O_2. In addition, (Oliveira et al., 2014) indicated the stability of H_2O_2 was lower at high pH values.

(Tekin et al., 2006) showed that pH did not seem to affect the treatment efficiency as long as it was equal to or greater than 7. Therefore, the pH was adjusted to7 before Fenton's coagulation. In this situation, fewer hydroxyl radicals were generated due to the presence of fewer free iron ions. (Chu et al., 2012) found that at natural pH 9.1, almost no removal of phenol and COD was observed.

Comparison Based on Dosage of Catalyst

The photocatalytic efficiency of organic degradation increased with the increase of the amount of TiO_2 (Laoufi et al., 2008). This rise in the percentage of organic degradation may be explained by increasing the total active surface area with increasing catalyst dosage and resulted in increasing the number of hydroxyl radicals and superoxide radicals. A linear relationship exists between the initial rates of reaction and the dosages of the catalyst regardless of the catalyst conformation in photocatalytic removal (Das et al., 2013). The higher catalyst activity occurs under high light incident intensity because the photons are present in excessive amounts leading to more reactive species generation and more destruction of organic compounds (Laoufi et al., 2008; Wang et al., 1999; Stepnowski et al, 2002).

Normally, the removal efficiency rapidly increases with a rise in catalyst dosage because greater catalyst dosages result in a rise of the number of active sites existing for adsorption (Akpan & Hameed, 2009; Twesme et al., 2006; Jain & Shrivastava, 2008). However, there were no significant changes beyond a certain concentration of catalyst of TiO_2 and would not result in any change in the efficiency of degradation (Alhakimi et al., 2003; Laoufi et al., 2008). A reverse effect occurs when the TiO_2 concentration increases to higher than the optimum value, the degradation rate declines due to the interference of the light by the suspension (Chakrabarti & Dutta, 2004; Ehrampoosh et al., 2011). It may be due to the scattering of the light and reduction in light penetration through the effluent due to the obstruction of a large number of solid particles (Das et al., 2013; Gaya & Abdullah, 2008; Singh et al., 2013; Chan et al., 2003). This, in turn, results in a reduction of the available active sites. Many researchers have detected a decline in organic degradation efficiency with a rise in catalyst dosage beyond a certain limit (Kabir et al., 2006; Wang et al., 1999). Optimal catalyst concentration was obtained at 100 mg L^{-1} by using by using the photocatalyst of TiO_2 for removing aliphatic and aromatic organic pollutants in refinery wastewater (Saien & Nejati, 2007). A similar observation was made by (Shahrezaei et al., 2012), who reported that, at the optimum catalyst concentration of 100 mg L^{-1}, a maximum reduction in COD of more than 83% was achieved from petroleum refinery wastewater by using the photocatalyst of TiO_2 while the percentage removal of COD reaches a maximum for a catalyst loading of 1000 mg L^{-1} by (Das et al., 2013).

Comparison Based on Fenton Reagent Dosages

The concentration of hydroxyl radicals depends on the absolute amounts of H_2O_2 and Fe^{2+} in the photo-Fenton process. Rodrigues et al., (2009) reported that the rate of degradation increased with an increase in the concentration of the ferrous ion. Higher dosages of H_2O_2 and Fe^{2+} resulted in decreased COD removal. This was explained considering that the hydroxyl radical may be scavenged by the reaction with excess Fe^{2+} and H_2O_2. Moreover, an enormous increase in the ferrous ions led to an increase in the unutilized quantity of iron salts, which contributed to an increase of the total dissolved solids content of the effluent stream, and this was not permitted (Kang & Hwang, 2000; Kitis et al., 1999). Thus, laboratory scale studies are required to establish the optimum loading of ferrous ions to remove the organic compounds. The concentration of hydrogen peroxide plays a crucial role in deciding the efficiency of the photo-Fenton process. Usually, it is observed that the percentage degradation of the pollutant increase with an increase in the dosage of hydrogen peroxide (Kang & Hwang, 2000). However, the previous studies did not recommend the excess amount of hydrogen peroxide. Moreover, the presence of hydrogen peroxide is harmful to many of the organisms, and it affects significantly the overall degradation efficiency (Chu et al., 2012).

Chu et al. (2012) reported that hydrogen peroxide was the scavenging of generated hydroxyl radicals after the optimum H_2O_2 dosage. Thus, the dosage of hydrogen peroxide should be utilized completely in reactions. In addition, (Ertugay & Acar, 2013) indicated that the COD removal increased to 50.7% as the H_2O_2 dosage increased to 125 mg L^{-1}. However, removal efficiency would decrease when H_2O_2 dosage was higher than 125 mg L^{-1}. Martins et al. (2010) explained that the iron load had the highest impact on TOC removal of the Phenolic wastewater after using Fenton process. The TOC removal increased as the Fe^{2+} concentration increased due to increase the production rate of the hydroxyl radicals, which led to a higher effluent mineralization level. Nevertheless, an excess of iron could have a radical scavenger effect. Oliveira et al. (2014) indicated that the Fe^{2+} was responsible for speeding up the formation of hydroxyl radicals. The degradation was slower in the experiments using lower iron concentrations due to the insufficient amount of catalyst for the same amount of oxidant. Martí et al. (2003) explained that the success of the Fenton treatment depended on the formation of hydroxyl radicals, which were successfully produced in the presence of both iron and H_2O_2. In Fenton process, hydrogen peroxide and iron are two major chemicals that determine the operation costs and efficacy. In order to maximize the effectiveness of the process, it was important to determine the optimal operational H_2O_2/Fe^{2+} molar ratio.

Understanding the roles of H_2O_2 and iron in the removal of organic compounds by Fenton process helps to determine the optimal reagent dosages. H_2O_2 and iron are used to produce the hydroxyl radicals necessary to oxidize organic substances according to the following reaction (Equation 13) (Martí et al., 2003):

$$\text{Hydroxyl radicals } (\bullet OH) + \text{organic substances} \rightarrow \text{Oxidation Products} \tag{13}$$

Consequently, particular attention must be paid to Fe^{2+} and H_2O_2 dosages in order to avoid the undesired hydroxyl radicals scavenging reactions occurring in the presence of an excess of each two reagents. Martí et al. (2003) reported that any addition in H_2O_2/Fe^{2+} molar ratio over the optimal Fenton ratio decreased the removal efficiency.

It seems that excessive hydrogen peroxide has a scavenging effect on hydroxyl radicals (Equation 14):

$$H_2O_2 + \bullet OH \rightarrow HO^{\bullet}_2 + H_2O \tag{14}$$

This reaction leads to the production of hydroperoxyl radical, which has weaker oxidizing power compared to hydroxyl radical (Martí et al. 2003). (Ertugay & Acar, 2013; Martí et al., 2003) explained that the excess amount of hydrogen peroxide could cause the autodecomposition of H_2O_2 to oxygen and water, and the recombination of hydroxyl radicals. Thereby decreasing the concentration of hydroxyl radicals reduced the pollutant removal efficiency (Ertugay & Acar, 2013).

On the other hand, when Fenton ratio was below the optimal Fenton ratio, COD removal was decreased because of the scavenging effect of excess Fe^{2+} (Cristóvão et al., 2014). It seemed that when a large amount of Fe^{2+} was available, Fe^{2+} and organic compounds compete to react with hydroxyl radicals. Thus, Fe^{2+} consumed hydroxyl radical resulting in reduced COD removal efficiency (Cristóvão et al., 2014).

Dosages of Fenton reagents reported for Fenton process to treat the petroleum wastewater were very different. For example, (Tony et al., 2012) obtained 50% COD removal after using photo-Fenton process under the optimal H_2O_2/Fe^{2+} ratio 10 whereas Silva et al. (2015) indicated that the favorable H_2O_2 to Fe^{2+} molar ratio was 22.7. The large discrepancies in reported optimal ratios of H_2O_2 to Fe^{2+} were attributed to variations in the petroleum wastewater characteristics. For very high H_2O_2/Fe^{2+} values (150-268), the process was not efficient due to excess H_2O_2 which led to the scavenging of radicals (Oliveira et al., 2014).

Comparison Based on the Initial COD Concentrations

It is found that the efficiency degradation of COD is greatly influenced with increasing the initial concentration of COD of the effluent because of the formation of hydroxyl radicals in water (Das et al., 2013). A similar trend was observed when photon absorption was increased by decreasing the initial concentration of furfural solution ($C_5H_4O_2$), which led to higher catalyst activation with a subsequent improvement of photocatalytic degradation (Faramarzpour et al., 2009). At higher concentrations of contaminants, the clashes between the catalyst and organic contaminants are great. Thus, the higher concentrations of contaminants can improve photodegradation (Li et al., 2006).

However, the percentage removal of COD decreases as the initial concentration of COD increases after a certain value. A current study by Paschoalino et al. (2012) revealed that the reason for this phenomenon is likely due to the decrease in the formation of hydroxyl radicals on the catalyst surface with the increase in pollutants concentration. At the same time, the active sites decrease when the adsorbed pollutants on the catalyst surface increase because of coverage of active sites by reaction intermediate, which inhibits the direct contact between pollutants and hydroxyl radicals (Li et al., 2006; Paschoalino et al., 2012).

Comparison Based on Reaction Time

The hydroxyl radicals ($\cdot OH$) can degrade organic pollutants to intermediates, and the intermediates are further degraded to CO_2 and H_2O (Shahrezaei et al., 2012). Thus, a required duration to complete the photo-Fenton process should be observed. According to (Karthikeyan et al., 2011), the percentage removal of COD increased linearly up to 4 h and was followed by a non-linear increase up to 50% in 6 h. The initial linear increased in COD reduction may be attributed to the chemical oxidation of the dissolved organics in the wastewater with hydroxyl radical. Thereafter, the reaction rate diminished as the hydrogen peroxide was consumed, which was the primary source for the generation of the hydroxyl radicals.

CONCLUSION

In the chapter, the trend and performance of different chemical applications for petroleum wastewater treatment were evaluated. The effectiveness and applicability of the recent and different updated processes were introduced and compared mainly based on organic removals. In general, the variations in treatment efficiency can be attributed to the different types of petroleum wastewater. Some types of petroleum wastewater with high organic content may require combination treatment process with Fenton to enhance their treatability. Accordingly, Fenton, Photo-Fenton and Fenton-like, Photocatalyst of TiO_2/Fenton and ZnO/Fenton applied to improve the treatment efficiency. AOPs were recently used (Fenton, Photo-Fenton and Fenton-like, Photocatalyst of TiO_2/Fenton and ZnO/Fenton) to improve the oxidation potential and to reduce the reaction time consumed when applying a combination treatment process. AOPs are an efficient method in treating petroleum wastewater.

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Chapter 6

Applications of Advanced Oxidation Processes in Palm Oil Mill Effluent Treatment

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ABSTRACT

This chapter presents a review on limited studies that have been conducted using advanced oxidation processes (AOPs) in treating biologically treated palm oil mill effluent. Palm oil mill effluent is the by-products of palm oil production that is normally treated using a series of biological processes. However, despite being treated for a long period of retention time, the effluent still possesses high concentration of organics, nutrients, and highly colored, and will pollute the environment if not treated further. Advanced oxidation processes that utilized hydroxyl radicals as their oxidizing agents have the potential of further treating the biologically treated POME. Fenton oxidation, photocatalysis, and cavitation are the main AOPs that have been studied in polishing the biologically treated POME. Depending on the experimental conditions, the removal of organics, in terms of COD, TOC, and color, could reach up to more than 90%. Nevertheless, each of this process has its own limitations and further studies are needed to overcome these limitations.

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INTRODUCTION

Palm oil is a major industry in Southeast Asia and its production is increasing rapidly with the growth of plantation areas across the countries including Malaysia, Indonesia and Thailand (Aris et al., 2008). In 2014, 62.34 million tonnes of palm oil were traded globally with Malaysia producing 20 million tonnes of them (Ng and Cheng, 2015). The trend of palm oil production in Malaysia is also increasing; the exports of palm oil, palm kernel oil and other relating products have increased to 16.2 million tonnes in 2016 (Din, 2017). This can also be witnessed by the increase in oil palm plantation area from 320 ha in 1970 to 5.74 million ha in 2015 (Din, 2017; Rupani et al., 2010). Additionally, the number of mills has grown from 10 in 1960 to 407 in 2008 (Wu et al., 2010) and 453 in 2016 (Din, 2017).

Unfortunately, the expansion of the oil palm industry comes with its environmental cost. The current extraction process of palm oil includes wet process and dry process. The wet process, which is used in Malaysia requires a large volume of water (Wu *et al.,* 2009). It is estimated that the production of one-tonne crude palm oil utilises 5 to 7.5 tonnes of water (Rupani *et al.,* 2010). Consequently, more than 50% of the water becomes palm oil mill effluent (POME). It has been estimated that the quantity of POME generated annually in Malaysia is almost 2.2 x 10^7 m^3. With such amount, the wastewater will pollute the environment if adequate treatment is not provided.

CHARACTERISTICS OF PALM OIL MILL EFFLUENT

The characteristics of raw POME are dependent on several factors such as harvesting period, raw material quality (FFB) in terms of age and type, extent of the milling process, activities being conducted at the respective mill, processing technique, the discharge limit set by the factory as well as climate or weather (Irenosen *et al.,* 2014). Besides, the wastewater quality may differ according to batch, day and mills (Madaki & Seng, 2013).

Fresh POME is usually a viscous brownish colloidal mixture of water, oil and fine cellulosic fruit residue (Mat Rani, 2014) with unpleasant odour (Azuar *et al.,* 2015; Irenosen *et al.,* 2014). Some physicochemical properties of raw POME are shown in Table 1. Generally, raw POME is high in temperature, organics, solids, oil and grease as well as nutrients. The high temperature of POME, ranging from 80 – 90 °C is mainly due to the use of large amounts of steam and hot water in sterilization process. The pH for raw POME is slightly acidic in nature because of the organic acids content in complex forms (Madaki & Seng, 2013).

An important characteristics of raw POME is that it has a high concentration of organics. This is due to the fact that POME has a high amount of protein, carbohydrate, nitrogenous compounds, lipids and minerals which partly contributed to organic contents of the wastewater (Rupani *et al.,* 2010). Additionally, the high organic matters in POME is also contributed by the presence of different sugars such as arabinose, xylose, glucose, mannose and galactose (Ujang *et al* 2010). The solids in raw POME mainly come from oil-bearing cellulosic materials of the oil palm fruit (Ujang *et al.,* 2010). A variety of suspended components ranging from cell walls, organelles, short fibres, a spectrum of carbohydrates and nitrogenous compounds, free organic acids as well as mineral constituents also can be found in POME (Kanu & Achi, 2011).

Table 1. Characteristics of raw POME determined in previous studies

Parameters	Vijayaraghavan et al. (2007)	Salim et al. (2008, 2010)	Ibrahim et al. (2012)	Wang et al. (2015)	Jusoh (2017)
Temp. (°C)	83 - 85	-	54	80-90	-
pH	3.4 - 3.6	4.59 - 5.01	5.32	4.2	4.7 ± 0.15
Biochemical Oxygen Demand (BOD5)	25,545	26,200 - 27,800	10,197	25,000	88,783 ± 18,142
Chemical Oxygen Demand (COD)	55,775	64,200 - 65,800	50,500	51,000	144,078 ± 29,754
Total Organic Carbon (TOC)	-	11,730 - 12,870	-	-	11442 ± 1,377
Total Solid (TS)	-	-	31,533	-	-
Total Suspended Solids (TSS)	18,479	34,800 - 35,200	4,007	18,000	21,880 ± 5,159
Oil and Grease (O&G)	8,020	1,300 - 1,900	15,800	6,000	11,508 ± 1,910
Ammonia-N (NH3-N)	36	52 - 72	-	35	342 ± 38
Phosphorus	-	123 - 161	-	-	428 ± 43

Notes: All parameters are in mg/L except for pH

POME TREATMENT SYSTEM

Similar to other agricultural based wastewaters, POME comprised of biodegradable materials with COD/BOD$_5$ ratio of about 2. Hence, biological methods have been commonly used for the treatment of POME. Due to POME high strength characteristics, anaerobic digestion process is normally used at the initial stage, followed by aerobic process.

Anaerobic System

Different types of anaerobic system have been developed to treat POME. These include anaerobic suspended growth processes (Chin & Wong, 1983; Cail & Bafford, 1985a; Cail & Bafford, 1985b), attached growth anaerobic processes (Borja & Banks, 1995; Vijayaraghavan & Ahmad, 2006), anaerobic sludge blanket processes (Borja et al., 1996; Zhang et al., 2008), membrane separation anaerobic treatment processes and hybrid anaerobic treatment processes (Najafpour et al., 2006; Zinatizadeh et al., 2007).

Chin and Wong (1983) have reported thermophilic anaerobic digestion with higher BOD and COD values of 28,200 mg/L and 67,400 mg/L, respectively. The BOD and COD of the supernatant was decreased to 250 mg/L and 970 mg/L, respectively, within 35 days. The thermophilic condition was also studied by Borja and Banks (1993) using semi-continuous anaerobic digester. The system achieved COD removal of 85% of 65,000 mg/L. The study was conducted at 15.1 g COD/L of organic loading rate (OLR) and four days of retention time. The semi-continuous anaerobic digestion was previously studied by Cail and Barford (1985a) under mesophilic condition. It obtained 75% removal of 70,000 mg/L of COD value within six days of HRT and at OLR of 12.6 g COD/L day. Wong *et al.* (2013) has also studied the mesophilic condition using acidogenic suspended closed anaerobic bioreactor (SCABR). It was reported that COD removal decreased from 87.08% to 38.2% with the reduction of HRT from 12 to 2 days; however, OLR values have increased from 6.67 to 38.29 g COD/L day.

Poh and Chong (2014) have reported on thermophilic condition using upflow anaerobic sludge blanket-hollow centred packed bed (UASB-HCPB). COD and BOD removal of 90% were achieved within two days of HRT and at OLR of 27.65 g COD/L day; lower OLR can cause unstable characteristics of effluent. Another study conducted using immobilised cell bioreactor anaerobic digestion was by Borja and Banks (1994) reported COD removal of 96.2% after six days of retention time at 10.6 g COD/L day of OLR. A study was carried out using an up-flow anaerobic sludge fixed film (UASFF) bioreactor by Zinatizadeh et al. (2006) reported 90% of COD removal attained in two days of retention time with the loading rate of 23.15 g COD/L day.

Borja and Banks (1995) have investigated the degradation of POME by comparing the efficiency between anaerobic filter (AF) and anaerobic fluidised bed reactor (FBR). Both processes, which had a HRT of six hours and OLR of 40 g COD/L day for FBR manage to remove 78% of COD. However, the AF was only capable to work up to OLR of 20 g COD/L day; higher OLR would lead to clogging of the media. Borja et al. (1996) used a two-stage up-flow anaerobic sludge blanket (UASB) system containing acidogenic UASB reactor and methanogenic UASB reactor. These reactors were attached to a pair of up-flow anaerobic reactors in a two-stage treatment. It was found that the methanogenic reactor can acclimatise more rapidly as compared to acidogenic reactor due; 90% of COD removal was gained from the methanogenic reactor at maximum OLR of 30 g COD/L day. Singh *et al.* (2013) has also carried out a study on immobilized UASB bioreactor using Clostridium LS2. COD removal of 66% was attained from initial COD of 30 g /L after 12 hr of retention time.

An up-flow anaerobic contact filter was used on POME with the presence of microflora isolated from cow dung (Vijayaraghavan & Ahmad, 2006). The maximum COD removal of 73% was acquired from initial COD of 20,000 mg/L. The pH was identified to increase the COD removal; as the COD removal decreased at lower pH. It could be due to metabolic reaction affected by shifting in the intermediate production pathway from acid production phase to solvent production phase (Byung & Zeikus, 1985; Khanal et al., 2004). Yacob *et al.* (2006) studied a start-up operation using a semi-commercial closed anaerobic digester. They used the digester to create microbial population from seed sludge belonging to the same type of waste, which helps to improve the acclimatising process. It removed 95% of COD removal at 17 days as compared to 81% of COD removal using conventional open digester within 20 days of retention time.

A field-scale pilot bioreactor was studied in a combination of an anaerobic hybrid reactor (AHR) with an anaerobic baffled filter (ABF) (Shin *et al.,* 2014). The treated wastewater has stable characteristics when OLR is reduced from 7 to 6 g COD/L day which have removed 70% of COD removal at 40 days. However, Choi *et al.* (2013) reported better COD removal of 93.5% as an anaerobic downflow filter (ADF) was added to AHR and ABF with OLR of 8.5 – 23 g COD/L day and HRT ranging from 0.7 to 2.4 days. AHR was performed under mesophilic and thermophilic conditions achieved 90 – 95% of COD removal at 15 g COD/L day of OLR (Jeong *et al.,* 2014). They found that the thermophilic condition has better COD removal of 93 – 95% as compared to 90 – 93% in the mesophilic. Wang *et al.* (2015) have performed a study using pilot-scale anaerobic expanded granular sludge bed (EGSB) reactor reported 83% of COD removal achieved in 10 days of HRT at 6.45 g COD/L day of OLR. Teng *et al.* (2013) attained 83.1% of COD removal after 40 days of HRT at OLR of 1.34 – 1.37 g COD/L day using anaerobic bench scale reactor (ABSR).

Aerobic System

Aerobic digestion is a system that can be operated efficiently for POME at a shorter hydraulic retention times (HRT) (Wu *et al.,* 2010). Various treatment of aerobic digestion for POME has been reported. These include pressurized activated sludge process (Ho and Tan, 1988), aerobic treatment with 5% inoculums of Trichoderma viride (T. viride) spores and mycelium (Karim and Kamil, 1989), aerobic treatment with single culture and mixed culture (Bhumibhamon *et al.,* 2002), aerobic treatment using Yarrowia lipolytica (Oswal *et al.,* 2002), rotating biological contactor (RBC) with Saccharomyces cerevisiae (Najafpour *et al.,* 2005) and activated sludge reactor (Vijayaraghavan *et al.,* 2007).

Ho and Tan (1988) treated secondary treatment of anaerobically digested POME liquor using a pressurised activated sludge process. The study was conducted to obtain a high rate oxygen transfer at elevated pressure in the reactor. The results of BOD, COD, total solids, suspended solids and oil (and grease) reduction were 98.4%, 97.7%, 87.5%, 99.2% and 93.3%, respectively. These reductions were achieved at the ratio of organics to mixed liquor suspended solids (MLSS) ranging from 0.4 to 0.7 kg BOD/ kg MLSS per day.

Trichoderma viride was initially reported by Church *et al.* (1973) in the aerated lagoon and the oxidation ditch to treat corn and pea canning wastes. T. viride removed 95% of COD with short HRT as compared to anaerobic digestion. These findings were continued by Karim and Kamil (1989) on POME and resulted with 95% of COD removal after 10 to 14 days of fermentation. It was found that T. viride could grow well and compete against the indigenous flora in the raw POME with recovered crude protein content and a yield of the mycelium of 37.6 - 40.7% and 1.37 – 1.42 g/l (dry weight), respectively.

The treatment of oil and grease in POME has been carried out using single culture bacteria and mixed culture bacteria (Bhumibhamon *et al.,* 2002). It was found that the single culture removed 80.6 – 87.7% and 90 – 96% of oil (and grease) and COD, respectively in 48 hours. It was concluded that the single cultures of Acinetobacter sp., Bacillus sp., and Pseudomonas sp., were more beneficial for POME degradation than mixed culture.

Oswal *et al.* (2002) studied the ability of tropical marine yeast of Yarrowia lipolytica NCIM 3589 to degrade POME. Previously, the yeast was studied by Zinjarde and Pant (2000) to degrade alkanes in crude oil. Removal of 95% COD within as short as two days of retention time was reported. Almost 99% of COD removal was achieved when POME was sequentially treated with a flocculant and a consortium developed from garden soil (Oswal *et al.,* 2002). The continuous bench scale of RBC was used with Saccharomyces cerevisiae and POME as an initial biomass loading and by fixing biofilm (Najafpour *et al.,* 2005). The treatment showed high removal of COD of 88%, suspended solids of 89% and total Kjeldahl nitrogen (TKN) of 80% due to high biomass retained in RBC. The disc biomass played a major role in the organic biodegradation and could tolerate high organic loadings and hydraulic shock. The study was conducted at the lowest volumetric flow rate of 1.1 l/h of POME and 55 hours of HRT.

Vijayaraghavan et al. (2007) used an activated sludge process for the treatment of anaerobically digested POME and diluted raw POME. The activated sludge process was observed to oxidise anaerobically digested POME better than diluted raw POME. The experiment ends up with the higher removal of 98% COD, 93% oil (and grease) at 60 hours of HRT. It is due to the presence of partially degraded organic and oil molecules which are more amenable to aerobic digestion.

Ponding Treatment System

The most commonly treatment method employed in Malaysia is the ponding system covering more than 85% (Rupani *et al.,* 2010; Bello & Abdul Rahman, 2017). The ponding system comprised of cooling, anaerobic, facultative, and aerobic or algae ponds, arranged in series. Each of this pond has its specific purpose in the treatment and is determined by the capacity of the palm oil mill, the amount of effluent discharges, company policy as well as the availability of the suitable land (Salihu & Alam, 2012). A typical layout of the ponding system is shown in Figure 1 and a brief explanation of the ponds' function is given in Table 2.

Anaerobic treatment is usually applied as a pre-treatment before facultative and aerobic digestion. The anaerobic pond has the longest retention times in ponding system of about 20 to 200 days (Bala *et al.,* 2014). During anaerobic digestion, the organic and inorganic matters are degraded into simpler end products such as methane (CH_4) and carbon dioxide (CO_2). Other than anaerobic digestion, organics and solids concentration in raw POME is also reduced through sedimentation process. As a result, the organics strength of POME has been significantly reduced producing fermented POME that is more amenable to aerobic treatment (Chan *et al.,* 2010).

The applications of anaerobic digestion alone would not be sufficient to treat the wastewater. Hence, further treatment in the facultative pond is necessary for a period of about 20 days. Aerobic pond has been applied as a complement treatment for partially digested POME for over the past 20 years in Malaysia (Abdurahman *et al.,* 2013). The partially digested organics in POME are more amenable to aerobic digestion as compared to diluted POME (Vijayaraghavan *et al.,* 2007). Aerobic treatment also offers some advantages as compared to chemical and physical treatment such as low operational cost, application of environmental friendly microbes, no involvement chemicals and no secondary pollution (Chan *et al.*, 2009). The aerobic condition in the aerobic pond is achieved by the use of mechanical surface aerators.

In some ponding systems, algae pond is used in addition to the aerobic pond. In algae pond, algal species will take up phosphates, carbon dioxide and nitrogen compounds such as ammonia and nitrates for algal biomass production hence, removing these contaminants from POME. At the same time, algae supply the oxygen needed by heterotrophic bacteria for organic materials biodegradation.

Figure 1. Typical layout of ponding system commonly used in Malaysia

Table 2. Function of ponds in the ponding system

Pond Type	Function
Cooling pond	To reduce the temperature of the wastewater
Anaerobic pond	To treat the high strength wastewater (preliminary treatment)
Facultative pond	To further reduce the strength of the wastewater
Aerobic pond	To further polish the wastewater

An investigation by Ma and Ong (1985) reported that ponding system is able to remove more than 99% of BOD in raw POME. Their work has shown that the composition of biodegradable organic materials in raw POME are significantly removed from initial concentrations of 30,000 mg/L to only 100 mg/L through the application of ponding system. In a more recent study, Jusoh (2017) also reported BOD and COD removals up to 99% and 97%, respectively, in the anaerobic pond. After passing through a series of ponds, the final BOD and COD were reduced to average values of 261 mg/L and 1800 mg/L. Nevertheless, despite the high percentage of removal in the pond system, the level of organics in the treated wastewater is still high and poses threat to the receiving water body. Color remains as one of the challenges in treating POME. The effluent remains colored even after being treated. The color has been attributed to the presence of tannin-lignin, phenolics, carotene and suspended solids that originate from the fruit bunch (Schmidt *et al.,* 2015; Rungpichayapichet *et al.,* 2015; Bello et al., 2013; Burin *et al.,* 2010; Bhatia et al., 2007). Tannin-lignin in POME contributes to the brown and yellow color and has a musty smell (Mohammed and Chong, 2014).

POME Tertiary Treatment

Despite being treated by a series of biological process the treated effluent is still high in organic and inorganic matters and requires further treatment. Hence, tertiary treatment that is positioned at the end of the conventional treatment processes is required. Table 3 provides the characteristics of the treated POME from several studies. As depicted, the characteristics vary according to plants and even vary within the plant itself. Despite the relatively low BOD_5 value, the COD values were much higher. The high COD/BOD ratio indicate the non-biodegradable nature of the effluent, which limits the application of biological process as the tertiary treatment. The nutrient contents and color are still high, which will significantly affect the receiving water body. Most of the data collected indicate values that are greater that the allowable limit set the Department of Environment, Malaysia.

Table 3. Profile of performance of a POME ponding treatment system

Parameter	Raw POME (Jusoh, 2017)	(Jusoh, 2017)	(Siew, 2006)	(Omar, 2008)	(Aqilah et al., 2013)	(Shahrifun et al., 2015)	Allowable limit[a]
pH	4.7±0.15	8.0±0.23	8.1	8.6	9.0	8.0	5.0-9.0
BOD_5 (mg/L)	108817±14492	261±27	160	N/A	160	260	100[b]
COD (mg/L)	165071±8266	1798±180	1854	579	1600	3511	1000[c]
TOC (mg/L)	17208±2073	716±58	N/A	179	N/A	N/A	-
TSS (mg/L)	24463±22969	6220±4029	1138	70	14,787	1745	400
VSS (mg/L)	21597±19512	4353±2449	N/A	N/A	N/A	N/A	-
TP (mg/L)	597±64	147±14	N/A	N/A	N/A	N/A	-
TN (mg/L)	4400±1262	169±21	N/A	N/A	N/A	N/A	200[d]
AN (mg/L)	421±62	94±13	N/A	N/A	N/A	N/A	150[d]
O&G (mg/L)	14647±1839	1255±473	N/A	N/A	N/A	N/A	50
Colour (ADMI)	14130±955	3960±332	N/A	547	N/A	N/A	-

[a] Environmental Quality (Prescribed Premises) (Crude Palm Oil) (Ammendment) Regulations 1982 (P.U.(A) 183/82)

[b] BOD_3 (mg/L)

[c] Values for the period of 1-7-1981 to 30-6-1982. No new value stipulated since then

[d] Filtered sample

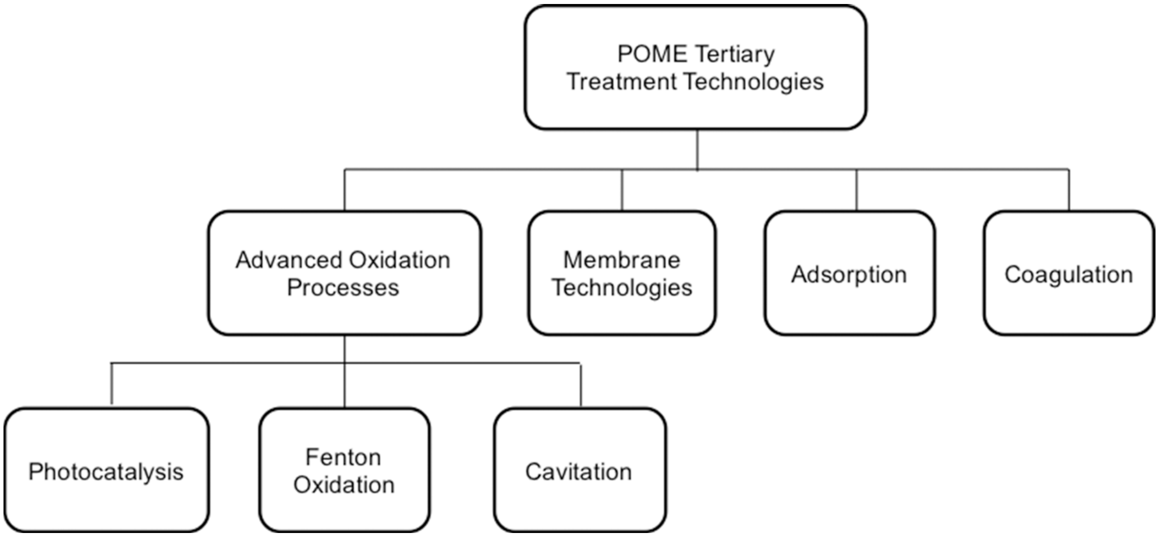
Tertiary Treatment Technologies

Different treatment technologies have been studied for tertiary treatment of POME. These include membrane filtration, coagulation, adsorption, and AOPs. Figure 2 illustrates the common tertiary treatment technologies applied for POME.

Application of membrane technology in treating POME has been investigated for many years (Wu *et al.,* 2007). The technology was implemented on recycling and reuse of wastewater (Idris *et al.,* 2010). Idris *et al.* (2010) have used ultrafiltration (UF) membrane system for treatment of biologically treated POME. The experiment was conducted by varying the effects of transmembrane pressure and using different molecular weight cut-off (MWCO). It showed that the degradation of biologically treated POME increased with the reduction of transmembrane pressure from 1.5 to 0.5 bar. The removal of 64% of COD, 84% of colour and 66% of turbidity was obtained at 0.5 bar of transmembrane pressure. The results of this study were in contrast with the results obtained by Wu *et al.* (2007), which explained that the removal of COD, colour and turbidity were increased with the increase in the transmembrane pressure. Biologically treated POME contained high amounts of protein, which have the potential for membrane fouling (Li *et al.,* 2006; Bowen and Gan, 1991), delayed widespread application of membrane processes (Ahmad *et al.,* 2005) and reduction in permeate flux (Idris *et al.,* 2010). These factors have increased the operational cost which includes membrane cleaning cost, process downtime and replacement cost of the membrane (Maartens *et al.,* 2002).

Facta *et al.* (2010) conducted an experiment with additional treatment of silent discharge ozoniser for colour removal using a high-frequency resonant power converter. The colour of POME decrease from 100 mg/L Pt.Co to 20 mg/L Pt.Co when 800 mg/L of ozone was injected within five minutes. POME treatment also has been conducted using membrane bioreactor (MBR) with considerable removal of organic components; however, the POME remained coloured (Yuniarto *et al.,* 2008; Ahmad *et al.,* 2005).

Figure 2. Treatment technologies for POME
(Bello & Abdul Raman, 2017)



Jusoh (2017) and Ahmad *et al.* (2008) found that carotenes had been the cause of colour in POME. It is a component of POME (0.019%) which contributes to colour pollution.

Mohammed and Fong (2014) explored the potential of applying natural, chemically and thermally modified banana peel as biosorbent for the treatment of biologically treated POME. Three types of adsorbent were tested namely natural banana peel (NBP), methylated banana peel (MBP), and banana peel activated carbon (BPAC). The performance of the adsorbents was based on COD, color and TSS removal. The effects of biosorbent dosage, contact time and initial pH were investigated. As expected, the increase in the dosage enhanced the removal performance due to the greater availability of the adsorption surface area. However, beyond certain dosage, the effect was no longer significant. Increase of contact time also increase the removal performance until equilibrium adsorption was reached. Based on the studied biosorbents, the optimum condition was found at contact time of 24 h, dosage of 30 g/100 ml, and pH of 2. The BPAC was found to be the best biosorbent as compared to NBP and MBP. The maximum removal of color, TSS, COD, BOD, and tannin and lignin using BPAC obtained at pH of 2, contact time of 30 h and adsorbent dosage of 30 g/100 ml were 96.0%, 100%, 100%, 97.4%, and 76.7%, respectively.

The use of coagulation process for the treatment of POME has been reported by many researchers. Different types of coagulants have been tested, which include polyaluminium chloride (PAC) (Poh et al., 2014; Ahmad et al. 2006), chitosan (Ahmad et al., 2006), alum (Ahmad et al., 2006), natural seeds such as *Moringa oleifera* seeds (Bhatia et al., 2007) and *Cassia obtusifolia* seeds (Shak and Wu, 2015). Poh at al. (2014) applied PAC coagulant to reduce the strength of anaerobically digested POME after micro-bubble floatation. Optimum coagulant dosage was observed to be 2 g/L. Although the larger particles were removed by micro-bubble floatation while the smaller particles were removed by the coagulation, significant removal of the pollutants were achieved after the coagulation process. The treated effluent could meet the standards. The combination of micro-bubble and PAC coagulation managed to achieve COD and TSS removal of 93.3% and 99.9%, respectively. Ahmad et al. (2006) compared the performance of chitosan, alum and PAC in removing 2000 mg/L residual oil and 10,000 mg/L suspended solids from POME. Using 0.5 g/L of chitosan, the coagulation-sedimentation process was able to achieve more than 95% removal of both pollutants within 45 minutes. Alum and PAC required 8.0 and 6.0 g/L, respectively to achieve the same removal performance and at a longer time of about 90 minutes. Hence, chitosan was proven to be more efficient and economical in treating the POME.

Advanced oxidation processes have been used in treating different types of contaminants and wastewaters. As for POME, they have been applied mainly as polishing or tertiary treatment. Studies on AOPs application in POME treatment are currently limited to Fenton oxidation, photo-catalysis and cavitation (Bello and Abdul Raman, 2017).

POME Tertiary Treatment using Advanced Oxidation Processes

While many processes merely transfer the contaminants from one phase to another, chemical oxidation offers an alternative for complete destruction of the contaminants or transforming them into simple and less hazardous by-products. Of the oxidants commonly used in water and wastewater treatment, Advanced Oxidation Processes (AOPs) provide an attractive option with the use of hydroxyl radicals ($HO^\bullet$), a very reactive species as the oxidizing agent. Although the idea of AOPs has been in existence since the mid 20th century, active research efforts in this field has only taken place in the last 20 years (Aieta *et al.*, 1988).

As mentioned earlier, AOPs are a category of chemical oxidation processes which produce and utilise $HO^{\bullet}$ as their key oxidant (Aieta *et al*., 1988; Legrini *et al*., 1993). As shown in Table 4, $HO^{\bullet}$ is the second most reactive common oxidising agent known to mankind after fluorine. The typical rate constants for reaction between $HO^{\bullet}$ and organic or inorganic materials are in the order of 10^6 to 10^9 $M^{-1}s^{-1}$ (Farataziz & Ross, 1977). These rates, as shown in Table 5, are about 10^9 times higher than its closest competitor, ozone (O_3) (Andreozzi *et al.*, 1999).

Reaction mechanisms of $HO^{\bullet}$ with various materials consist of a series of chain reactions that continue and finally lead to carbon dioxide, water and inorganic salts. They can be classified into four types, namely hydrogen abstraction, electrophilic addition, electron transfer, and radical-radical reactions. These have been discussed in detail by Legrini *et al.* (1993).

There are several techniques that can be used to generate $HO^{\bullet}$. Generally, the techniques comprise of a reaction between an oxidant with at least a co-oxidant or a catalyst. More recently, $HO^{\bullet}$ has also been generated using cavitation techniques (Jusoh *et al*., 2017; Dular *et al.*, 2016). They can be broadly classified into two main categories, i.e. homogeneous and heterogeneous, depending on the number of phases involved in the reactions. Advanced Oxidation Processes have also been categorised as photochemical degradation (O_3/UV, H_2O_2/UV), photocatalysis (TiO_2/UV, photo-Fenton) and chemical oxidation processes (O_3, O_3/H_2O_2, Fenton) (Chiron *et al*., 2000). Alternatively, they can also be grouped based on the main oxidant used in the process. A list of the AOPs found commonly in the literature is given in Table 6.

Fenton oxidation

Fenton oxidation (FO) (also termed as Fenton Reagent) generates $HO^{\bullet}$ through the reaction between ferrous (Fe^{2+}) and hydrogen peroxide (H_2O_2) under acidic condition (Bello and Raman, 2017) as in Eq.

Table 4. Oxidation potentials of several oxidising agents (Legrini et al., 1993)

Species	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

Table 5. Second order rate constants for ozone and $HO^\bullet$ for several compounds (Andreozzi et al., 1999)

Organic compound	Rate constant (M^{-1} s^{-1})	
	Ozone, O_3	Hydroxyl radical, $HO^\bullet$
Benzene	2	7.8×10^9
Toluene	14	7.8×10^9
Chlorobenzene	0.75	4×10^9
Trichloroethylene	17	4×10^9
Tetrachloroethylene	< 0.1	1.7×10^9
n-Butanol	0.6	4.6×10^9
t-Butanol	0.03	0.4×10^9

(1). In this first stage, the reaction between Fe^{2+} and H_2O_2 occurs rapidly ($k = 41.7 - 79\ M^{-1}s^{-1}$: Sychev and Isak, 1995), which produces large amount of $HO^\bullet$ and Fe^{3+}, which rapidly decomposes the pollutants.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^\bullet + OH^- \qquad (1)$$

As soon as the initial Fe^{2+} is consumed and transformed into Fe^{3+}, the chain reactions are propagated by the subsequent Fenton-like reaction (Eqn. 2) which forms the second stage of the FO system. This latter reaction generates $HO_2^\bullet$ and regenerates the Fe^{2+} ion for further reaction. However, since the Fenton-like reaction is a slower process ($k = 9.1 \times 10^{-7}\ M^{-1}s^{-1}$: Sychev and Isak, 1995) and $HO_2^\bullet$ is a less reactive species as compared to $HO^\bullet$, the degradation process in the second stage tends to be much slower. When the FO process is initiated by the Fenton-like reaction, the reactions proceed slower from the start. However, as more Fe^{3+} is converted to Fe^{2+}, the reactions become faster and the extent of the overall degradation is similar to that initiated with the Fenton reaction.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \qquad (2)$$

In addition to oxidation mechanism, the FO system is also capable of removing pollutants via coagulation (Kuo, 1992; Lin and Lo, 1997). As shown by Eqns. 3 to 7, ferric ions generated in Fenton oxidation may form hydroxo-complexes with OH^- and may polymerise at pH between 3.5 and 7 causing coagulation.

Table 6. List of commonly reported Advanced Oxidation Processes

Reaction phase	Main oxidant	Processes
Homogeneous	O_3	O_3/high pH; O_3/H_2O_2; O_3/UV; O_3/H_2O_2/UV
	H_2O_2	H_2O_2/UV; H_2O_2/Fe^{2+}; H_2O_2/Fe^{3+}; H_2O_2/Fe^{2+}/UV; H_2O_2/Fe^{3+}/UV; H_2O_2/Fe^{3+}-oxalate
Heterogeneous	O_3	O_3/solid catalyst
	H_2O_2	H_2O_2/iron oxide
	None	UV/TiO_2; UV/TiO_2/O_2; UV/TiO_2/H_2O_2; UV/metal oxides, cavitation

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5\, OH]^{2+} + H_3O^+ \quad (3)$$

$$[Fe(H_2O)_5\, OH]^{2+} + H_2O \leftrightarrow [Fe(H_2O)_4\, (OH)_2]^+ + H_3O^+ \quad (4)$$

$$2[Fe(H_2O)_5\, OH]^{2+} \leftrightarrow [Fe_2\, (H_2O)_8\, (OH)_2]^{4+} + 2H_2O \quad (5)$$

$$[Fe_2\, (H_2O)_8\, (OH)_2]^{4+} + H_2O \leftrightarrow [Fe_2\, (H_2O)_7\, (OH)_3]^{3+} + H_3O^+ \quad (6)$$

$$[Fe_2\, (H_2O)_7\, (OH)_3]^{3+} + [Fe(H_2O)_5\, OH]^{2+} \leftrightarrow [Fe_3\, (H_2O)_5\, (OH)_4]^{5+} + H_2O \quad (7)$$

In a real situation, the precipitation of iron is a required step in the FO process. The added iron needs to be removed from the treated wastewater before the wastewater can be released from the treatment plant. This provides an additional removal mechanism that partly compensates for inefficiency of the oxidation process but at the same time generates sludge which needs further treatment and disposal.

In the presence of organic substrate (RH), the primary product of the oxidation would be the organic radical, $R^\bullet$, which possesses mainly reducing properties and may be consumed through the reactions with H_2O_2, Fe^{3+}, and O_2.

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \quad (8)$$

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet \quad (9)$$

$$R^\bullet + Fe^{3+} \rightarrow \text{Product} + H^+ + Fe^{2+} \quad (10)$$

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \quad (11)$$

The application of Fenton oxidation as tertiary treatment is an attractive option as the high strength biodegradable compounds have significantly been degraded by the preliminary and secondary treatment systems. The target of POME polishing treatment is mainly to remove the residual COD, colour and nutrients.

Aris *et al.* (2008) have studied the removal of COD and colour of a biologically treated POME using two types of Fenton's oxidation, namely, ambient-Fenton and solar-Fenton. For ambient Fenton study, the experiments were conducted in the laboratory under ambient light, while the experiments for solar-Fenton were conducted in an open space directly under sunlight irradiation. The experiments were designed using Central Composite Design (CCD) with the aid of MINITAB™ (ver. 13.32) statistical software. The H_2O_2 dosage was ranged from 800 mg/L to 1500 mg/L, while Fe^{2+} ranged from 50 mg/L to 400 mg/L. The reactions were carried out at the initial pH of 3 and was set to 7 after an hour of oxidation. After settling of 30 minutes, the samples were analyzed for COD and color. The initial COD and color before treatment was 1854 mg/L and 1138 Pt-Co, respectively. The removal of COD for ambient Fenton ranged from 6.5% to 75% while the removal for solar-Fenton ranged from 16.0% to 82.4%. The color removal for ambient Fenton and solar-Fenton ranged from 56.3% to 92.4% and 60% to 95.1%, respectively. Such variation in the results is expected to be caused by the dosage of Fe^{2+} and H_2O_2 used in the study. Color appears to have higher removal percentage as compared to COD. Highest removal of COD and color were 82.4%, and 95.1%, respectively, achieved by solar-Fenton which indicate the viability of the process in treating the biologically treated POME.

Similar results were recently observed by Saeed *et al.* (2016) using Fenton oxidation. They treated biologically treated POME under optimum condition of pH 3.5 for 90 min achieved 85% of COD removal. Previously, Saeed *et al.* (2015) optimize the operating parameters for Fenton process in post-treatment of POME using CCD statistical approach. Reagents dosage, initial pH and reaction time were found to significantly affect the removal performance. With initial COD of 2800 mg/L and color of 2260 Pt.Co. respectively, they achieved 84.5% and 91.1% of COD and colour removal, respectively, using homogeneous Fenton oxidation under the optimum conditions of 4.57 g/L H_2O_2, 1.88 g/L Fe^{2+}, pH of 2.9 and 30 min of reaction time. All those mentioned studies show the same trend for higher colour removal efficiency than COD removal efficiency could possibly be due to the degradation of the colour causing pollutants (Aris *et al.,* 2008).

Kee (2007) investigated the mechanisms in solar-Fenton oxidation that are involved in treating biologically treated POME. About 85% and 95% of TOC and color, respectively were removed after 60 minutes of solar-Fenton reaction (pH 3) followed by coagulation (pH 7) and sedimentation. Within 15 minutes of reaction, the results showed that solar-Fenton oxidation was responsible for more than 87.6% of total TOC removed, while another 12.4% was caused by the coagulation-sedimentation process. As the reaction was prolonged to 60 minutes, more organics were oxidized leaving only about 4% being removed via coagulation-sedimentation. Contribution of color removal by coagulation-sedimentation process was more significant as compared to TOC removal. This is partly due to color contributed by the presence of iron added in the treatment process; precipitation of ferric hydroxides or other iron complexes significantly lowered the colour of the solution. Further treatment of the wastewater using sand filtration reduce the TOC and color up to 92.2% and 97.1%, respectively.

An aerated heterogeneous Fenton oxidation using nano zero valent iron (NZVI) was applied on a diluted anaerobically treated POME by Taha and Ibrahim (2014). The study was carried out using Box-Behnken Design and Response Surface Method. The dosages of NZVI and H_2O_2 ranged from 1.2 to 3.7 g/L and from 0.60 to 2.30 g/L respectively; the aeration rate tested was between 0 to 50 l/h with reaction time ranging from 30 to 240 minutes. Using initial pH of 2.0, they obtained highest COD removal of 75% at optimum conditions. They also observed that the concentration of tannic acid, which is responsible for the POME color, was reduced by 40% after the pH was adjusted to 2.

The enhancement of Fenton-NZVI using ultrasound has been reported by Taha et al. (2014). The effect of pH was crucial for the generation of Fe^{2+} from NZVI. Significant production of Fe^{2+} was only observed at pH 2, apparently took place after the removal of iron oxides layer on the surface of NZVI. The shockwave and cavitation created by ultrasound radiation enhanced the collisions of NZVI particles and thus, improved the production of Fe^{2+} and the reaction process. The intensity and exposure duration also affect the performance of the system. The combination of higher intensity and longer sonication time in Fenton process accelerate the COD removal of POME. Through the process, 80% of COD content was removed within 2 hours instead of 24 hours of silent degradation.

The modification of conventional Fenton was explored by Aqilah *et al.* (2013) for POME polishing at different combination of UV, Ferrioxalate/H_2O_2, TiO_2 and O_3. The biologically treated POME had a COD and BOD of 1600 mg/L and 160 mg/L, respectively. As the pH of the reactions were not adjusted but maintained at about 9, the removal of COD by Fenton-based oxidation was quite low, in the range of 31% to 49%. The application of photo Ferrioxalate was the best with color removal of 64%. The low performance is expected as Fenton-based reactions require optimum pH between 3 to 3.5. Two steps treatment of UV/Ferrioxalate/TiO_2 followed by UV/O_3 for two hours and three hours, respectively, attained complete COD and colour removals. These combinations provide the best performance but consumed much more time in the process as compared to common technique of Fenton oxidation.

Parthasarathy *et al.* (2016a) have combined Fenton oxidation and physico-chemical treatment as a polishing technology for POME. In this case, they used chitosan coagulation in four set of experiments including coagulation using chitosan, chitosan plus $FeSO_4$, chitosan coupled with H_2O_2 and chitosan with Fenton. Chitosan (2500 mg/L) and Fenton (Fe^{2+} of 2500 mg/L and H_2O_2 of 500 mg/L) managed to remove 73% of COD, while chitosan with H_2O_2 is the most promising alternative for POME treatment could possibly be attributed by the neutral pH or the interaction between iron and chitosan leading to the reduction of the active sites of the iron.

Photocatalysis

The use of metal oxide semiconductor in the presence of UV light, termed as photocatalysis, has gained wide attention for the degradation of refractory organics since its initial study in the mid' 70s (Pelizzetti *et al*., 1990; Legrini *et al*., 1993). Many catalysts have been tested, but TiO_2 in either the hybrid mixture of rutile (approx. 70%) and anatase form or pure anatase form seem to be the best catalyst for various pollutants in term of efficiency, stability, and cost (Tanaka *et al.,* 1989; Gogate and Pandit, 2004; Ganiyu *et al.,* 2015). It is capable of absorbing UV light up to about 400 nm wavelength for the initiation of the photocatalytic process (Goslich *et al*., 1997).

Pelizzetti and Minero (1993) provided a detailed discussion on the mechanism of the TiO_2 photocatalysis process. The photocatalytic process is initiated by the absorption of UV radiation by the semiconductor. With the photons' energy, at least equal to the energy of the semiconductors band gap, electrons are promoted from the valence band to the conduction band forming electron-hole pairs (Eqn. 12). The electrons reduce the dissolved oxygen (if present) forming superoxide radical ions, $O_2^{\bullet-}$, whereas the remaining holes are capable of oxidising adsorbed H_2O or OH^- to reactive $HO^\bullet$ (Eqns. 13 to 15). Unfortunately, when not enough electron acceptors are available in water, considerable numbers of electron-hole pairs recombine, thus reducing the efficiency of the process.

$$TiO_2 + hv \rightarrow TiO_2\,(e^- + h^+) \tag{12}$$

$$TiO_2\,(h^+) + OH^-_{ad} \rightarrow TiO_2 + HO^\bullet_{ad} \tag{13}$$

$$TiO_2\,(h^+) + H_2O_{\,ad} \rightarrow TiO_2 + HO^\bullet_{ad} + H^+ \tag{14}$$

$$TiO_2\,(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \quad (15)$$

The concentration, surface area and the nature of the catalyst play an important role in deciding the overall rates of degradation (Goslich *et al.,* 1997; Gogate & Pandit, 2004). Additionally, characteristics of the wastewater, pH, temperature, O_2 concentration and presence of H_2O_2 have significant effects on the efficiency of the photocatalytic process (Tanaka *et al*, 1989; Bakar and Aris, 2000).

The applications of photocatalysis as tertiary treatment of POME have been carried out by several researchers. Tan *et al.* (2014) have investigated the effect of TiO_2 loading, ranging from 1 to 10 wt%, on the degradation of biologically treated POME. They reported that increase of TiO_2 loading from 1 - 5 wt% significantly remove the COD, TOC and color. However, further increase of TiO_2 reduce the performance, mainly attributed to the increase in turbidity that reduce the penetration of the light. A maximum removal of about 43%, 63% and 70% of COD, TOC, and colour, respectively was achieved at the optimum condition. Ng and Cheng (2015) have investigated on UV-responsive TiO_2 photocatalyst in removing COD and BOD in biologically treated POME. The optimum catalyst loading was found as the degradation rate increased when the catalyst loading increases from 0.1 to 1.0 g/L and decreases beyond that due to shielding effect of the UV light. The organic pollutants achieved 52% degradation under optimum condition of 1.0 g/L TiO_2 and 70 mL/min O_2.

Ng *et al.* (2016) have investigated the chemical composition of silver-modified titania (Ag/TiO_2) to degrade POME under visible light irradiation. They obtained COD removal of 26.8% after 480 min of irradiation at 1.5 g/L of optimum catalyst loading; beyond that the degradation efficiency decreased due to light scattering and aggregation of the photocatalyst particles. Although doping was intentionally used to enhance the TiO_2 performance under visible light, the performance is considerably less than under UV irradiation. This finding agrees with that found by Cheng *et al.* (2016). The photocatalyst activity was studied by Cheng *et al.* (2015) comparing Pt/TiO_2 photocatalyst under UV and visible irradiation for polishing of the biologically treated POME. While 90% and 11% conversion were observed for UV and visible light, respectively, further investigation is needed for establish the effectiveness of Pt/TiO_2 in photocatalytic oxidation of biologically treated POME.

Ng and Cheng (2016a) have conducted a study using UV-responsive ZnO as catalyst for biologically treated POME polishing. They attained 50% COD removal at 1.0 g/L of optimum catalyst loading irradiated for 240 min. They found that as UV exposures prolonged to 22 hr, the COD removal can be enhanced further. Ng *et al.* (2017) recently proven that TiO_2 is still better photocatalyst compared to ZnO for the photocatalytic polishing of POME. More than 80% degradation of the organic pollutants was achieved by TiO_2 as compared to 74% by ZnO after 22 hr of UV irradiation. The difference in their photocatalytic activity can be explained by higher stability of TiO_2 without deterioration activity even after three consecutive cycles, whilst 30% of ZnO was lost in only 1st-cycle of photoreaction.

Ng and Cheng (2016b) also investigated the factors that affect the UV/titania system. Using Response Surface Method, namely Central Composite Design, three main factors that were identified according to their significance level are oxygen loading, POME initial concentration, and titania loading. The interaction effect between oxygen loading and POME initial concentration was also observed. Under optimum conditions, COD removal of about 53% was obtained.

Cavitation

Cavitation as defined by Suslick *et al.* (1997) and Gogate and Pandit (2004) is a process of formation, growth and implosive collapse of cavities in liquids at a slight interval of time releasing a large magnitude of energy. The condition to form the cavitation is when the vapour pressure of the liquid is increased higher than the pressure of the liquid at the current temperature. The collapsing cavities created the hot spots, which increase the temperature, pressure and velocity of fluid up to 727 °C, 2000 atm and 100 - 300 m/s, respectively (Pang *et al*., 2011). There are several advantages of cavitation technique as discussed by Suslick *et al*. (1997) and Arrojo *et al*. (2007). These include generation of hot spots, release of highly reactive free radicals, continuous cleaning as well as increase in the surface area of the solid catalysts, enhancement in the mass transfer rates due to turbulence generated as the outcome of acoustic streaming, does not require any chemical addition and lower energy consumption as compared to other AOPs (Arrojo *et al*., 2007).

The cavitation can be formed using four different techniques, namely, optic cavitation, particle cavitation, acoustic cavitation (AC) and hydrodynamic cavitation (HC) (Gogate, 2010; 2002; Walt, 2002). Optic cavitation is produced using photons of high-intensity light (laser) rupturing the liquid continuum (Ramirez-San-Juan *et al*., 2010; Alehossein and Qin 2007). The cavitation process can be explained by the formation of photons from the nonlinear absorption and/or avalanche ionisation due to the focusing of a laser beam to the liquids. The laser attributed to an increase in the temperatures and pressures as the absorption coefficient of photons is high and resulted in rapid vaporisation of liquid producing acoustic shock waves. Particle cavitation is form from any other type of elementary particles. The generate cavitation leads to form a void and changes in the stress state in the surrounding epoxy matrix which give rise to increased plastic deformation and plastic hole growth (Guild *et al.*, 2010; Gogate, 2002). AC in simple terms is the phenomenon of growth and collapse of cavities under an ultrasonic field (Yusof *et al*., 2016; Ashokkumar, 2011). The cavitation is formed from the passage of ultrasound through a liquid medium causing mechanical vibration and acoustic streaming within the fluid. In HC, cavitation is generated when the liquid passed through a constriction such as an orifice plate or a venturi tube. The constriction employed in the cavitation chamber provides pressure variation in the fluid, which resulted in the pressure of the liquid to fall below its threshold pressure (vapour pressure) (Gogate, 2008). However, only AC and HC offer better possibility in bringing desired chemical changes in wastewater treatment practice (Gogate & Pandit, 2004). Optic cavitation and particle cavitation fail to induce chemical changes in bulk solution as both techniques are typically used for a single-bubble cavitation. The following discussions will therefore focus only on AC and HC.

Ultrasound (US) cavitation integrated with activated carbon (AC) was studied by Parthasarathy *et al.* (2016b) for intense POME polishing. The study was carried out using biologically treated POME with COD and TSS in the range of 4700±550 mg/L and 1800±282 mg/L, respectively. Using AC alone, complete removal of COD and color was achieved at AC dosage of 200 g/L and contact time of 6 hours. With US alone, 50% amplitude and 90 min cavitation time managed to achieve maximum COD removal of about 79.5% and TSS removal of 95.8%. The combination of both that was carried out for 15 min at 50% US power amplitude followed by 30 min of AC adsorption at 50 g/L dosage achieved nearly 100% of COD removal and 83.3% of TSS removal. The lower dosage and the shorter contact time of AC could be the reason for the low TSS removal as compared to the COD removal.

Jusoh (2017) investigate the performance of HC for the polishing of POME using multiple configurations and arrangements of orifice plate. Based on iodine liberation, the HC plate configuration and arrangement were found to have significant effects on the generation of the $HO^{\bullet}$. Single, double and triple plates arrangement were tested and the highest was generated by the double-plate arrangement. Furthermore, the $HO^{\bullet}$ generation was also affected by the type of plate used as well as the distance between those plates. The HC performance under the effect of pH, H_2O_2 dosing and aeration had significantly increased the iodine liberation as compared to HC alone. The cavitation formation released more $HO^{\bullet}$, measured based on the iodine liberation, which was higher in acidic pH. The addition of H_2O_2 was also observed to affect the HC performance. The iodine liberation increased up to the optimum H_2O_2 dosage of 100 mg/L, beyond which the liberated iodine decreased. Not much improvement on iodine liberation was observed while using aeration. The optimized system was then investigated to treat the biologically treated POME. However, the treatment performance of 20 litres of the wastewater recirculated at optimum pump capacity of 45 psi was not encouraging. Colour was only removed up to 14.7%, while COD removal fluctuated with some runs having COD value higher than the initial one. The increase in COD concentration was found under the effect of pH. The addition of H_2O_2 and aeration was found to have significant effect in

Table 7. Summary of AOPs application for POME tertiary treatment

Process	Conditions	Removal	Reference
Fenton	H_2O_2: 1150 mg/L; Fe^{2+}: 200 mg/L pH: 3; t = 60 min; COD_i: 1095 mg/L; $Color_i$: 1800 ADMI; TOC: 430 mg/L	TOC: 85% Color: 95%	Kee (2007)
	H_2O_2: 800 - 1500 mg/L Fe^{2+}: 50 - 400 mg/L pH: 3; t = 60 min; COD_i: 1854 mg/L $Color_i$: 1138 Pt-Co	COD: Fenton: 75% Solar-Fenton: 82.4% Color: Fenton: 92.4% Solar-Fenton: 95.1%	Aris *et al.* (2008)
	H_2O_2: 4.57 g/L; Fe^{2+}: 1.88 g/L pH: 2.9; t: 30 min; COD_i: 2800 mg/L $Color_i$: 2260 Pt-Co	COD: 84.5% Color: 91.1%	Saeed *et al.* (2015)
Heterogeneous Fenton	H_2O_2: 0.6 - 2.3 g/L; NZVI: 1.2 - 3.7 g/L; pH: 2 Aeration: 0 - 50 L/h; t = 30 - 240 min COD_i: 4568 mg/L	COD: 75%	Taha and Ibrahim (2014)
Photo-Fenton/O_3	Fe^{3+}: 8 g/L; H_2O_2: 16 g/L; Oxalate: 16g/L; TiO_2: 200 mg; pH: 9; t: 5 hr; COD_i: 1600 mg/L; BOD_i: 160 mg/L	Complete removal of COD and color	Aqilah *et al.* (2013)
Fenton + coagulation	Fe^{2+}: 2500 mg/L; H_2O_2: 500 mg/L; chitosan: 2500 mg/L	COD: 73%	Parthasarathy *et al.* (2016a)
Photocatalysis	TiO_2: 1 - 10%; t: 4 hr	COD: 43%; TOC: 63%; color: 70%	Tan *et al.* (2014)
	TiO_2: 1 g/L; 70 mL/min O_2; t: 4 hr	COD: 52%	Ng and Cheng (2015)
	TiO_2: 1.5 g/L; t: 8 hr	COD: 26.8%	Ng *et al.* (2016)
	ZnO: 1g/L; t: 4 hr	COD: 50%	Ng and Cheng (2016a)
Ultrasound + activated carbon	Power amplitude: 50%; AC: 50 g/L; t: 45 min; COD_i: 4700 mg/L	COD: almost 100%	Parthasarathy *et al.* (2016b)
Hydrodynamic cavitation	H_2O_2: 100 mg/L; Pressure: 45 psi	Color: 14.7	Jusoh (2017)

removing the COD. The colour removal is significantly affected by pH and H_2O_2 but not by aeration. The reaction of $HO^\bullet$ with the organic constituents in biologically treated POME may cause the increase in tannin/lignin and phenolic concentration as well as fluctuation in carotene removal. The strong correlation was found between tannin/lignin and phenolics as both compounds can be formed through their reaction pathway. The degradation of biologically treated POME, particularly phenolics and tannin/lignin was found to form catechol and ρ-benzoquinone as by-products.

CONCLUSION AND THE WAY FORWARD

As Malaysian palm oil industry is moving forward to fulfil the global demand, the production of palm oil gets higher and more wastewater generated during the palm oil processing are being discharged. Furthermore, the performance of the commonly used treatment system, i.e. open ponding system, has apparently failed to meet the regulations. Even those that fulfil the regulations are still high in non-biodegradable organic constituents, nutrients and color and pollute the receiving water. Apparently, the environmental issues with regards to POME issue is still unsolved. The quality of the receiving waters has been deteriorating by the discharge of the incomplete treated POME. As the regulations are expected to become more stringent, more efforts are needed to identify a technical and cost effective method to address the issue.

Applications AOPs to treat the wastewater have been reported but apparently limited to Fenton oxidation, photo-catalysis and cavitation (Table 7). The AOPs, particularly Fenton related processes have shown promising results; however, their applications are limited to lab- and pilot-scale study. Generation of sludge, extreme pH requirement, long reaction time, stability of the system, cost effectiveness and capability to integrate with the existing treatment technologies remains as issues for AOPs. Furthermore, the high volume of POME to be treated remains as the major constraint of the processes as it reflects to the cost of the chemicals, adsorbents and finally the operational cost of the system. Hence, more studies are still needed to overcome these challenges.

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Chapter 7

Concentrated Landfill Leachate Treatment by Electro-Ozonation

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ABSTRACT

Municipal solid waste has continued to be a major problem in many nations of the world. The primary methods of treating landfill leachate include physical-chemical and biological treatment processes. Pressure-driven membrane processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO), are among the utmost promising and capable ways for treating landfill leachate. The concentrated leachate created from pressure-driven membrane processes typically represents 13%–30% of total incoming landfill leachate. Concentrated leachate is a dark brown solution with high levels of pollutants. Treating concentrated leachate is extremely difficult, and thus, a combined treatment system is suggested. In the present study, concentrated landfill leachate was treated using a combined treatment technique that included electro-ozonation. The removal efficacies of chemical oxygen demand (COD), color, and nickel were monitored at original pH (7.3) as well as current and voltage of 4 A and 9 V, respectively.

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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). A sanitary landfill is assessed based on environmental risk evaluation; planned size; designed cell advance; extensive site preparation; full leachate management; daily and final cover; full gas management; compaction; fence and gate; maintained record of waste volume, type, and resource; and absence of scavenging and trading. A main component of isolation is the management and treatment of leachates (Liermann, 2009). Sanitary landfills are the prevalent way of solid waste disposal. This method has benefits; however, their main drawback is leachate production that should be managed well.

Leachates are generated when moisture mixes with refuse in a landfill; pollutants are dissolved into the liquid phase, after which they accumulate and then percolate. Leachates vary from one landfill to another in the short- and long-terms periods because of variations in climate, hydrogeology, and waste composition. Improvements in landfill engineering are intended to reduce leachate production and collection, as well as improve treatment prior to discharge (Visvanathan et al., 2000).

The primary methods of landfill leachate treatments include physical–chemical and biological treatment processes. In general, combinations of physical, chemical, and biological techniques are applied because of the difficulty in obtaining satisfactory results by a single method (Aziz, 2011).

Biological treatment methods are including anaerobic and aerobic methods. Some of the most and popular physical/chemical methods are membrane filtration, ozonation, adsorption and electrochemical treatments. Goals of current chapter are (1) trends on electrochemical oxidation methods, ozonation methods and concentrated landfill leachate, and (2) investigate performance the electro-ozone reactor in treating concentrated landfill leachate.

LANDFILL LEACHATE

Moisture penetrates into the wastes in a landfill after a while we will have the landfill leachate. Characteristics of leachates differ from one landfill to another in the short- and long-terms periods due to differences in climate, hydrogeology, and waste composition (Visvanathan et al., 2000).

Landfill leachates are considered as wastewater that has the strongest environmental impact. The most significant feature of leachates is the high concentrations of particular contaminants.

Urban landfill leachates consist of contaminants that can be classified into four main groups as follows: (1) dissolved organic matter; (2) inorganic compounds such as calcium, potassium, sodium, ammonium, calcium, magnesium, sulfates, and chlorides; (3) iron and heavy metals such as nickel, lead, copper, chromium, cadmium, and zinc; and (4) xenobiotic organic materials (Aziz et al., 2011; Tengrui et al., 2007).

Concentrated Landfill Leachate

Concentrated leachate is a dark brown solution with a high chemical oxygen demand (COD) and a low biochemical oxygen demand (BOD) to COD ratio, which make it difficult to biodegrade (Zhang et al., 2013). Thus, a combined system should be used to treat concentrated leachate. Shengli et al. (2011)

investigated the treatment of concentrated landfill leachate via coagulation and fly ash adsorption. He et al. (2015) studied concentrated landfill leachate treatment through oxidation with Fenton's reagent.

CHEMICAL TREATMENT PROCESSES

Electrochemical Oxidation Method

Electrochemical methods have been used for the treatment of organic materials with high toxicity and low biological degradability. Electrochemical methods, such as electrocoagulation, electro-oxidation, and electro-photo-oxidation, have been frequently applied for treatment of wastewaters from textile, tannery, and oil industries. Treatment of landfill leachates by electrochemical methods is another important research area. The electrooxidation method was specifically examined in most of the studies in this field (Deng, 2007).

Electrochemical oxidation is the utmost prevalent electrochemical process for eliminating organic pollutants from wastewaters. It is a procedure based on the effluent electrolysis and in its simplest form, consists in the oxidation of contaminants in an electrolytic cell, which is formed by two electrodes connected by an external circuit, so that electrochemical reactions can take place. During the electrochemical reaction, electrons transfer occurs between the electrodes' surface and the species present in solution and contaminants oxidation takes place, either through direct electron transfer to the anode (direct anodic oxidation), or by chemical reaction with electrogenerated species at the anode, such as physically adsorbed "active oxygen" (physisorbed hydroxyl radical) or chemisorbed "active oxygen" (oxygen in the lattice of a metal oxide anode) generated from water discharge (Martínez-Huitle & Brillas, 2009).

During the electrochemical oxidation of an aqueous effluent the oxidation mechanisms may follow two different routes: (i) Electrochemical conversion, in which organic compounds are partially oxidized and transformed into a variety of more biodegradable reaction by-products, being a subsequent treatment still required, generally a biological one; (ii) Electrochemical combustion, where organic compounds are completely mineralized and transformed into water, carbon dioxide and other inorganic species, being no further purification required (Fernandes, 2014).

Ozonation

Advanced oxidation processes (AOPs), arising in 1970s, are highly competitive technologies for the destruction of a wide range of recalcitrant organic pollutants resistant to conventional approaches. They successfully function in the advanced treatment of low concentrated effluents, and can also be used as pretreatment to enhance the biodegradability of wastewater (Xiao et al., 2015).

Ozone (O_3) is widely used in drinking water and wastewater treatment as disinfectant and oxidant (Li et al., 2015). It is well known that ozone is a strong oxidant, the oxidation potential of which is 1.52 times higher than that of chlorine (Wu et al., 2015). The strong oxidants mainly involve ozone molecular, fleshly-generated oxygen atoms and hydroxyl radicals during ozonation (Azbar et al., 2004). Among these oxidants, hydroxyl radicals can partially oxidize non-biodegradable organics because of non-selectively breaking down the molecular structure of them, which is usually called indirect reaction. Ozone molecular also reacts with organic compounds by the way of direct oxidation. Some of researches had reported that ozonation has the merit of enhancing the biodegradability of the organics containing toxic and inhibitory compounds from the effluents (Zhang et al., 2013).

The use of ozone is advantageous because of its very strong oxidizing properties and the fact that it does not form chlorinated by products. The redox reactions of ozone typically proceed through radical-type chain mechanisms. The reaction formation is very sensitive to the applied conditions, such as pH and ionic media (Benbelkacem et al., 2003). Ozone decomposition reaction occurs when the pH value increases; thus, the formation of hydroxyl radical (OH^-) increases in the presence of a solution with a high pH value.

In overall, when augmented to natural water, ozone is consumed in two steps: rapid ozone consumption (OC) and slow decay. The amount of ozone consumed during the first stage can be represented by the instantaneous ozone demand, which corresponds to the difference between the administered ozone and the amount of ozone measured after a few seconds. The rapid reaction step is followed by a moderate or slow ozone decay stage (Chaturapruek et al., 2005).

The mechanisms of the ozone breakdown involve producing hydrogen peroxide, especially in basic solution. These results provide kinetic evidence for the initiation step, which corresponds to a two-electron transfer process or an oxygen atom transfer from ozone to a hydroxide ion (Equations 1 and 2). The mechanistic implication of these reactions will be used to describe the role of ozone as a disinfectant in water purification and organic oxidation processes (Rivas et al., 2003; Benbelkacem et al., 2003; Chaturapruek et al., 2005; Tezaoui et al., 2007).

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \tag{1}$$

$$2O_3 + H_2O_2 \rightarrow 2OH + O_2 \tag{2}$$

At an acidic reaction pH, the ozonation reaction limits the generation of hydroxyl free radicals by the O_3/HO technique as illustrated in Equations (3 to 6) (Peixoto and Filho, 2010). This result justifies the antagonistic effect of interaction between ozone and the reaction pH.

$$O_2 + OH^- \rightarrow O_2^- + HO_2 \tag{3}$$

$$HO_2 \leftrightarrow O_2^- + H^+ \tag{4}$$

$$O_3 + O_2 \rightarrow O_3 + O_2 \tag{5}$$

$$O_3^- + H^+ \leftrightarrow HO_3 \tag{6}$$

Temperature has an important influence on the half-life of ozone. Table 1 shows the half-life of ozone in water, which is much shorter than in air, proving that ozone decomposes faster in water. The solubility and stability of ozone decrease at higher temperatures (Rosal et al., 2006). Ozone cannot be dissolved in water at temperatures above 40 °C because of its half-life at these temperatures is very short (Lenntech, 2012).

Effects of Ozone on Leachate Biodegradability

Combination of biological and chemical oxidation processes is usually applied to enhance the effluent biodegradability standards. The chemical oxidation processes, including ozonation, can lead either to a total degradation of chemical compounds or to the transformation of resistant highly hydrophobic organics into more polar molecules. These processes can be preferably used to transform recalcitrant organic wastewater constituents to biodegradable organics (Derco et al., 2001). Ozonation increases the biodegradability of high-molecular-weight organic compounds through the decomposition of large organic molecules, thereby increasing the effectiveness and turning them into compounds that are easily assimilated biologically (Bila et al. 2005).

The most biodegradable organic material is produced after oxidation with only ozone (Hagman et al. 2008). During ozonation, biodegradability of leachate is enhanced due to fragmentation of organic compounds from long chains to lower chains degraded to carbon dioxide (Geenens et al. 2001).

Background of Study

Landfill leachate carries some forms of pollutants, such as ammonia, nitrogen (NH_3-N), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), colour, heavy metals, and suspended solids. Leachate composition depends on different factors, such as the kind of waste and site hydrology, as well as age, type, and operation of the landfill (Foul et al., 2009). In general, the following landfill leachate treatment options are available: (1) spray irrigation on abutting grassland, (2) leachate recirculation through the landfill, (3) sewage and leachate co-treatment, (4) leachate evaporation using landfill-generated methane as fuel, and (5) biological or physical/chemical treatment (Mojiri, 2014; Mojiri et al., 2014). One of the useful physical/chemical treatment methods is ozonation.

Ozonation processes are attractive means for the treatment of landfill leachates due to the high oxidative power that ozone possesses (Murray and Parsons, 2004). As one of the most powerful oxidants with an oxidation potential (E_0) of 2.08V, ozonation alters the molecular structure of refractory organic compounds in landfill leachate, turning them into compounds that are easily assimilated biologically. Depending on the pH values, which play major roles in the ozone decomposition, ozone oxidation follows the two main pathways: either a direct electrophilic attack of the ozone molecule to the recalcitrant

Table 1. Half life time of ozone dissolved in water as a function of temperature (pH 7)

Temperature (^oC)	Half-Life (min)
15	30
20	20
25	15
30	12
35	8

(Source: Lenntech, 2012)

pollutants or a generation of •OH radicals due to the ozone decomposition process and followed by a subsequent attack of the radicals on the pollutants (Lin et al., 2011).

Ozone has recently been given much attention because of its powerful chemical oxidant property and high capacity for oxidation and disinfection in landfill leachate treatment technology (Wu et al., 2004). Ozonation products are generally less complex, are constituted of smaller molecules, and are more biodegradable than their precursors (Bila et al., 2005). Several applications and techniques involving ozone have been conducted on landfill leachate treatment as summarized in Table 2. Because the lack of ozonation in removal of COD and ammonia, the researcher have been suggested combined systems.

Temperature has an vital influence on the half-life of ozone. The solubility and stability of ozone decrease at higher temperatures (Rosal et al., 2006). Ozone cannot be dissolved in water at temperatures above 40 °C because of its half-life at these temperatures is very short (Lenntech, 2012).

Lin and Chang (2000) studied treatment of landfill leachate by combined electro-fenton oxidation and sequencing batch reactor method. Their results showed a good performance to remove COD and colour.

Haapea et al. (2002) and Geenens at al. (2001) reported that COD removal was improved from 30 – 40% using ozonation in pre-treatment of landfill leachate to 81 – 95% used biological activated sludge after ozonation process

Lei et al. (2007) investigated treatment of landfill leachate by combined aged-refuse bioreactor and electro-oxidation. The removal efficiencies of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), total nitrogen (TN) and ammonia nitrogen (NH_3–N) of landfill leachate treated by the two-stage bioreactor system were 98.5%, 99.9%, 98.0%, 64.2% and 99.9%, respectively. The optimum electrolysis time of leachate was 30 min.

Table 2. Summary of ozone applications on leachate treatment

Initial Concentration	Experimental Conditions	Removal (%)	Reference
COD: 2300 – 5000 (mg/L), (mg/L), pH: 7.9 – 9.02	Ozone dosage: 0.001 mol /L, contact time: 60 min, sample volume: 1L	COD: 30%	Rivas et al. (2003)
COD: 3945 (mg/L), NH_3-N: 800 (mg/L), pH: 4.5	Ozone dosage: 3 (g/L)	COD: 48%	Silva et al. (2004)
COD: 2422 – 3954 (mg/L), (mg/L), NH_3-N: 750 - 800 (mg/L), pH: 8 – 8.5	Ozone dosage: 40 g/h (3 – 5 g/L).	COD: 40%	Bila et al. (2005)
COD: 5850 (mg/L), NH_3-N: 1380 (mg/L), pH: 9	Ozone dosage: 2.8 (g/L)	COD: 85%	Calli et al. (2005)
COD: 7622 – 8000 (mg/L), (mg/L), NH_3-N: 2390 - 2620 (mg/L), pH: 7.8 – 8.1	Ozone dosage: 3mg /L, contact time: 40 min, pH: 8.01,	COD: 35%, NH_3–N: 50%	Kurniawan et al. (2006)
COD: 5230 (mg/L), Colour: dark brown	Ozone dosage: 80 g/m3, contact time: 60 min, pH: 8.7, cample volume: 150 mL	COD: 27%, Colour: 87%	Tizaoui et al. (2007)
COD: 743 (mg/L), NH_3-N: 714 (mg/L), pH: 3.5	Ozone dosage: 112 mg/L, contact time: 60 min, pH: 8.7, sample volume: 1L (two fold diluted)	TOC: 28%	Cortez et al. (2011)

Zhang et al. (2010) investigated evaluation of electro-oxidation of biologically treated landfill leachate using response surface methodology. Their results showed a good performance to remove ammonia and COD. The removal efficiencies were 98.4% and 66.4%, respectively.

García-Morales et al. (2013) integrated advanced oxidation process (ozonation) and electrocoagulation treatments for dye removal in denim effluents. For this purpose, integrated advanced oxidation process comprising ozone and electrocoagulation techniques were used. After ozone was applied 64% colour removal, 78% turbidity removal and 3% COD reduction was observed. With the electrocoagulation treatment a 22%, 21% and 9% of colour removal, turbidity removal and COD reduction were achieved, respectively. However; using the integrated process, 65% colour removal, 76% turbidity removal and 37% COD reduction could be attained.

TRENDS ON ELECTRO-OZONATION IN SHANGHAI, CHINA

China is one of the fastest growing countries in the world and has, as a result, a growing waste management problem (Themelis and Mussche, 2013). Most Chinese MSW usually includes residential, institutional, commercial, street cleaning and non-process waste from industries (World Bank, 2005).

The common categories of MSW in China include kitchen waste, paper, plastic, fabric, metal, glass, pottery, brick and stones, batteries, and discarded household appliances, etc. There are three major treatment and disposal methods named landfilling, composting and incineration in China.

CONCENTRATED LANDFILL LEACHATE SAMPLING AND METHODOLOGY OF STUDY

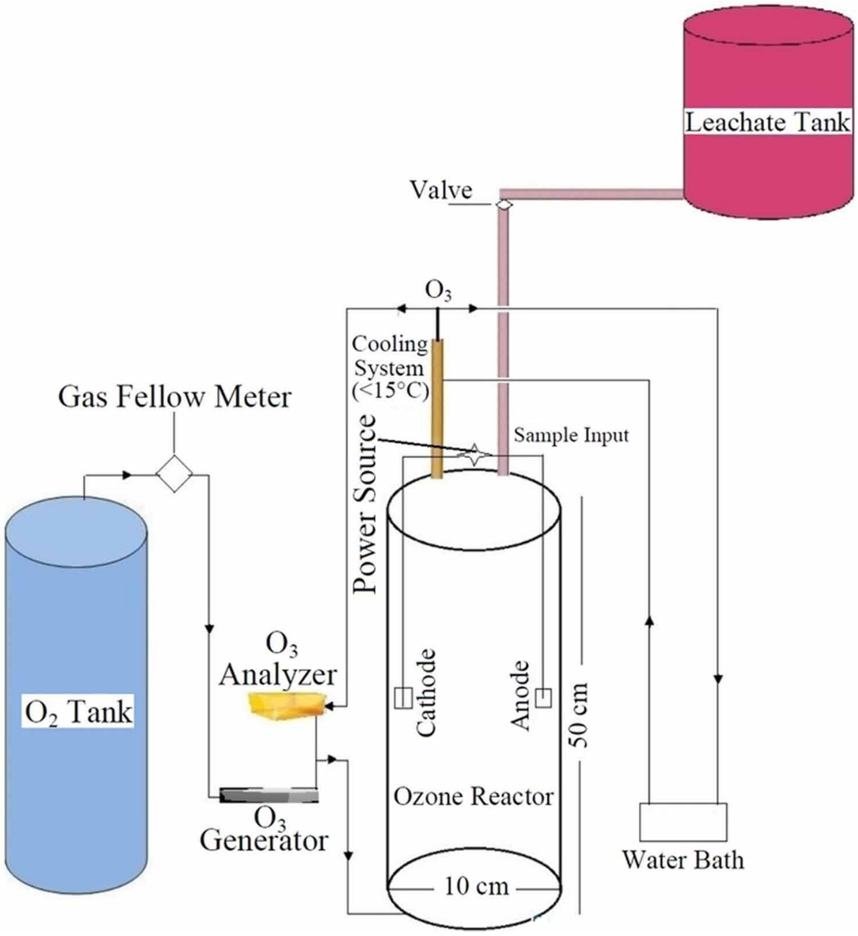
8 samples of concentrated landfill leachate during July 2015 to November 2015 were collected from Shanghai Laogang Leachate Treatment Plant, Shanghai, China. It is an old landfill leachate since Shanghai Laogang Landfill was started in 1989 along the shore of the East China Sea and commissioned at the end of 1991. This site receives around 10000 Tons of municipal wastes per day from across Shanghai. It is a covered landfill site with membrane reactors for treating generated leachate. Concentrated landfill leachate characteristic is shown in Table 3.

A cylinder with a volume of 3.5 L (height = 50 cm, diameter = 10 cm) was used as the ozonation reactor. The reactor was reinforced by a cross-column ozone chamber to develop ozone gas diffusion (Fig. 1). The cooling system and water bath supported the ozone reactor in maintaining the internal reflex temperature at <15 °C as the optimal half-life of the dissolved ozone (30 min) in water (Lenntech, 2012). Ozone was formed using a generator fed with pure dry oxygen. Ozone dosage was measured via an ultraviolet gas ozone detector (Lontec, Qingdao). Reaction time was contrasted between 30 min and 120 min to determine the optimal reaction time (Tizaoui et al., 2007). Furthermore, the ozone reactor was supported with anode and cathode plates (Ti/RuO_2–IrO_2, 18 cm × 8 cm) as the electric power supply source. The plates were arranged parallel (distance was 5 cm) to each other and were dipped in leachate. Electronic power (Digital CC&CV DC Power Supply, Everfine, Hangzhou, China) was used. Based on preliminary experiments, the voltage and current were 9 V and 4 A, respectively; this is in line with findings of Bashir et al. (2009) and Rada et al. (2013). The reactor was filled with 2500 mL concentrated leachate. The O_3 fellow rate was fixed at 1000 mL/min for all runs based on preliminary experiments and ozone analyzer capacity. All chemical physical or biological analysis for leachate and bottom ash characteristics are carried out in accordance with the Standard Methods (APHA, 2005). In this study, the expensive part of research is energy consumption for ozone generator same most ozonation methods. Electrical power for electrochemical part of this reactor can be supplied with a 9V solar panel.

The input and output ozone gas concentrations varied from 40 mg/L to 120 mg/L and were measured by an ultraviolet gas ozone detector (Lontec, Qingdao). The ozone consumed (OC) through the elimination of a certain sum of COD by ozonation under the experimental situations is given in Equation 7 (Abu Amr et al., 2013):

$$OC = \frac{Q_G}{V} \times \frac{\int_0^t \left(1 - \frac{C_{AG}}{C_{AG0}}\right) dt}{\left(COD_0 - COD\right)}. \tag{7}$$

Figure 1. Schematic diagram of reactors design and experiments procedures



Where, Q_G shows the gas flow rate (mL/min), V illustrates volume of samples (mL), C_{AG} clarifies the off-gas ozone concentration (g/m^3), CAG0 represents the input ozone concentration (g/m^3), t is the time (min), and COD_0 and COD are the initial and final COD (mg/L), respectively. For monitoring ozone utilization, three different fellow rates (1000, 600 and 400 mL/min) were considered during 60 min react time (Oloibiri, 2013).

Statistical Analysis

The elimination efficacies of COD, colour, and Ni were calculated by assessing the goal parameters before and after treatment. Elimination effectiveness was evaluated using Equation (8):

$$\text{Removal}\left(\%\right) = \frac{\left(C_i - C_F\right)100}{C_i}. \tag{8}$$

Where, C_i and C_f are first and ultimate concentrations of the parameters, respectively. Experimental design was utilized for optimum removal. The RSM is a throng of mathematical and statistical systems that are valuable to chemical reaction optimization and industrial processes and are routinely utilized for experimental designs (Mojiri et al., 2014). In this study, RSM was applied to calculate the relationship between responses (COD, colour and Ni removal, %) and independent variables as well as to improve the relevant situations of variables to calculate the best rate of responses. RSM was launched through the support of the Design Expert 7 software. The two significant independent variables measured in this study were contact time (A), and initial concentration of O_3 mg/L (B). The time, and initial concentration of O_3 (mg/L) were 30 to120 mins, and 40 to 120, respectively (Abu Amr, 2013). For current study, a quadratic model is a suitable model, as shown in Eq. (9). The impacts of the interaction of all variables on responses were then analyzed (Table 4).

$$Y = \beta_0 + \sum_{j=1}^{k}\beta_j X_j + \sum_{j=1}^{k}\beta_{jj} X_j^2 + \sum_{i}\sum_{<j=2}^{k}\beta_{ij} X_i X_j + e_i$$

$$Y = \beta_0 + \sum_{j=1}^{k}\beta_j X_j + \sum_{j=1}^{k}\beta_{jj} X_j^2 + \sum_{i}\sum_{<j=2}^{k}\beta_{ij} X_i X_j + e_i \tag{9}$$

where, Y shows the response; X_i and X_j represent the variables; β_0 illustrates a constant coefficient; β_j, β_{jj}, and β_{ij} are the interaction coefficients of linear, quadratic and second-order terms, respectively; k shows the number of study factors; and e is the error (Mojiri et al., 2013).

TRENDS ON REMOVAL EFFICACIES OF A CASE STUDY IN SHANGIA, CHINA

Table 3 shows that the concentrated landfill leachate exhibits high-intensity colour (2113 Pt. Co), as well as high COD concentration (3018 mg/L), BOD_5 (285 mg/L), and nickel concentration (29.67 mg/L).

Table 3. Characteristics of concentrated landfill leachate, and domestic sludge

No.	Parameter	Leachate Average value	Activated Sludge	Standard discharge limit[a]
1	pH	7.34	6.81	-
2	Colour (Pt. Co)	2113	-	40.0
3	BOD_5 (mg/L)	285	48.11	30.0
4	COD (mg/L)	3018	114	100.0
5	BOD_5/COD	0.09	-	-
6	NH_3-N (mg/L)	49.00	-	25.0
7	Total organic carbon (mg/L TOC)	51.39	-	-
8	Total nickel (mg/L)	29.67	0.33	0.10
9	Cl (mg/L)	1280	-	-

[a]The Chinese discharge standards (2008)

Table 4. Experimental variables and results for the electro-ozonation reactor

Run	Reaction Time (min)	Ozone Dosage (mg/L)	COD removal (%)	Colour removal (%)	Ni removal (%)
1	21.00	80.00	42.92	77.04	35.92
2	75.00	128.00	66.11	89.17	55.29
3	129.00	80.00	55.81	86.25	44.26
4	75.00	32.00	33.63	70.95	27.39
5	75.00	80.00	55.79	85.52	44.45
6	75.00	80.00	55.14	86.13	44.27
7	21.00	80.00	43.78	76.67	35.91
8	30.00	40.00	34.13	71.87	28.64
9	75.00	32.00	32.16	70.87	27.11
10	75.00	80.00	55.01	84.99	43.91
11	75.00	128.00	66.32	89.32	55.33
12	30.00	40.00	33.47	71.07	27.49
13	120.00	120.00	61.42	89.24	50.12
14	129.00	80.00	54.17	83.18	44.18
15	120.00	40.00	35.13	72.18	33.12
16	30.00	120.00	55.17	86.00	47.13
17	120.00	120.00	61.13	89.38	50.25
18	120.00	40.00	35.89	71.98	29.19
19	30.00	120.00	53.87	82.41	43.16
20	75.00	80.00	55.28	85.88	44.56

*pH= 7.3; Current= 4A; Voltage= 9V

Ammoniacal nitrogen, NH_3–N, was 49.0 mg/L it is in line with findings of Wang et al. (2016) and Zhang et al. (2013). A BOD_5/COD of 0.09 with low biodegradability was observed. Zhang et al. (2013) stated that a 0.09 BOD_5/COD ratio for concentrated leachate was in line with the current research. He et al. (2015) reported 26.6 mg/L nickel concentration for concentrated leachate, which is close to the value derived in the present research.

In addition, contaminant concentration overpassed the acceptable limits issued by the Effluent Limitations for USW Landfills in China (2008). This experiment was conducted at original pH (7.34) to reduce treatment cost and to follow up actual conditions. pH was mostly around 7.5 during experiments and after treatment. This result indicates that pH remains unchanged after electro-ozonation, which is in line with the findings of Mohajeri et al. (2010). Kreetachat et al. (2007) showed that pH changes of 5−10 in the system minimally affected COD and total organic carbon removal efficiencies. Rehman et al. (2012) investigated colour and COD removal from poultry litter leachate using an ozonation process at original pH. The 3D surface plots of COD, colour, and nickel removal during electro-ozonation treatment are presented in Fig. 2. The ANOVA outcomes of the response parameters and response rate under optimum conditions during electro-ozonation treatment are shown in Tables 4 to 6.

COD is the amount of oxygen requirement of an organic matter that is susceptible to oxidation via a powerful chemical oxidant. COD wastes are normally not easily biodegraded and frequently encompass compounds that inhibit biological activities (Viessman et al., 2009). COD removal efficacy (Table 4) varied from 32.1% (reaction time = 75 min, O_3 dosage = 32 mg/L) to 66.3% (reaction time = 75 min, O_3 dosage = 128 mg/L) during treatment using the electro-ozonation reactor. Optimal COD removal (64.8%) was achieved at a reaction time of 97.0 min and an O_3 dosage of 120 mg/L in the electro-zonation reactor.

Terry (2010) reported 60% COD removal by using ozone and oxygen in a simple kinetic model prediction. Sallanko and Okkonen (2009) stated that 1 g of ozone decreased the amount of COD by 1.5 g. With increased dosages, the effectiveness of ozone in removing COD decreased rapidly. Abu Amr et al. (2013) reported up to 79% COD removal from landfill leachate through the use of ozone/Fenton's reagent during an advanced oxidation process (AOP) with 90 min reaction time. In the AOP, ozone has been verified as a powerful oxidizing agent because it induces the formation of oxygen atoms and hydroxyl radicals. Ozone can directly or indirectly break organic compounds into simpler and smaller molecules (Yasar et al., 2007).

Colour removal efficacy (Table 4) varied from 70.8% (reaction time = 75 min, O_3 Dosage = 32 mg/L) to 89.3% (reaction time = 120 min, O_3 dosage = 120 mg/L) during the treatment with electro-ozonation reactor. Optimal colour removal (90.0%) was achieved at a reaction time of 117.4 min and O_3 dosage of 120 mg/L in the electro-ozonation reactor. Rehman et al. (2012) stated that ozonation at an initial pH of 7 can eliminate 77% of the colour of landfill leachate. Abu Amr and Aziz (2012) removed 98% colour from the landfill leachate by using ozone/Fenton's reagent in the AOP. Li et al. (2010) reported that electrochemical oxidation of landfill leachate under proper situations can eliminate utmost COD and meaningfully diminish the colour of the leachate. Muthukumar et al. (2004) stated that ozone can effectively decolorize wastewater dye because it attacks conjugated double bonds, which are often associated with colour. Lee et al. (2007) stated that decolorization efficiently occurs at a low pH through direct ozonation reaction at the unsaturated chromophoric bonds of dye molecules. At high pH, indirect reactions of ozone may oxidize the whole-dye molecules; other non-colour organic compounds, which can contribute to the formation of non-toxic breakdown products, are subsequently converted into CO_2 and H_2O.

Figure 2. The 3D surface plots of (A) COD removal, (B) color removal, and (C) Ni removal in Normal-SBR

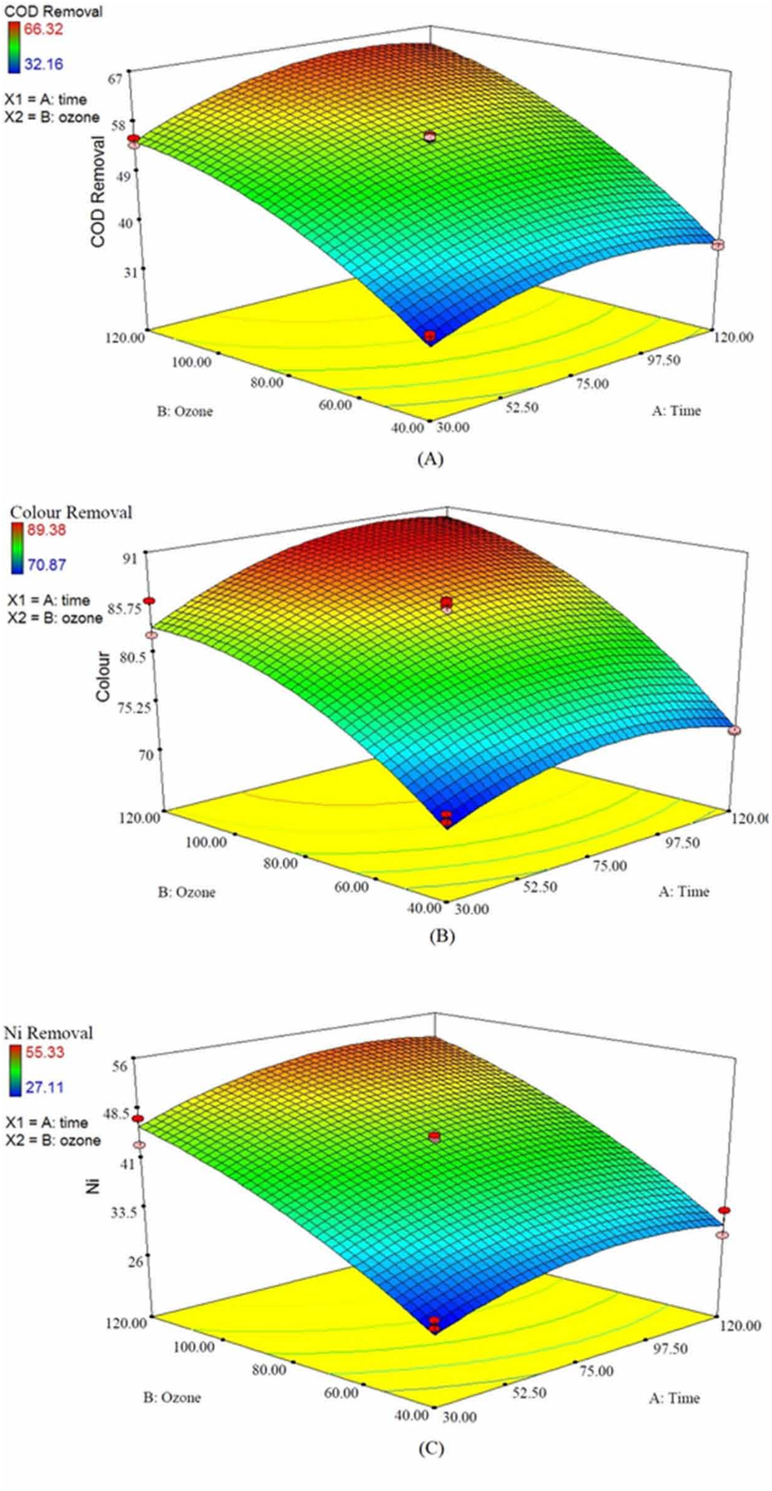


Table 5. ANOVA results for response parameters

Response	Final equation in terms of actual factor	Prob.	R^2	Adj. R^2	Adec. P.	SD	CV	PRESS	Prob. LOF
COD	$-1.128 + 0.358A + 0.697B - 0.002A^2 - 0.002B^2$	0.0001	0.9814	0.9748	31.832	1.86	3.76	102.38	0.0751
Colour	$48.327 + 0.218A + 0.487B + 0.0006AB - 0.001A^2 - 0.002B^2$	0.0001	0.9743	0.9652	26.326	1.35	1.67	55.14	0.0387
Ni	$2.883 + 0.276A + 0.472B - 0.001A^2 - 0.001B^2$	0.0001	0.9708	0.9604	26.066	1.85	4.57	26.22	0.0067

*Prob.: Probability of error; R^2: Coefficient of determination; Adj. R^2: Adjusted R^2; Adec. P.: Adequate precision; SD: Standard deviation; CV: Coefficient of variance; PRESS: Predicted residual error sum of square; Prob. LOF: Probability of lack of fit

**In final equations, where A is contact time (h), B is ozone concentration (mg/L),

Values of "Prob > F" less than 0.05 indicate model terms are significant.

Table 6. The value of response at optimum conditions

Independent Factors		Responses		
A (h)	B (mg/L)	COD rem. (%)	Colour rem. (%)	Ni rem. (%)
96.9	120.0	64.8	90.4	52.9

A: Contact Time and B: O_3 Concentration

The efficiency in the elimination of Ni (Table 4) through the action of an electro-ozonation reactor varied from 27.1% (reaction time = 75 min, O_3 Dosage = 32 mg/L) to 55.2% (reaction time = 75 min, O_3 dosage = 128 mg/L). The ideal condition for Ni elimination (52.9%) by using the electro-zonation reactor was attained at a reaction time of 96.7 min and O_3 dosage of 120 mg/L. Ozone oxidizes transition metals to their high oxidation state, which usually causes them to form less soluble oxides that are easily separated by filtration. Generally, ozone oxidizes these heavy metals to form metallic oxides or hydroxides, which precipitate off and can be easily removed from water. Ozone is used to eliminate heavy metals from the effluent produced by various industries (Upadhyay and Srivastava, 2005). The oxidative properties of ozone are useful in the removal of soluble metals and decomplexion of bound heavy metals (Portjanskaja, 2010). Electrochemical treatments contain of applying a constant voltage over time (potentiostatic) to the refluent being treated, or alternatively, of passing a constant current over time (galvanostatic) over the refluent. An electrolytic cell serves as the reactor in which this procedure occurs. As the continuing current flows, the negative electrode (cathode) reduces the chemical species by giving them electrons; by contrast, the positive electrode (anode) oxidizes the chemical species by receiving electrons from them (Oprea et al., 2009).

Chemical electro-oxidation can be achieved indirectly or directly (Bashir et al., 2009). One form of indirect electro-oxidation occurs in the presence of vast concentrations of chlorides, Cl^-; first, active chlorine is formed on the anode, and hypochlorite, HClO, which exerts a potent oxidizing effect, is produced in rapid succession. This reflex is mostly appropriate for saline refluent leachates because it eliminates a number of pollutants (for example, ammonium is partly transformed into nitrogen gas, N_2). As a result, the second kind of indirect electrooxidation leads to the output of hydrogen peroxide, H_2O_2, which also demonstrates a powerful oxidizing impact on recalcitrant organic substances (Bashir et al., 2009). Additional example of indirect electro-oxidation occurs in the occurrence of metal ions (Ag^{2+}, Co^{3+}, Fe^{3+}, and Ni^{2+}) in a solution. These ions act as mediators and are oxidized in the anode, as they become more reactive by moving from a low valence state to a high valence state. Thus, they invade the organic complexes present in the solution and form hydroxyl radicals, which can consequently oxidize organic compounds (Rada et al., 2013). In the current study, the concentrated landfill leachate was considered to exhibit a high concentration of Cl (chloride). During the electrochemical oxidation, Cl^- was released at the anode to make Cl_2. Subsequently, Cl_2 was chemically transformed into OCl^- to efficiently oxidize the pollutants (Mussa et al., 2015). A series of reactions involving indirect oxidation during the electrooxidation process is shown in Equations 10 to 16 (Deng & Englehardt, 2007).

Anodic reactions:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{10}$$

$$6HOCl + 3H_2O \rightarrow 3ClO_3^- + 4Cl^- 12H^+ + 1.5O_2 + 6e^- \tag{11}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{12}$$

Bulk reactions:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{13}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{14}$$

Cathodic reactions:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{15}$$

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \tag{16}$$

Contaminant removal via electrochemical ozonation is achieved using two different approaches: indirect oxidation, in which a mediator is electrochemically caused to perform oxidation; and direct anodic oxidation, in which contaminants are demolished on the anode surface (Li et al., 2010). Most metal cations are possibly eliminated at the cathode, whereas some contaminants (e.g., organic compounds) are certainly oxidized at the anode. Furthermore, an oxidation reaction could arise in bulk solution by an oxidant produced by the electrodes. Electrochemical oxidation has been extensively studied as an effective means of controlling contamination in wastewaters treatment (Deng & Englehardt, 2007).

The use of ozone as a pre-treatment method can improve biological treatment. Ozone is effective in improving the BOD/COD ratio, and thus, coupling chemical and biological processes is a viable option. Therefore, enhancing biodegradation through ozone pre-treatment has been attempted (Adhyapak et al., 2011). Ordono and Rollon (2012) stated that the complexes susceptible to ozonolysis are those inclosing C=C double bonds, specific functional groups (e.g. OH, CH_3, OCH_3) and atoms carrying. So this method could improve the biodegradability.

This system could remove rest of pollutants near the China Standard so it may be installed there. For installing this system just the size of system should be increased to actual size. It has potential value as new environment friendly method for reducing pollution. Beside it, Its installation is too easy and no need hiring professional workers.

Ozone consumption indicates the quantity of ozone that can be used to eliminate a certain volume of COD. Oloibiri (2013) found that the amount of COD removed increased with ozone consumption. Abu Amr (2013) reported that ozone consumption (OC) was between 0.32 and 1.6 (kg O_3/kg COD). Oloibiri (2013) determined that ozone utilization ranged from 0.23 mg to 0.48 mg COD eliminated per mg of ozone consumed. Similar ranges were reported by Tizaoui et al. (2007). Table 7 shows the results of the OC tests. In the current study, OC ranges from 0.30 to 1.4 (kg O_3/kg COD), which agrees with the findings of previous studies.

CONCLUSION

Electrochemical oxidation and ozonation are most important physical/chemical treatment methods. The electrochemical oxidation procedure is mainly appealing because the electrons provide a versatile, efficient, cost-effective, easily automatizable, clean technology. Therefore, the electrochemical oxidation treatment has been successfully used for the oxidative decontamination of wastewaters and landfill leachates. Ozone (O_3) is widely used in drinking water and wastewater treatment as disinfectant and oxidant. It is well known that ozone is a strong oxidant, the oxidation potential of which is 1.52 times higher than that of chlorine. In this study a combined system containing electro-ozonation was used to treat concentrated leachate. CCD and RSM were utilized to optimize parameters. The main conclusions of current research are presented below.

(1) The designed electro-ozonation could eliminate 64.8%, 90.4%, and 52.9% of COD, colour, and Ni, respectively at the optimum of contact time (96.9 min) and O_3 dosage (120.0 mg/L). (2) Ozone consumption ranged between 0.3-1.4 Kg COD removed per Kg ozone consumed.

Table 7. Results of ozone consumption testing

O_3 Generated (g/m^3)	Q_G	O_2 gas required (L) to generate 1 kg O_3	C_{AG0} (g/m^3)	C_{AG} (g/m^3)	OC (Kg O_3/Kg COD)	$COD - COD_0$ (mg/L)
120	400	3333.3	120	77	1.39	1324
80	600	7500.0	80	48	0.76	1515
40	1000	25000	40	26	0.30	2082

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Chapter 8

Photocatalysis (TiO_2/ Solar) in Water and Wastewater Treatment

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ABSTRACT

Advanced oxidation processes (AOPs) have gained growing importance for the removal of organic pollutants from water. Heterogeneous photocatalysis has been rapidly expanding for water treatment. This approach has economic and sustainability advantages compared with other processes. The main advantage of this process is its capability to gain complete oxidation or mineralization of organic contaminants at conditions of near ambient temperature and pressure. This chapter aims to review the mechanism involved in this process, characteristics of semiconductor photocatalyst, difference between suspended and immobilized photocatalyst system, comparison between the use of natural sunlight and commercial lamp, also the reactor involved. Potential advantages and limitations, as well as the application of photocatalysis in water and wastewater are also discussed.

INTRODUCTION

Water scarcity is strongly connected to the problem of water quality. Drastic urban development has deteriorated the quality of water and in some cases, made it unsafe for consumption (Naddeo et al., 2013). Due to continuous population growth, urbanization and industrialization, increasing water demands are stressing the existing water resources (Hashim et al., 2013). Over the last few decades, the occurrence of micro-pollutants in the environment has become a worldwide issue of increasing environmental concern. Micro-pollutants, also termed as emerging contaminants, consist of a vast and expanding array of anthropogenic as well as natural substances. Micro-pollutants are the thousands of inorganic and organic trace pollutants occurring at nano gram per liter (ng/L) to microgram per liter (µg/L) level of

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concentration (Luo et al., 2014). Micro-pollutants may exert toxic effects, even at such low concentrations, particularly when present as mixtures.

Micro-pollutants originate from different sources such as agricultural, industrial and everyday uses, for instance, personal care products, pharmaceuticals, and cleaning agents (Metz & Ingold, 2014). Routine analytical determinations of these parameters are never carried out because samplings and analyses are complex as well as time and money consuming (Guidotti et al., 2000). The low concentration and diversity of micro-pollutants not only complicates the detection and analysis procedures, but also creates challenges for water and wastewater treatment processes. With current condition of the environment, generally, organic micro-pollutants have become the center of attention to be eliminated in water and wastewater. Focusing on these pollutants which are resistant to biodegradation, the use of an alternative chemical oxidation method that can destroy these recalcitrant compounds is a matter of great concern. Among them, Advanced Oxidation Processes (AOPs) might probably constitute the best option in the near future (Cheng et al., 2016).

Over the last few decades, AOPs have gained growing importance for the removal of organic pollutants from water. The main advantage of AOPs compared to other technologies is the capability to gain complete oxidation or mineralization of organic contaminants through a process that operates near ambient temperature and pressure (Matilainen and Sillanpää, 2010). Photocatalysis which is also another AOP, has been rapidly expanding for water and air treatments (Al-Rasheed, 2005). This approach has economic and sustainability advantages in comparison with other processes, which require high energy costs (Marin et al., 2011). The mechanism, influential factors, advantages, and application of this AOP process will be discussed comprehensively in the following section.

Photocatalysis can be classified as homogeneous or heterogeneous processes, depending on whether they occur in a single phase or they make use of a heterogeneous catalyst like metal supported catalysts, carbon materials, or semiconductors, such as TiO_2, ZnO, and CdS (Oliveira et al., 2014). Homogeneous process is characterized by chemical changes depending on the interactions between the chemical reagents and target compounds (Ribeiro et al., 2015). Photo-Fenton reaction is categorized as a homogeneous process because it occurs when a light source is present, hydrogen peroxide (H_2O_2) will decompose by ferric (Fe^{2+}) ions present in the aqueous phase and resulting in the formation of hydroxyl radicals (Chong et al., 2010).

Heterogeneous photocatalysis is a chemical oxidation process in which a metal oxide semiconductor immersed in water and irradiated by near UV light ($\lambda < 385$ nm) which then results in the formation of free hydroxyl radicals (Umar and Aziz, 2013). The basic principle of semiconductor photocatalysis relies on the formation of an electron-hole pair upon the absorption of a photon with energy equal or bigger than the semiconductor band gap (Robertson et al., 2012). These two highly reactive entities are involved in a series of reductive and oxidative reactions on the semiconductor's surface (Chong et al., 2010).

MECHANISM OF PHOTOCATALYSIS

In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of TiO_2 photocatalyst, an energetic light source, and an oxidizing agent such as oxygen and air. The electronic structure of a semiconductor plays a key role in this process. Figure 1 shows the schematic diagram illustrating the mechanism of a TiO_2-based photocatalysis. A semiconductor consists of the valence band and the conduction band. The energy difference between these two levels is said to be the band gap energy (E_g).

Without excitation, both the electrons and holes are in the valence band. As illustrated in Figure 1, only photons with energies greater than the band gap energy can result in the excitation of the electrons in the valence band to the conduction band. With sufficient energy, the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band is completed, as shown in the equation below.

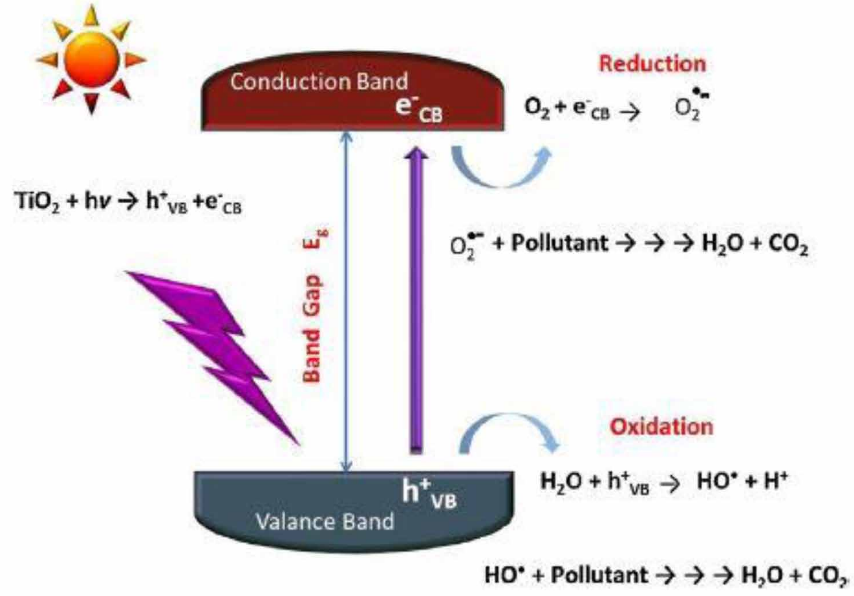
$$TiO_2 \xrightarrow{hv} e^-_{cb}\left(TiO_2\right) + h^+_{vb}\left(TiO_2\right) \tag{1}$$

The electron and hole can recombine, releasing the absorbed light energy as heat, and this will prevent the occurrence of redox reactions. In order to avoid recombination, the presence of a suitable scavenger or the surface defect state is important to trap the electron or hole throughout the process (Bahnemann, 2004). In the valence band of the TiO_2 particle, the positive hole can react directly with the adsorbed pollutants, but reactions with water are far more likely to occur since the water molecules are far more populous than contaminant molecules (Al-Rasheed, 2005). The oxidation of water or hydroxide ion (OH^-) by the hole produces the hydroxyl radical ($\dot{O}H$).

$$TiO_2\left(h^+_{vb}\right) + H_2O \rightarrow TiO_2 + \dot{O}H + H^+ \tag{2}$$

$$TiO_2\left(h^+_{vb}\right) + OH^- \rightarrow TiO_2 + \dot{O}H \tag{3}$$

Figure 1. Schematic diagram illustrating the mechanism of a TiO_2-based photocatalysis
(Source: Etacheri et al., 2015)



It is generally accepted that oxygen plays an important role in photocatalysis. In the conduction band, from a reaction with H$^+$, which is formed earlier in the splitting of water, oxygen (O_2) is reduced to form superoxide ion ($\dot{O}_2^-$) (Konstantinou and Albanis, 2004). This important reaction prevents the electron from recombining with hole and results in an accumulation of oxygen radical species that can participate in attacking contaminants.

$$TiO_2\left(e_{cb}^-\right) + O_2 + H^+ \rightarrow TiO_2 + H\dot{O}_2 \rightarrow \dot{O}_2^- + H^+ \tag{4}$$

From the reaction producing superoxide ions in the conduction band, the intermediate hydroperoxyl radical ($H\dot{O}_2$) can be further protonated to react with hydrogen ions (H^+), which subsequently forms hydrogen peroxide (H_2O_2) (Chong et al., 2010).

$$TiO_2\left(e_{cb}^-\right) + H\dot{O}_2 + H^+ \rightarrow H_2O_2 \tag{5}$$

H_2O_2 can act as an oxidizing agent in this photocatalytic process and produces more amounts of hydroxyl radicals (Akpan and Hameed, 2009). By yielding more hydroxyl radicals at a time, this can doubly increase the degradation rate of pollutants in the treatment process. Hence, the process results in considerable savings and a simpler operation of the equipment involved.

$$H_2O_2 + hv \rightarrow 2\dot{O}H \tag{6}$$

$$H_2O_2 + \dot{O}_2^- \rightarrow \dot{O}H + O_2 + OH^- \tag{7}$$

$$H_2O_2 + TiO_2\left(e_{cb}^-\right) \rightarrow \dot{O}H + OH^- + TiO_2 \tag{8}$$

Hydroxide radicals and superoxide ions can rapidly attack pollutants on the surface, and possibly in solution as well. Both of these substances (OH● and O_2●$^-$) are the most important products formed in TiO_2 photocatalysis (Al-Rasheed, 2005). Since this process breaks down the contaminant molecules continuously, no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. The TiO_2 particle itself is unchanged and no consumable chemicals are required (Al-Rasheed, 2005).

SEMICONDUCTOR PHOTOCATALYST

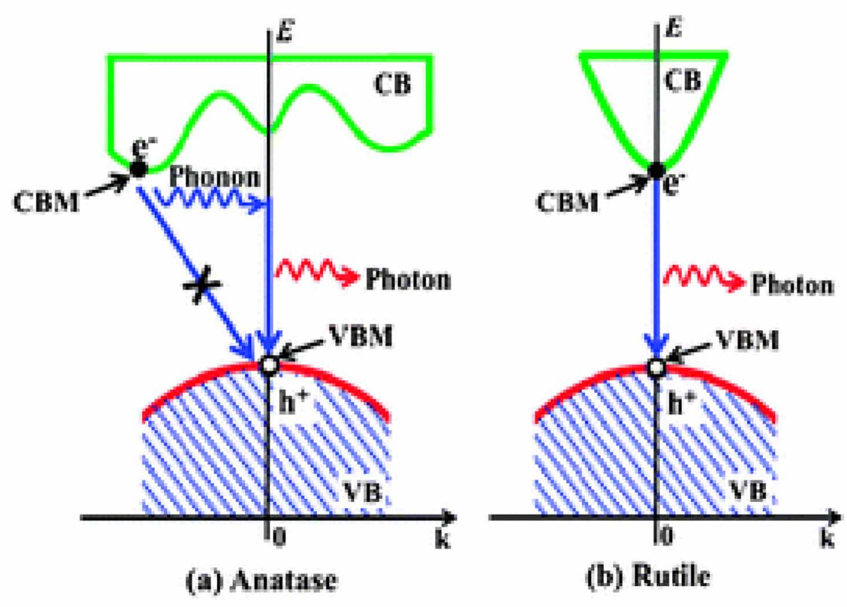
Semiconductor, such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS, are materials whose valence band and conduction band are separated by an energy gap or band-gap. When a semiconductor molecule absorbs photons with energy equal or greater than its band-gap, electrons in the valence band can be excited and jumped up into the conduction band, and thus charge carriers are generated. In order to have a photo-catalyzed reaction, the e^- - h^+ recombination, subsequent to the initial charge separation, must be prevented as much as possible (Gerven et al., 2007).

Characteristic of Semiconductor Photocatalyst

Titanium dioxide (TiO_2) is chosen as a catalyst since it has excellent pigmentary properties, high ultraviolet absorption, and high stability to be used in the photocatalytic degradation of chemicals in water and air (Al-Rasheed, 2005). TiO_2 is a naturally-occurring mineral with optical and electronic properties that makes it suitable for applications of photovoltaics, sensors, and photocatalysis (Pelaez et al., 2012). Studies have demonstrated the ability of TiO_2 to accelerate the sunlight-mediated inactivation of microorganisms and the degradation of organic and inorganic materials (Rengifo-Herrera & Pulgarin, 2010). Many other semiconducting oxides have been tested as catalysts; however, TiO_2 in the anatase form performed the most interesting and efficient features such as high stability, good performance, low toxicity and low cost (Uyguner-Demirel & Bekbolet, 2011).

TiO_2 semiconductor exists in four mineral forms that are, anatase, rutile, brookite, and titanium dioxide (B). Anatase type TiO_2 which has a crystalline structure has the band gap energy of 3.2 eV whereas rutile type TiO_2 has the band gap energy of 3.0 eV (Mahmood et al., 2013). It must be noted that although both anatase and rutile type TiO_2 absorb UV radiation, rutile type can also absorb radiation that is nearer to visible light. However, anatase exhibits higher photocatalytic activity than rutile type due to its conduction band position which demonstrates stronger reducing power as compared to rutile type (Li Puma et al., 2008). Figure 2 shows the molecular structure of TiO_2 for anatase and rutile.

Figure 2. Molecular structure of TiO_2 (a) Anatase (b) Rutile
(Source: Zhang et al., 2014)



(a) Anatase

(b) Rutile

Incomparable to other semiconductor photocatalysts, TiO_2 is inexpensive and can be supported on various substrates such as glass, fibers, stainless steel, inorganic materials, and sand, which allows a continuous re-use. Besides that, photo-generated holes are extremely oxidizing and photo-generated electrons reduce sufficiently to produce superoxides from dioxygens (Li Puma et al., 2008). In general, TiO_2 photocatalysts are commercially available and display the main features related to surface area, adsorption affinity for many organic compounds and lower recombination rate (Fresno et al., 2014).

Slurry vs. Immobilized TiO_2 System

Suspended TiO_2 provides higher efficiency than the immobilized system, due to a higher ratio of catalyst active site to reaction volume. If immobilized TiO_2 is used, degradation performance drops up to 60-70% since the system offers lower reaction surface rate for the photocatalysis reaction to take place. In every photocatalytic system, the main concern is to have maximum removal efficiencies of compounds. Therefore, it is better to implement suspended TiO_2 under solar irradiance, as to ensure the unlimited solar photons can enter the solution and combine with the photocatalyst particles to generate hydroxyl radicals in a large amount. Table 1 shows the advantages and disadvantages of using slurry and immobilized system in photocatalysis.

OPERATIONAL FACTORS INFLUENCING THE PHOTOCATALYTIC REACTION

During the photocatalysis process, some operating factors influencing the efficiency of this process are determined, such as pH, TiO_2 concentration, and the initial concentration.

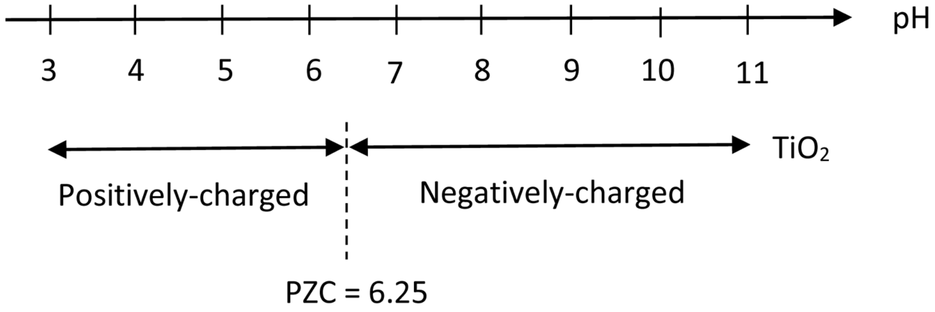
pH

In heterogeneous photocatalytic water system, pH is one of the most important operating factors that affect the charge on the TiO_2 particles and the position of the conduction and the valence bands. Due to the nature of TiO_2 catalyst used, any variation in the operating pH is known to affect the isoelectric point or the surface charge of TiO_2. Figure 3 illustrates the surface charge of TiO_2. At PZC of TiO_2, the interaction between the photocatalyst particles and water contaminants is minimal due to the absence of electrostatic force (Zamora, 2013). The point of zero charge (PZC) of the TiO_2 is widely reported at pH 6.25 (Li et al., 2005).

Table 1. Slurry and immobilized systems in photocatalysis

	Slurry	Immobilized
Advantages	-Simplicity in terms of preparation of application. -Higher surface rate of reaction. -Higher degradation efficiencies.	-Do not require separation step. -Time and cost-saving.
Disadvantages	-Require post treatment for catalyst recovery. -Agglomeration of TiO_2.	-Difficult to be synthesized. -Lower surface rate. -Significant reduction in system efficiency.

Figure 3. Surface charge of TiO_2



When operating pH<PZC (TiO_2), the surface charge for the TiO_2 becomes positively charged and gradually exerted an electrostatic attraction force towards the negatively charged compounds. Such polar attractions between TiO_2 and anionic organic compounds can intensify the adsorption onto the TiO_2 surface for subsequent photocatalytic reactions (Gogniat et al., 2006). This is particularly important when the anionic organic compounds present in a low concentration level. Above pH 6.25, the negative charge at the surface of the TiO_2 increases with increasing pH. Moreover, the pH of the solution affects the formation of hydroxyl radicals by the reaction between hydroxide ions and photo-induced holes on the TiO_2 surface (Shifu and Gengyu, 2005).

Many reports have used the point of zero charge (PZC) of TiO_2 to study the pH impact on the photocatalytic oxidation performance (Chin et al., 2006; Chong et al., 2009; Ochuma et al., 2007; Toor et al., 2006). The pH level which is below pH 3 is not preferable to be used because too acidic condition can be harmful when applied on site. While at a pH level above 11, or too alkaline condition, literature study had proven that the photo-degradation rate will decrease (Zhang et al., 2008). Yip et al. (2006) observed that the removal rate of PAHs, consisting of naphthalene, benzo(a)pyrene, and benzo(g,h,i) perylene, in aqueous solution, were enhanced at pH 7.

Similar result was found by Begum and Gautam (2011), who reported maximum degradation of lindane (98%) at pH 7. This indicates that the pollutant undergoes acid-base equilibrium, which means PZC of TiO_2 surface facilitate better absorption of active groups. On the other hand, high degradation rate of pyrene was obtained by Luo and his co-researchers (2008) at acidic pH level. In their work, they assumed pyrene to have negative charges located on its atoms, which can facilitate the adsorption onto the TiO_2 positive surface under a low pH condition, thus promoting better photocatalytic degradation. Table 2 shows the review of pH done by previous studies. It must be stressed that appropriate pH control strategies must be implemented at every different location of a photocatalytic water treatment process for efficient photocatalytic reaction to proceed.

Concentration of Titanium Dioxide (TiO_2)

Concentration of TiO_2 in the photocatalytic water treatment system affects the overall photocatalysis reaction rate in a true heterogeneous catalytic regime, where the amount of TiO_2 is directly proportional to the overall photocatalytic reaction rate (Gaya and Abdullah, 2008). A linear dependency holds until certain extent when the reaction rate starts to aggravate and becomes independent of TiO_2 concentra-

Table 2. Review of pH in previous studies

Contaminant	Photocatalytic System	Working Range	Findings	Reference
Azo dyes in aqueous solution	Solar/TiO_2	pH < 6	Higher degradation rate at acid pH.	Konstantinou & Albanis, 2004
Pesticide (propham, propachlor, and tebuthiuron) in aqueous suspension	UV/TiO_2	Propham = 5	Different photocatalytic behaviour of the compounds at different pH values.	Muneer et al., 2005
		Propachlor = 3		
		Tebuthiuron = 11		
Textile dyes	Solar/TiO_2	1.0-12.0 for various pollutants	In alkaline solution, •OH is easier to be generated and thus, the degradation efficiency is enhanced.	Akpan & Hameed, 2009
β-blockers (atenolol & propanolol)	UV/TiO_2	3 < pH < 10	Conversion was favored at near-neutral conditions.	Ioannou et al., 2011
Pesticides and phenolic in wastewater	Solar UV/TiO_2	2.0-12.2 for various pollutants	The degradation efficiency is enhanced at high pH due to abundance of OH^- ions in alkaline conditions.	Ahmed et al., 2011

tion. This is attributed to the geometry and working conditions of the photo-reactor where the surface reaction is initiated upon light photon absorption (Bamba et al., 2008).

When the amount of TiO_2 increases above a saturation level, this can create a light screening effect that reduces the surface area of TiO_2 being exposed to light illumination, and hence, the photocatalytic efficiency. A large number of studies have reported the effect of TiO_2 loadings on the process efficiency (Chong et al., 2009; Gaya and Abdullah, 2008; Ochuma et al., 2007). Rubio-Clemente et al. (2014), in their review of TiO_2-assisted photocatalytic degradation of PAHs in aqueous solution reported that in any solar reactor system, the initial rates were found to be directly proportional to catalyst concentration, until it reached a limit of catalyst concentration at which the rate of photocatalysis will become constant or even decrease.

The reason generally for such a constant level is associated to the decrease of the number of active sites on the photocatalyst surface because of the aggregation of TiO_2 particles, which in turn decrease the number of hydroxyl and superoxide radicals. Similar results have been reported for photocatalytic degradation of thiram, tebuthiuron, and atrazine (Kaneco et al., 2006; Muneer et al., 2005). Pang et al. (2009) indicated that the degradation of methamidophos increases with catalyst concentration from 2.0g/L to 12.0g/L and further increase in TiO_2 results in reduced degradation due to reduced visible light penetration.

Although the number of active sites in solution will increase with catalyst loading, a point appears to be reached where light penetration is compromised because of excessive particle concentration. The tradeoff between these two opposing phenomena results in an optimum catalyst loading for the photocatalytic reaction (Adesina, 2004). This suggests that the amount of TiO_2 to be used should maintain a balance between these two opposing effects. Table 3 shows the review of TiO_2 concentration done by previous studies. In order to ensure efficient absorption of photons and to avoid excess catalyst, the photocatalytic reactor should be operated at optimum catalyst loading.

Table 3. Review of TiO_2 concentration in previous studies

Contaminant	Photocatalytic System	Working Range	Findings	Reference
Azo dyes in aqueous solution	Solar/TiO_2	Maximum degradation rate: 400-500 mg/L	Decrease in the degradation percentage at higher catalyst loading.	Konstantinou & Albanis, 2004
Pesticide (propham, propachlor, and tebuthiuron) in aqueous suspension	UV/TiO_2	0.5-7.5 g/L	Degradation rate increases with the increase in catalyst concentration.	Muneer et al., 2005
Textile dyes	Solar/TiO_2	0.5-15.0 g/L for various pollutants	Initial rates were directly proportional to catalyst concentration until it reached an optimum point.	Akpan & Hameed, 2009
β-blockers (atenolol & propanolol)	UV/TiO_2	50-3000 mg/L	Decreased performance at increased catalyst loadings.	Ioannou et al., 2011
Pesticides and phenolic in wastewater	Solar UV/TiO_2	0.1-12 g/L for various pollutants	Degradation rate initially increases with catalyst loading and then decreases at high values.	Ahmed et al., 2011

Initial Pollutant Concentration

Previous investigations have reported the dependency of the TiO_2 photocatalytic reaction rate on the concentration of water contaminants (Chong et al., 2009; Ochuma et al., 2007; Toor et al., 2006). Under similar operating conditions, a variation in the initial concentration of the water contaminants will result in different irradiation time necessary to achieve complete mineralization or disinfection. Owing to the photonic nature of the photocatalysis reaction, excessively high concentration of organic substrates is known to simultaneously sature the TiO_2 surface and reduces the photonic efficiency leading to photocatalyst deactivation (Saquib and Muneer, 2003). This may be due to the fact that at higher concentrations more pollutant molecules could occupy more active sites, thus inhibiting the generation of the oxidants (Yang et al., 2012).

The removal of lindane from drinking water was investigated by Senthilnathan and Philip (2009) by photo-degradation using TiO_2. The degradation pattern was inversely affected by the initial lindane concentration, which was why they came to the conclusion that at higher initial concentration, competitive adsorptions on the active sites increases thus inhibit the formation rate of hydroxyl radicals. Lair et al. (2008) studied the photocatalytic degradation of naphthalene using TiO_2. They found that the degradation efficiency decreased gradually as the initial concentration of naphthalene was increased up to 5 mg/L.

The photocatalytic degradation of 4-nitrophenol (4-NP) was shown to decrease from 100% to 40.9% as the initial concentration increases from 0.02 to 0.1g/L (Parida and Parija, 2006). Lathasree et al. (2004) studied the effect of initial concentration (40-100 ppm) on the photocatalytic degradation of phenol using ZnO as catalyst. The initial rates of photo-degradation were high at the lower concentration range but it decreased as concentration increased. For chlorophenols, the initial rate was observed to increase with the increase in the initial concentration range 40-60 ppm and decreased as concentration increased further. Table 4 shows the review of initial pollutant concentration done by previous studies.

Table 4. Review of initial pollutant concentration in previous studies

Contaminant	Photocatalytic System	Working Range	Findings	Reference
Azo dyes in aqueous solution	Solar/TiO_2	-	Degradation efficiency of the dye decreases as the dye concentration increases further.	Konstantinou & Albanis, 2004
Pesticide (propham, propachlor, and tebuthiuron) in aqueous suspension	UV/TiO_2	Propham = 0.25-0.75 mM	Degradation rate increases with the increase in substrate concentration until it reaches a point where further increase in substrate concentration led to decrease in degradation rate.	Muneer et al., 2005
		Propachlor = 0.20-1.35 mM		
		Tebuthiuron = 0.25-1.0 mM		
Water	UV/TiO_2	-	High concentration of organic substrates is known to reduce the photonic efficiency.	Chong et al., 2010
β-blockers (atenolol & propanolol)	UV/TiO_2	5-30 mg/L	Conversion decreased with increasing concentration.	Ioannou et al., 2011
Pesticides and phenolic in wastewater	Solar UV/TiO_2	0.003-1.5 mM	As the concentration of the target pollutant increases, the pollutant degradation rate decreases.	Ahmed et al., 2011

Light Intensity and Wavelength

The photonic nature the photonic nature of the photocatalysis reaction has outlined the dependency of the overall photocatalytic rate on the light source used. The photochemical effects of light sources with different wavelength emitting ranges will have a profound consequence on the photocatalytic reaction rate, depending on the types of photocatalysts used – crystalline phase, anatase-to-rutile composition and any state of photocatalyst modifications. Using commercial Degussa P25 TiO_2, which has a crystalline ratio of anatase 70/80:30/20, a light wavelength at $\lambda<380$nm is sufficient to photonic activation (Bahnemann, 2004).

Light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength (Ahmed et al., 2011). Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency (Pareek et al., 2008). Rincón and Pulgarin (2004) reported that the residual disinfecting ability of the photocatalyst largely depends on the duration of light intensity without any temporal interruptions. They investigated the effect of light intensities at 400 and 1000mW/cm^2 on bacterial lethality and regrowth and found that the higher intensity without any temporal interruptions can cause irreversible damage to the E. coli.

Kaneco et al. (2009) investigated that the effect of irradiance on the solar photocatalytic destruction of thiram with various light intensities on sunny and cloudy days. The degradation efficiency increased rapidly with in the light intensity up to 0.4wM/cm^2, and above the intensity the efficiency increased gradually. The solar photocatalytic efficiency of bisphenol A (BPA) was reported to increase rapidly with increase in the light intensity up to 0.35wM/cm^2, and then the efficiency increased gradually (Kaneco et al., 2004). The review of studies suggested that the effect of light intensity on the photocatalytic degradation rate must be determined to ensure successful application of the photocatalytic oxidation system.

Oxidizing Agent

Electron/hole recombination is one of the main drawbacks in the application of TiO_2 photocatalysis as it causes waste of energy. In the absence of suitable electron acceptors or donors, the recombination step is predominant and thus it limits the quantum yield. Hence, it is crucial to prevent electron-hole recombination in order to ensure an efficient photocatalysis. Oxygen is required as electron scavenger to keep the photocatalytic reaction, and the amount of oxygen going into the system is an important parameter. The air (oxygen) flow into the photocatalytic system should be well regulated, as poor flow of oxygen can bring about an adverse effect on the photocatalytic reaction as reported by Chakrabarti and Dutta (2004).

Since hydroxyl radicals appear to play an important role in photocatalytic degradation, several researchers have investigated the effect of addition of electron acceptors such as H_2O_2, $KBrO_3$, and $K_2S_2O_8$ on the photocatalytic degradation of various pesticides and herbicides (Bahnemann et al., 2007; Singh and Muneer, 2004; Rahman et al., 2006; Wei et al., 2009) to enhance the formation of hydroxyl radicals as well as to inhibit electron/hole pair recombination. In most of the cases, the order of enhancement is $UV/TiO_2/KBrO_3 > UV/TiO_2/K_2S_2O_8 > UV/TiO_2/H_2O_2$.

The degradation efficiency of the UV/TiO_2/oxidant process is slightly greater in an acidic medium than in a basic medium. $KBrO_3$ was shown to be the more efficient acid as compared to H_2O_2 for improving the degradation rate of tebuthiuron, propachlor, chlortoluron, and thiram (Bahnemann et al., 2007), imazapyr (Carrier et al., 2006), dimethoate (Chen et al., 2007a) and glysophate (Shifu & Yunzhang, 2007). In contrast, H_2O_2 was reported to be efficient for propham and propachlor (Muneer et al., 2005), triclopyr and daminozid (Qamar et al., 2006), as well as dicamba and floumeturon (Rahman & Muneer, 2005a,b). The effect of oxidant addition on the photocatalytic degradation of trichlorfon is shown to be in order of: $K_2S_2O_8 > KBrO_3 > H_2O_2$ (Liu et al., 2009). Table 5 shows the review of oxidizing agent done by previous studies.

Table 5. Review of oxidizing agent used in previous studies

Contaminant	Photocatalytic System	Working Range	Findings	Reference
Azo dyes in aqueous solution	Solar/TiO_2	H_2O_2 & $S_2O_8^{2-}$	Beneficial but dependent on the substrate type and on various experimental parameters.	Konstantinou & Albanis, 2004
Pesticide (propane, propachlor, and tebuthiuron) in aqueous suspension	UV/TiO_2	Hydrogen peroxide, potassium bromate, and ammonium persulphate	All the additives enhanced the degradation rate of all the pesticide derivatives.	Muneer et al., 2005
Textile dyes	Solar/TiO_2	H_2O_2	Oxidizing agents have a greal deal of influence on the photocatalytic degradation of dyes.	Akpan & Hameed, 2009
β-blockers (atenolol & propanolol)	UV/TiO_2	0.07-1.4 mM	The use of hydrogen peroxide did not promote the extent of degradation of either subtrate.	Ioannou et al., 2011
Pesticides and phenolic in wastewater	Solar UV/TiO_2	$BrO_3^- > S_2O_8^{2-} > H_2O_2$; 0-4 mM/L	Electron acceptor is added to prevent electron-hole recombination, which is a waste of energy.	Ahmed et al., 2011

PHOTO-REACTOR

The limited part of the solar spectrum (l-400 nm) that can be used in photocatalysis with TiO_2 may be a disadvantage but, as the energy source is so cheap and abundant, even under these limitations its use is of interest. Therefore, degradation of the organic pollutants present in wastewater using irradiated TiO_2 suspensions has grown very quickly during the last few years. Although scientific research on these processes has been conducted for at least the last three decades, industrial commercial applications, engineering systems and engineering design methodologies have only been developed recently (Parent et al., 1996; Malato et al., 1999a; Blanco et al., 2000). Solar photochemical detoxification technologies (Coleccion Documentos CIEMAT, 2000) can provide the environmental waste management industry with a powerful new tool to destroy waste with clean energy from the sun.

It is worth to note that a major component of a photocatalysis system is the photo-reactor. This is a device which absorbs the incoming radiation, converts it into heat, and transfers this heat to a fluid flowing through the collector (Kalogirou, 2007). The specific hardware needed for solar photocatalytic applications is very similar to that used for conventional thermal applications with the following main differences (Jorgensen & Rangaprasad, 1991; Blake et al., 1997; Malato, 1999): The fluid must be exposed to UV solar radiation so the absorber must be transparent to this radiation and no thermal insulation is required as the temperature does not play a significant role in the photocatalytic process. Aluminum is the only metal surface that offers high reflectivity values in the UV spectrum. Photocatalytic reactors must be both transmissive and resistant to UV light. Common materials that meet these requirements are fluoropolymers, acrylic polymers and borosilicate glass and tubular photoreactor designs are the best option.

In TiO_2 heterogeneous photocatalysis, suspended catalyst systems give efficiencies higher than supported catalysts (Pozzo et al., 1997. After their use, titania powders can be agglomerated and sedimented (Watts et al., 1995; Fernandez-Ibanez et al., 2000 a, b). There are two types of reactors: non-concentrating and concentrating. The major difference between these two types of reactor is that a non-concentrating reactor, or also called as stationary collector, has no moving parts or light tracking device (Malato et al., 2009). Non-concentrating solar collectors are the choice for solar photocatalytic applications (Ajona & Vidal, 2000). They are more efficient than concentrator-based system due to the use of both direct and diffuse UV light and their intrinsic simplicity. The most frequently used reactor are parabolic trough reactor (PTR), thin film fixed bed reactor (TFFBR), double skin sheet reactor (DSSR), and compound parabolic collecting reactor (CPCR).

Parabolic Trough Reactor (PTR)

Parabolic trough collectors are made by bending a sheet of reflective material into a parabolic shape. A metal black tube, covered with a glass tube to reduce heat losses, is placed along the focal line of the receiver. When the parabola is pointed towards the sun, parallel rays incident on the reflector are reflected onto the receiver tube. It is sufficient to use a single axis tracking of the sun and thus long collector modules are produced. The collector can be orientated in an east-west direction, tracking the sun from north to south, or orientated in a north-south direction and tracking the sun from east to west. The advantages of the former tracking mode is that very little collector adjustment is required during the day and the full aperture always faces the sun at noon time but the collector performance during the early and late hours of the day is greatly reduced due to large incidence angles (cosine loss). North-south orientated troughs have their highest cosine loss at noon and the lowest in the mornings and afternoons when the sun is due east or due west.

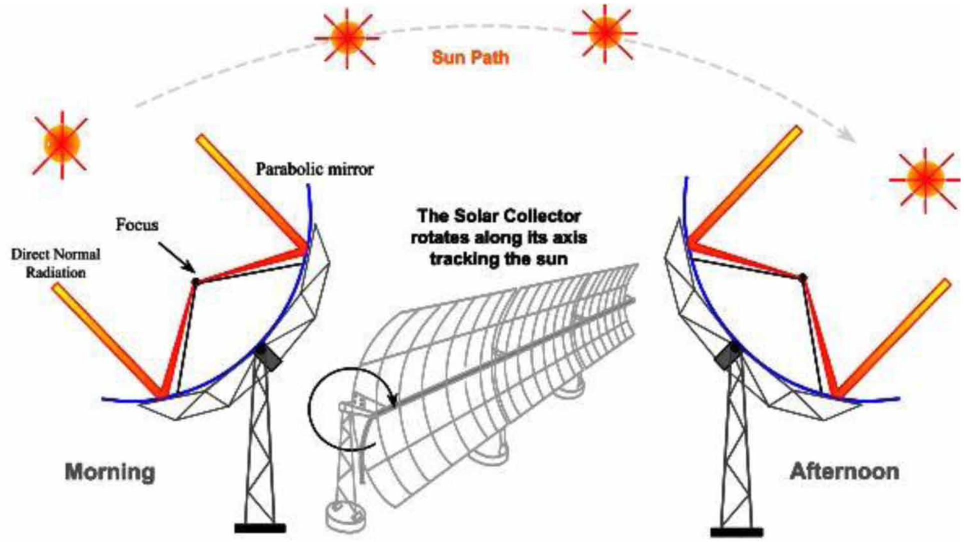
Parabolic trough collectors (PTC) can effectively produce heat at temperatures between 50°C and 400°C for solar thermal electricity generation or process heat applications. Parabolic trough technology is the most advanced of the solar thermal technologies because of considerable experience with the systems and the development of a small commercial industry to produce and market these systems. Parabolic trough collectors are built in modules that are supported from the ground by simple pedestals at either end. The receiver of a parabolic trough is linear. Usually a tube is placed along the focal line to form an external surface receiver. The size of the tube, and therefore the concentration ratio, is determined by the size of the reflected sun image and the manufacturing tolerances of the trough. The surface of the receiver is typically plated with selective coating that has a high absorptance for solar radiation but a low emittance for thermal radiation loss.

A glass cover tube is usually placed around the receiver tube to reduce the convective heat loss from the receiver, thereby further reducing the heat loss coefficient. A disadvantage of the glass cover tube is that the reflected light from the concentrator must pass through the glass to reach the absorber, adding a transmittance loss of about 0.9, when the glass is clean. The glass envelope usually has an anti-reflective coating to improve transmissivity. One way to further reduce convective heat loss from the receiver tube and thereby increase the performance of the collector, particularly for high temperature applications, is to evacuate the space between the glass cover tube and the receiver. Figure 4 shows the schematic diagram of a PTR.

Thin Film Fixed-Bed Reactor (TFFBR)

One of the first solar reactors not applying a light-concentrating system and thus being able to utilize the diffuse as well as the direct portion of the solar UV-A irradiation for the photocatalytic process is

Figure 4. Schematic diagram of a PTC



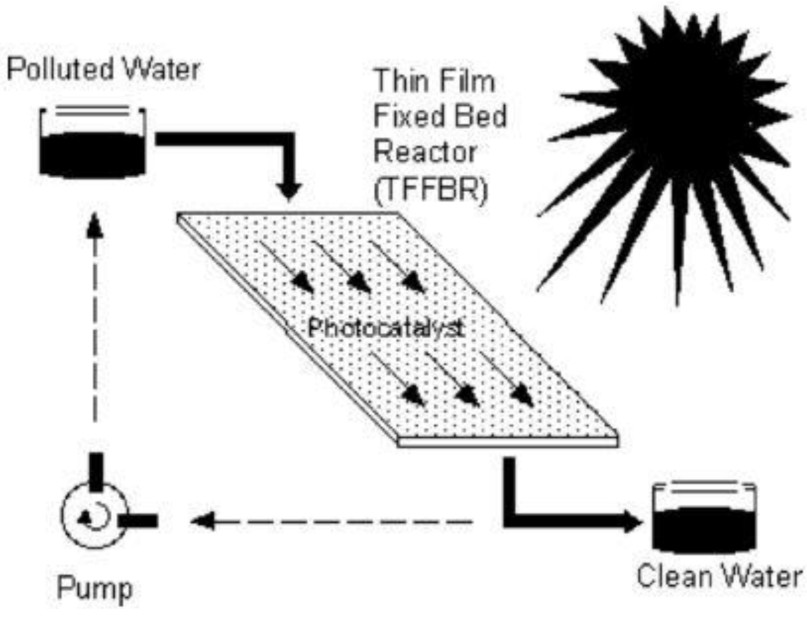
the thin film fixed bed reactor (TFFBR). It should be noted that under AM (air mass) 1.5 conditions the diffuse and direct portion of the solar radiation reaching the surface of the earth are almost equal. This means that a light concentrating system, e.g. a parabolic trough reactor can, in principal, only employ half of the solar radiation available in this particular spectral region. The most important part of the thin film fixed bed reactor is a sloping plate (width 0.6 m, height 1.2 m) coated with the photocatalyst (e.g. titanium dioxide Degussa P25) and rinsed with the polluted water in a very thin film.

The flow rate is controlled by a cassette peristaltic pump and can be varied between 1 and 6.5 L/h. Figure 5 shows one of the first TFFBR test reactors during its operation at the Plataforma Solar de Almeria in Spain. The efficiency of its performance was tested and compared with that of the PTR during several test campaigns employing both, model compounds dissolved in pure water and real wastewater samples from various industrial companies. In every case, it was observed that the efficiency of the TFFBR was superior to that of the PTR as expected based upon the above described insolation conditions effective in both systems.

Double Skin Sheet Reactor (DSSR)

A new kind of non-concentrating reactor is the double skin sheet reactor (DSSR). It consists of a flat and transparent structured box made of Plexiglass. The inner structure of the reactor is schematically drawn in Figure 6. The suspension containing the model pollutant and the photocatalyst is pumped through these channels. The comparison of the spectral irradiance of the sun (AM 1.5) with the transmission spectrum of the Plexiglass used to manufacture the double skin sheets evinces that the UV-A portion of the solar spectrum below 400nm nicely matches with the onset of the Plexiglass transmission. This type of reactor can utilize both the direct and the diffuse portion of the solar radiation in analogy to CPCR. After the degradation process the photo-catalyst has to be removed from the suspension either

Figure 5. First TFFBR operated at Plataforma Solar de Almeria



by filtering or by sedimentation for both reactors. The DSSR consists of a modified double-skin sheet (SDP 16/32) manufactured by the Rohm GmbH in Darmstadt (Germany). One module has a length of 1400 mm, a width of 980 mm and contains 30 channels each of which being 28.5 mm by 12 mm, and their total inner volume adds up to 14.4 L in a single sheet.

Compound Parabolic Collecting Reactor (CPCR)

CPCR, a non-concentrating type of reactor, is efficient for the post-reaction, separation and regeneration of the catalyst without major technical or economic problems (Geng et al., 2008). This type of technology can provide the environmental waste management industry with a powerful new tool to destroy waste with clean energy from the sun (Gálvez and Rodríguez, 2009). Wastes that can be destroyed include persistent organic contaminants that are present as pollutants in water and wastewater. Besides having the best optics for low concentration systems, the components of CPCR are simple, which also means easy and low manufacturing costs (Malato et al., 2007). Figure 7 shows the solar reflection on CPCR.

Due to the shape of CPCR that has a reflective surface below its absorber tube, it is able to collect both direct and diffuse solar radiation. The reflectors are made from polished aluminium since this material has very good reflection properties, especially in the UV-region of the solar spectrum (Bahnemann, 2004). The variety ranges of 'angle of acceptance' also enable this reactor to concentrate all the radiation that arrives within the complete perimeter of the absorber. As shown in Figure 8, the lower portion of the reflector (section P–R) is circular while the upper portion (section Q–P) is parabolic that reflects extreme rays (Rodríguez et al., 2004). While operating using this reactor, the design condition of several parameters was given in Table 6. Apart from that, Figure 9 shows the schematic diagram of the photocatalytic procedure using CPCR.

Figure 6. Schematic diagram illustrating the inner structure of DSSR

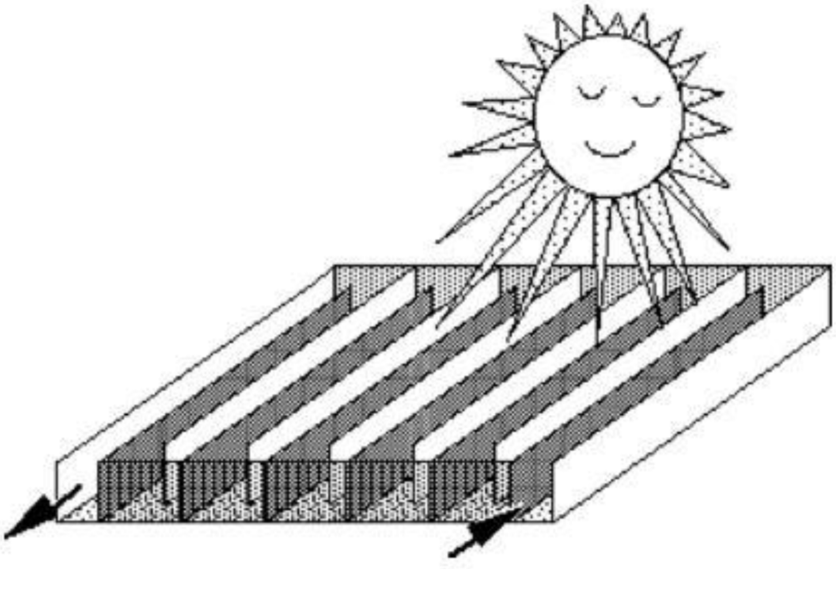


Figure 7. Solar reflection on CPCR
(Source: Gálvez and Rodríguez, 2009)

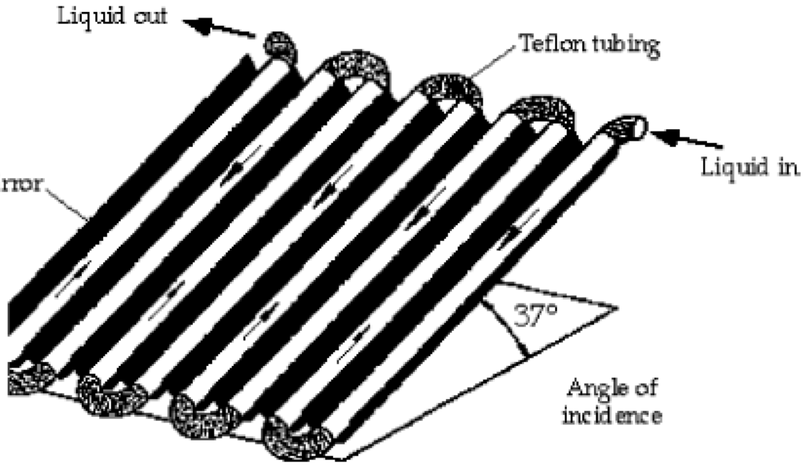


Figure 8. Schematic view of a single CPCR showing an angle of acceptance = 60˚ (Source: Rodríguez et al., 2004)

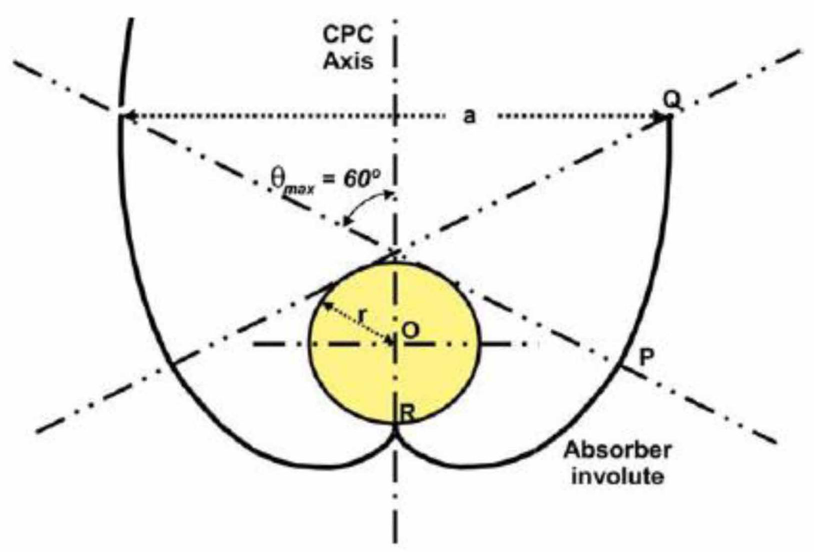
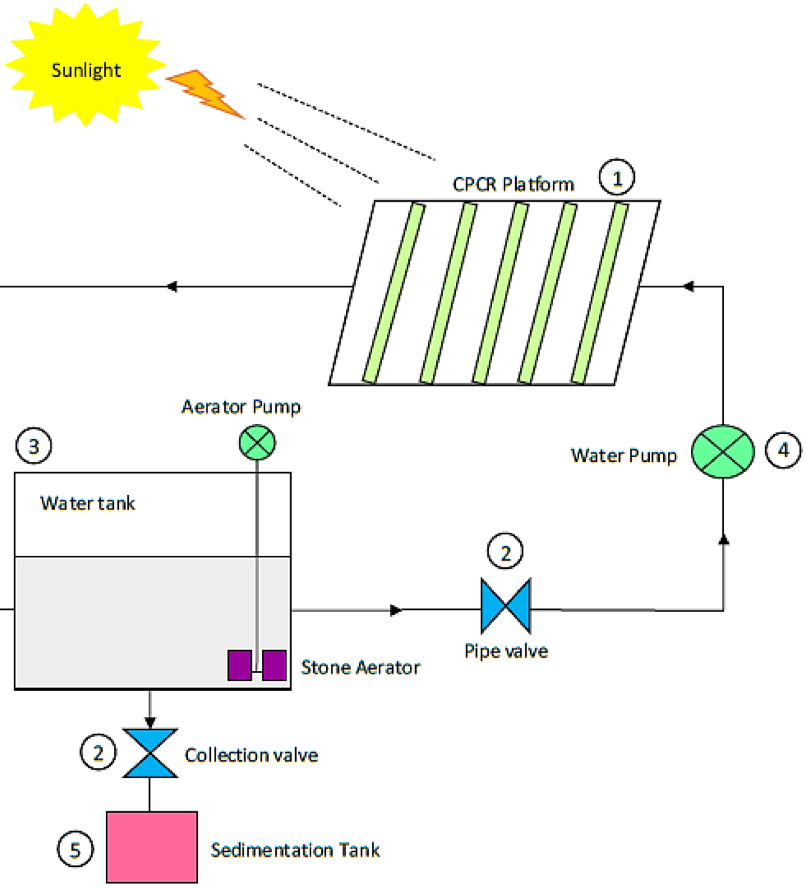


Table 6. Design condition for photocatalysis process

Parameter	Design Condition
Total sample	15 L
Flow rate	40 L/min
CPCR angle	37°
Water pump	550 W
Aerator pump	8 W

Figure 9. Schematic diagram on the photocatalytic procedure using CPCR



COMPARISON BETWEEN NATURAL SUNLIGHT AND COMMERCIAL LAMP

Table 7 presents the summary of results and comparison with several studies on heterogeneous photocatalytic treatment process. The first five studies investigated on the degradation of a PAH or OCP compound under various kinds of commercial lamp and suspended TiO_2 system. While the last study in the table implemented natural sunlight as the source of UV irradiation and suspended TiO_2 as the photocatalyst in this heterogeneous photocatalysis process.

By referring to findings in previous studies, the removal efficiencies obtained and optimum working conditions were different for each study. This might be owing to the type of reactor used, amount and nature of the pollutants, as well as the UV source itself. High removal of LIN (98%) was achieved by using mercury lamp as indicated by Begum and Gautam (2011). Senthilnathan and Philip (2012), who compared the efficiency of using commercial lamp and solar radiation in their research, obtained 98% and complete removals of LIN, respectively.

This can be further proven through the experimental results obtained in the present study. FLT, PYR, LIN, and DDT, which attained high removals of 66% to 90%, indicate an excellent performance of the natural sunlight used to initiate this TiO_2-based treatment process. Overall, the use of solar radiation

Table 7. Summary of results and comparison with previous studies

Reference	Photocatalytic System	Working Condition	Findings
1. Lair et al. (2008)	-**Mercury lamp** (125 W, $\lambda = 365$ nm) -NAP -Pyrex glass flask -25 mL mixture solution -30 m of irradiation time	-TiO$_2$ loading = 2.5 g/L -Initial concentration = 5 mg/L -pH = 4.4 (unbuffered)	-k = 2.2 μmol/min.
2. Begum and Gautam (2011)	-**Mercury lamp** ($\lambda = 254$ nm) -LIN -Photochemical reactor -150 mL mixture solution -60 m of irradiation time	-TiO$_2$ loading = 0.3 g/L	-98% removal of LIN was noticed, with k= 0.0626 mg/L·min.
		-Initial concentration = 7.5 mg/L	
		-pH = 7	
3. Senthilnathan and Philip (2012)	-**UV lamp** (125 W, $\lambda = 365$ nm) -LIN -Fixed bed continuous photoreactor -6 h of irradiation time	-Initial concentration = 100 μg/L	-98% removal of LIN was detected.
	-Sunlight -LIN -Fixed bed continuous photoreactor -6 h of irradiation time		-100% removal of LIN was detected.
4. Mahmoodi and Sargolzaei (2014)	-**UV lamp** (8 W, $\lambda = 365$ nm) -NAP -Photochemical reactor -100 mL mixture solution -170 min of irradiation time	-TiO$_2$ loading = 2.17 g/L	- 66% of NAP was removed.
		-Initial concentration = 20 mg/L	
		-UV intensity = 16 W	
5. Karam et al. (2015)	-**UV lamp** -NAP -Closed system reactor -150 min of irradiation time	-TiO$_2$ loading=0.175g/L	-58% removal of NAP was achieved.
		-Initial concentration = 25 mg/L	
		-UV intensity = 2 mW/cm^2	
		-pH = 7	
6. Present study (2017)	-**Sunlight** -FLT, PYR, LIN, DDT -CPCR -15 L mixture solution	-TiO$_2$ loading = 1.54 g/L	-FLT (88%; k = 0.0145 mg/L·min)
		-Initial concentration = 125 μg/L	-PYR (90%; k = 0.0176 mg/L·min)
		-pH = 7	-LIN (66%; k = 0.0111 mg/L·min)
			-DDT (79%; k = 0.0128 mg/L·min)

and commercial lamp are suitable to be implemented in the heterogeneous photocatalytic process, since both systems offer good removal efficiencies of the organic micro-pollutants present in the environment.

However, the solar photo-catalyst of TiO_2 process can be an advantageous technique for purifying water containing organic contaminants, especially in remote arid sunny places, where water supply will be a crucial problem in the future. Furthermore, the use of unlimited natural sunlight can hinder the high energy consumption, thus maintaining a sustainable environment in the water treatment industries. Successful implementation of this photocatalysis process to treat rainwater can be a great contribution towards improving living quality since substantial amount of water could be provided, and at once, could reduce the high demand on the existing water supply systems.

KINETIC MECHANISM IN PHOTOCATALYSIS

Photocatalysis is time dependent process and it is very imperative to determine the rate of photocatalysis for designing and evaluating the photocatalyst in removing the pollutants from water (Pete et al., 2014) The disappearance rate of organic compounds mostly follows a pseudo-first-order kinetics according to the Langmuir–Hinshelwood (L–H) model (Yang et al., 2010). When the concentration of contaminants are low, the degradation performance follows the apparent first-order rate law or the Chick-Watson model as below (Xu et al., 2013).

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app} \cdot t \qquad (10)$$

where k_{app} represents the pseudo first order rate (min^{-1}), whereas C_0 and C_t are the concentrations at time 0 and t, respectively.

Typically, the photocatalytic process can be characterized by the Langmuir-Hinshelwood model, which has been widely used to describe solid-liquid reactions (Lazar et al., 2012). In photocatalytic processes, the interaction of the organic compounds with the semiconductor surface plays a major role (Khataee et al., 2010). Adsorption of these compounds on the catalyst's surface is a prerequisite for a high efficient process. The Langmuir-Hinshelwood rate expression is given by the following equation:

$$\frac{1}{k_{app}} = \frac{1}{k} C_0 + \frac{1}{k, K} \qquad (11)$$

where k is the rate constant of surface reaction (g/L · min), K is the Langmuir adsorption constant (L/g), and C_0 is the initial concentration of pollutant (μg/L) (Khezrianjoo and Revanasiddappa, 2012).

POTENTIAL ADVANTAGES AND DISADVANTAGES OF PHOTOCATALYSIS

It was first discovered by Fujishima and Honda in 1976 about the photocatalytic process of titanium dioxide, which decomposes water into hydrogen and oxygen in the presence of light irradiation (Al-

Rasheed, 2005). It has since triggered many research studies on photocatalysis in the whole world (Akpan & Hameed, 2009a; Fisher et al., 2013; Ibhadon & Fitzpatrick, 2013; Kaneco et al., 2006; Li et al., 2005; Ochuma et al., 2007; Sichel et al., 2007). This photocatalysis treatment method of semiconductor has some great advantages and also disadvantages in its application.

Advantages of the Process

Photocatalytic treatment method offers several advantages. The most important merit of using heterogeneous photocatalysis is that its ability to completely mineralize the organic pollutants in the environment, such as pesticides, herbicides, and micro-pollutants such as endocrine disrupting compounds, which are not able to be destroyed in secondary water treatment (Madhavan et al., 2010). Rather than merely transferring them to another phase, it even destroys pollutants without the use of potentially hazardous oxidants, such as ozone and chlorination (McCullagh et al., 2010). Herbicides and pesticides that may contaminate water, such as 2,4,5-trichlorophenoxyacetic acid, 2,4,5-tricholorophenol, triazine herbicide and DDT have been successfully degraded (Ibhadon & Fitzpatrick, 2013).

The oxidation process that takes place in photocatalysis can be completed within a few hours only. Availability of highly active and cheap catalysts, such as TiO_2, capable of adapting to specially designed reactor systems also makes this method practical to be used (Devipriya & Yesodharan, 2005). Furthermore, the catalyst itself is unchanged during the process and no consumable chemicals are required. This results in considerable savings and a simpler operation of the equipment involved (Al-Rasheed, 2005). The reactions, mostly proceed under mild conditions, e.g. under ordinary temperature and pressure, and therefore are safe (Kohtani et al., 2012).

Besides that, the energy use of photo-exciting the catalyst is obtained from the sun and the oxygen necessary for the reaction can be directly obtained from the atmosphere. Both of these sources are free, and thus can supply unlimited sunlight and oxygen (Malato et al., 2009). Additionally, since the process gradually breaks down the contaminant molecule, no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. This also means that the end products formed are harmless products, which are carbon dioxide and water (Al-Rasheed, 2005).

Disadvantages of This Process

Despite the aforementioned advantages, there are also drawbacks of photocatalysis. One of them is that this method is unsuitable for a large-scale synthesis, because the rate of surface reaction on photocatalysts under irradiation are limited by electron-hole recombination, smaller surface area, lesser adsorptive and diffusive properties of substrates compared to those of the conventional catalysis. Therefore, up to now, scaling-up of the semiconductor photocatalysis has been successfully applied to water and wastewater treatment, in which solar photocatalytic degradation of water contaminants and persistent toxic compounds is carried out in the low concentration of the contaminants.

The photocatalytic treatment of contaminated water probably yields various intermediates in irregular and uncontrollable radical reactions, and they may be toxic. Hence, it is important to determine the photocatalytic degradation pathway to ensure zero content of intermediate products at the end of the process. In the TiO_2 photocatalysis of aromatic compounds, several researchers have reported initial hydroxylation of aromatic rings by hydroxyl radicals and sequential ring cleavage occurred throughout the photocatalytic treatment of intermediates (Abellán et al., 2007; Lambropoulou et al., 2008; Zhang, L. et al., 2008).

In addition, in water treatment, the catalyst surface coverage is dominated by water molecules, which are linked to the hydroxyl groups by hydrogen bonds. This can render the approach of the organic pollutants to the catalyst surface difficult, especially for those compounds that are very soluble. However, studies have shown that even poorly adsorbed pollutants can be degraded, presumable because the organic molecules degraded in these cases are not limited to those located in the surface layer (Jenks, 2013).

APPLICATION OF PHOTOCATALYSIS IN WATER AND WASTEWATER TREATMENT

In the last 10 years, heterogeneous photocatalysis has been demonstrated as a low cost and sustainable technology for the treatment of pollutants in the air and water including organics and heavy metals (Ahmed et al., 2011; Chong et al., 2010). Unlike reverse osmosis, nano and ultrafiltration, photocatalysis is a cheap and a potential technology for water treatment. As photocatalysis makes use of sunlight or UV radiation, the technology is inexpensive, environmentally friendly and can be applied worldwide. It requires minimal equipment, is highly deployable and appropriate for developing countries and remote sites with no access to electricity (Ibhadon and Fitzpatrick, 2013). Table 8 shows recent examples of water pollutants which are photocatalytically degraded by TiO_2.

CONCLUSION

In recent years, heterogeneous photocatalysis has been a promising technology used to remove various organic compounds present in very low concentrations. In order to urge the continuous pursue of better treatment strategies, a few recommendations were drawn for future research: Deep investigations on the identification of the reaction intermediates should be included in the future work. For practicing better ecological balance, future research should focus on the recovery and stability of the TiO_2 photocatalyst,

Table 8. Recent examples of pollutants photocatalytically degraded by TiO_2

Contaminant	Photocatalytic System	References
Pesticides & herbicides		
Organophosphate and Phosphonoglycine	UV/TiO_2 immobilized on silica gel	(Echavia et al., 2009)
Azimsulfuron	UV/TiO_2 coated on glass rings	(Pelentridou et al., 2009)
Swep residues	Simulated sunlight/TiO_2 (Degussa P25)	(Fabbri et al., 2009)
Others		
N,N-diethyl-m-toluamide (Insect repellent)	UV/TiO_2 (Degussa P25)	(Adams and Impellitteri, 2009)
β-naphthol	UV/TiO_2-SiO_2	(Qourzal et al., 2009)
15 emerging compounds	Solar UV/TiO_2 coated on glass spheres	(Miranda-Garcia et al., 2010)
Endocrine disrupting compounds	UV/TiO_2 (Degussa P25)	(Zhang et al., 2012)

(Source: Lazar et al., 2012)

so that it can be re-used in the subsequent batch treatment. In such a way, the efficiency of the process gains importance not only for the economic viewpoint, but also for clean disposal of the treated effluent. In a nutshell, heterogeneous photocatalysis can be an advantageous technique for purifying water and wastewater containing organic contaminants, especially in remote arid sunny places, where water supply will be a crucial problem in the future. Other than that, the use of unlimited natural sunlight as the UV source can hinder the high energy consumption, thus maintaining a sustainable environment in the water treatment industries.

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Chapter 9

Groundwater Treatment via Ozonation

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ABSTRACT

Groundwater is the source of drinking water that needs to be maintained from pollution. Groundwater pollution is a major problem caused by human activities that are invaluable to human health. When high levels of organic and inorganic substances do not exceed the standard of drinking water, various studies have been made by researchers to overcome the problem. Various alternatives such as in-situ and ex-situ treatment have been carried out to eliminate pollutants from groundwater. Among the treatment, ozone becomes a major alternative because of its effectiveness in treating raw water. Ozone treatment has several advantages such as disinfectants, oxidize of organic and inorganic pollutant, and remove taste and color from groundwater. The performance of ozonation process becomes better when combined with other treatments. Therefore, application of ozone can replace chlorine because of its good potential to improve quality of groundwater effluent and comply drinking water standard adopted by World Health Organization.

INTRODUCTION

This chapter consist of two (2) main topics. Topic 2 is divided into five (5) sub-topics which includes drinking water governance in Malaysia, groundwater characteristics, groundwater issues, groundwater pollutants and various techniques of remediate pollutant in groundwater. The topic also identifies the causes and problems of groundwater pollution which affects the quality of drinking water. Moreover, several case studies on groundwater pollution problems throughout the world are also discussed in this topic.

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The second topic also explores the application of ozone in in water. The ozone functions in water treatment are also described in this topic. The mechanism and oxidation reaction between ozone and pollutant are also explained here. Previous studies on ozone application in water treatment are also reported to support the use of ozone later. Comparisons between ozone alone and a combination with other water treatments is also presented in this chapter. Overall, this topic helps to give a thorough understanding on the potential use of ozonation in groundwater.

GROUNDWATER

Groundwater occurs naturally through the hydrologic cycle by an aerial recharge and losses from surface water. Precipitation is the source of an aerial recharge. As aerial recharge occurrences are over a broad area, the amount of rainfall received are proportional to the formation of groundwater. Water bodies such as rivers, lakes, wetlands, ocean, coast and estuaries are main sources of groundwater recharge from water losses (Li et al., 2016). However, as almost all surface water interacts with groundwater continuously, the formation is reversible (Stahn & Tomini, 2017).

Globally, groundwater is the most extracted raw material with an average extraction of 600 to 700 km^3 annually (Pandey et al., 2011). On the contrary, groundwater contributes less than 10% of total water usage in Malaysia. Most of the groundwater supply are for domestic usage largely at remote or rural areas. 40% of the water supply particularly in rural areas are provided by groundwater (Nazaruddin, 2017). Furthermore, this sourcing method is also found to be commonly used to support the demand from industrial sectors as well as population growth. Nazarudin et al. (2017) also stated that newly opened housing development areas that are remote and where water supply is limited or at over-populated area would benefit from this groundwater harvesting method. Meanwhile, the state of Kelantan has been drilling tube well in coarse sand aquifers since the past 40 years. 624,389 people living in Kota Bharu and Bachok extract groundwater for their daily usage (Sefie et al., 2015).

The failure in distinguishing the boundless potentials of the resources are the main cause for the limited exploitation of groundwater in Malaysia. As Malaysia is blessed with an abundance of rainfall, the principal in water sustainability and resources primarily in groundwater management will benefit the country in the snowballing demand of water (Ayob & Rahmat, 2017).

Drinking Water Governance in Malaysia

The quality of drinking water in Malaysia is ruled by the National Standard for Drinking Water Quality and WHO Guidelines for Drinking Water Quality (Ambu et al., 2014). Water quality index is used to assess the suitability of water for a variety of uses. Table 1 and Table 2 shows the water quality index and water quality classification respectively as proposed by the Department of Environment (DOE), Malaysia. The water quality can be classified based on several parameters such as Ammonical Nitrogen (AN), BOD, COD, DO, pH and TSS. In Malaysia, water supply can be classified from Class I to Class V, from clean to the worst quality of water.

Groundwater quality are characterised by criteria such as contents of microbiological, physical, chemical and radioactive constituents. Drinking water quality standard is provided for water to be used for human consumptions. It must be clear without unpleasant taste, colour and odour (EPA, 2012). Table 3 shows the comparison standard for microbiological parameters in Malaysia and other countries for

Table 1. DOE water quality index

		CLASS				
Parameter	**Unit**	**I**	**II**	**III**	**IV**	**V**
AN	mg/L	< 0.1	0.1 – 0.3	0.3 – 0.9	0.9 – 2.7	> 2.7
BOD	mg/L	< 1	1-3	3-6	6-12	>12
COD	mg/L	<10	10-25	25-50	50-100	>100
DO	mg/L	>7	5-7	3-5	1-3	<1
pH	-	>7	6-7	5-6	<5	>5
TSS	mg/L	<25	25-50	50-150	150-300	>300
WQI	mg/L	<92.7	76.5 -92.7	51.9-76.5	31.0-51.9	>31.0

microbiological characteristic. The presence of total coliform in drinking water is harmful to human health. According to Standard of European Council (EC), they allowed the presence of coliforms which should not exceeded 10 /100 mL of water sample. However, the standard quality of drinking water in Malaysia is more stringent compared to other countries such as Canada and United States. Table 4 below compare the groundwater quality standard from different countries in South East Asia and Asia.

In addition, National Hydraulic Research Institute of Malaysia (NAHRIM), Minerals and Geoscience Department (JMG), Department of Environment (DOE), water supply department and local councils are amongst the government agencies monitoring the quality of groundwater. Chemical, heavy metals and microbial are also raising concern in terms of pollution documented irrespective to the purpose of monitoring.

Table 2. Water quality classification

Sub-Index & Water Quality Index	Index Range		
	Clean	**Slightly polluted**	**Polluted**
BOD	91-100	80-90	0-79
NH_3-N	92-100	71-91	0-70
SS	76-100	70-75	0-69
WQI	81-100	60-80	0-59

Table 3. Microbial water quality standard (Chan, Zalifah, & Norrakiah, 2007)

	Malaysia	**UK**	**EC**	**WHO**	**Canada**	**US**
Faecal coliforms	0/100 mL	0/100 mL	0/100 mL	0/100 mL	0/100 mL	0/100 mL
Coliforms	0/100 mL	n/s	n/s	0/100 mL	10/100 mL	1/100 mL
Total bacteria count	n/s	n/s	10/100 mL	n/s	n/s	n/s
Total coliforms	0/100 mL	0/100 mL	0/100 mL	-	-	-
Faecalis streptococcus	0/100 mL	0/100 mL	0/100 mL	-	-	-

n/s: not stated

Table 4. Comparisons of the groundwater quality standard from different countries in South East Asia and Asia

Parameters	Unit	COUNTRY						
		Malaysia	**Thailand**	**Vietnam**	**Indonesia**	**Philippines**	**Korea**	**China**
pH		6 - 9	6.5 - 9.2	6.5 – 8.5	6-9	6.5-8.5	5.8–8.5	6.5–8.5
Turbidity	NTU	50	20		-		<1 NTU	≤3
Ammoniacal nitrogen	mg/L	0.3			0.5	0.05	<0.5 mg/L	0.02
Biochemical oxygen demand	mg/L	3			2			
Chemical oxygen demand	mg/L	25			10			
Dissolved oxygen	mg/L	5-7			6	5		
Colour	TCU	150	15	5 - 50		50		≤5
Electrical conductivity	μS/cm	1000				-		
Odour	-	N				-		-
Salinity	%	1				-		
Taste	-	N				-		-
Total dissolved solid	mg/L	1000	1,200			-		≤500
Total suspended solid	mg/L	50		750 - 1500		50		
Total coliform	Count/100 mL	5000	< 2.2	3		-	Non-detection/100 mg	≤3000
Total phosphate as P	mg/L				0.2	0.5	-	
NO_3 as N	mg/L				10	7	<10 mg/L	≤5.0
Iron	mg/L		1.0	1-5	0.3	1	<0.3 mg/L	≤0.2
Lead	mg/L			0,05	0.03	0.01	<0.01 mg/L	
Manganese	mg/L		0.5	0.1-0.5		0.2	<0.3 mg/L	≤0.05
Mercury	mg/L		0.001	0,001		0.001	<0.001 mg/L	≤0.0005
Nickel	mg/L					0.02	-	≤0.05
Zinc	mg/L		15.0	5.0		2	<3 mg/L	≤0.5
Arsenic	mg/L		0.05	0,05	0.05	0.01	<0.01 mg/L	≤0.01
Cobalt	mg/L				0.2		-	
Barium	mg/L				1	0.7	-	≤0.1
Boron	mg/L				1	0.5	-	
Fluoride	mg/L		1.0	1.0		1	<1.5 mg/L	≤1.0
Selenium	mg/L		0.01	0,01	0.01	0.01	-	≤0.01
Cadmium	mg/L		0.01	0,01	0.01	0.003	<0.005 mg/L	≤0.001
Chrom (IV)	mg/L			0,05	0.05		-	
Copper	mg/L		1.5	1,0	0.02		<1 mg/L	≤0.05
Sulfate	mg/L		250	200-400			<250 mg/L	≤150

Source: National Environmental Quality Act B.E.2535 (1992), (Ministry of Environment. Drinking Water Management Act, 2017), (National Technical Specifications on the Environment (Quy chuẩn kỹ thuật quốc gia về môi trường -QCVN), (Lee et al., 2017; Wang et al., 2016; Nguyen & Loan, 2012; DOE, 2005).

Groundwater Characteristics

Groundwater quality is identified by the physical, chemical and microbial characteristics. Physical characteristics includes temperature, turbidity, colour, odour and taste. Chemical characteristics are mainly the concentration of inorganic substances such as heavy metals, ammoniacal nitrogen, chemical oxygen demand, biochemical oxygen demand including the parameter such as pH and conductivity. In the determination of the presence of coliform organism, microbial characteristic is very important (Ojo, Otieno, & Ochieng, 2012).

Heavy metals in groundwater occur naturally under the Earth's surface or through groundwater recharge mechanism. Frequently, heavy metals entering groundwater from the interaction during weathering of soils and rocks (Belkhiri et al., 2017). The serious problems of high concentration were found in Bangladesh where the arsenic concentration is found to be greater than 1000μg/L. The presence of arsenic in water can lead to lung, kidney, liver and prostate cancer (Nordstrom, 2002; Smith et al., 2006). According to Mohora et al. (2014), more than 600 000 people in Vojvodina, north province of Serbia, use groundwater that contains high level of arsenic. Based on World Health Organization (WHO), the maximum allowable limit of arsenic for drinking water is 10 μg/L. Other than arsenic, iron and manganese are the majority constituent of metal elements found in the Earth crust. The presence of iron and manganese in groundwater caused by rain filtering process through soil, rock and mineral and dissolve the minerals containing iron and manganese in the soluble form as ferrous iron (Fe^{2+}) or complex form as ferric iron (Fe^{3+}). Fe and Mn as shown in Table 5, are the common heavy metals contaminated in groundwater. Other factors influencing the concentration of heavy metals includes environmental reaction or soil condition such as acidity or alkalinity, oxidation or reduction, sorption or ion exchange (Hashim, Mukhopadhyay, Sahu, & Sengupta, 2011).

Colour occurs naturally in the groundwater because of an interaction between water and the minerals, soils and rocks, or contamination from anthropogenic activities on the Earth's surface (WHO, 2017). Traces of colouring found in groundwater do not suggest direct toxicity level. However, intense colours could lead to the reduction of light penetration into the water (Mezzanotte, Fornaroli, Canobbio, Zoia, & Orlandi, 2013).

Anthropogenic activities may contaminate groundwater during water infiltration from the Earth's surface. Contaminant from landfill, pesticides, fertilizer, septic tank, treatment facilities migrated into groundwater directly through infiltration or water losses from polluted water bodies (Galitskaya et al., 2017). Hence, groundwater quality directly subjected to the condition of soils, rocks and surface waters.

Groundwater Pollution

Groundwater pollution has been found in many places. Organic chemicals such as trichloroethylene, 1,1, 1-trichloroethane, benzene, perchlorate, gasoline, pesticides and nitrates are among the main causes. Besides that, other sources such as industrial and municipal landfills, waste oil, leakage of storage tank and pipe, illegal garbage dump and abandoned oil and gas wells are also a direct cause to groundwater pollution albeit at different level of severity.

Organic and inorganic chemical pollution of groundwater might continue for several decades or longer. This is due to fact that the groundwater movement is generally slow, which may not be detected for several years. Factors that influence groundwater movement are geological formation, soil permeability, rainfall infiltration and hydraulic gradient. Slow uniform flow allows for only little mixing and dilution

Table 5. Initial concentration of groundwater pollutant from previous literature (Akbar, Aziz, & Adlan, 2015)

Groundwater Sources	Pollutant	Concentration (mg/L)	Author
Northern Greece	Fe Mn	0.165 0.235	Katsoyiannis, Zikoudi, & Hug (2008)
Bangladesh	As	1	Mondal, Balomajumder, & Mohanty (2007)
Greece Country	Fe Mn	0.1-1.13 0.009 – 0.016	Kim & Nriagu (2000)
Kelantan,Malaysia	Fe Mn	0.1-27 0.1-19	Akbar et al. (2015)
Tioman Island, Pahang, Malaysia	Fe Mn	0.6 -1 < 0.1	Plan, Pengurusan, & Tanah (2011a)
Jenderam Hilir, Selangor, Malaysia	Mn	1.9-5.6	Plan, Pengurusan & Tanah (2011b)

to occur. Now, presence of air in groundwater (which function to decompose or breakdown contaminant) also contributes to the problem.

On the contrary, dilution, microbial activity, soil adsorption behaviour and surface tension might contribute in altering, transferring or alternating the movement of the pollutants. groundwater pollution and protection of well head should be given more attention.

Groundwater may contain elements that are not visible to human eyes such as microorganisms, organic and inorganic compounds that could be harmful to human just like most naturally occurring substances, (Adelana, 2014). As water scarcity is becoming more serious in recent times, more and more studies on groundwater treatment emerge. However, feasibility of each study heavily relies on the overall environment factors such as air pollution levels and geolocation of the aquifer as different areas might yield different readings on soluble contaminants and harmful substances.

Several studies suggested that chemical compounds in groundwater continue to change during hydrologic cycle. According to Belkhiri et al. (2017), samples taken from industrialized area often result in acidic precipitation due to high concentration of nitrogen and sulphur; compounds associated with pollution due to industrial activities. Studies also suggested that higher concentration of sodium chlorides found in the precipitation reading on areas that are close to the ocean (Isa and Aris, 2015).

Moreover, Sapari et al. (2011) also pointed out that soil quality also determines the acceptable values of parameter associated with groundwater quality. Carbon dioxide is not only dissolved in groundwater, but it is a natural component found in abundance in soil that would dissolve in groundwater; and as part of hydrologic process, formed acidic reaction that would further influence the changes of chemical compound in groundwater (Belkhiri et al., 2017). Consequently, these processes would influence turbidity, colour, pH, total dissolved solids and heavy metals; all of which are parameters that are associated with the assessment of groundwater quality.

Case Study 1: Groundwater in Kelantan

Only 65% of the total population are covered by the public water supply in Kelantan. This figure also represents the number of population consuming both water supply from public utilities and groundwater.

The remaining 35% of the population in Kelantan merely extracts groundwater for drinking purpose and daily usage (Idrus et al., 2014).

The quality of groundwater system provided by Water Supply and Environmental Sanitation Programme (BAKAS) in 2013 is investigated by the Kelantan State Health Department (Idrus et al., 2014). The purpose of the investigation was to identify the level of groundwater quality in 9 districts involving 454 wells. The districts involved are Bachok, Gua Musang, Kota Bahru, Kuala Krai, Machang, Pasir Mas, Pasir Puteh, Tanah Merah and Tumpat. Sampling of groundwater was performed between March to December of 2013.

49% out of the 454 samples are contaminated with total coliform as revealed from the microbiological study. The highest level was recorded in the district of Kota Bahru. 14% of the samples are reported to be polluted by E-coli. Meanwhile, through chemical studies it was discovered that the highest contamination level was iron (39%) followed by manganese (29%), ammonia (6%) and the lowest which is aluminium (1%). Average level of iron and manganese were 0.76 mg/L and 0.27 mg/L respectively. The concentration of both heavy metals exceeded the National Standard of Drinking Water, above 60% (MOH, 2016). The highest level of iron and manganese violation were recorded at the district of Kuala Krai and Kota Bahru. However, nitrate level, turbidity and pH met the drinking water quality in all 454 wells, except for the turbidity level in the district of Tanah Merah, 11.18 NTU.

National Hydraulic Research Institute of Malaysia (NAHRIM) located a total of 37 monitoring wells in Kelantan (Anuar Sefie, 2017, pers. comm, 25 July). The area covered were mainly residential and agricultural. As reported in 2014, the average level of iron was 0.54 mg/L, 44.37% higher than the drinking water standard. The highest level of iron recorded is 7.53 mg/L at Kampung Wakaf Zin. The monitoring well was located at an agricultural area. The lowest level of iron is 0.02 mg/L which was recorded at Kampung Tegayong, Pondok Pasir Tumbuh and Kampung Tawang. Meanwhile the average level of manganese is 0.11 mg/L, only 4.81% higher than the drinking water standard. The highest level of manganese is 0.66 mg/L which was recorded at Kampung Padang Mokkan which is an agricultural area. The highest level of sodium and potassium were both within the drinking water standard.

Case Study 2: Groundwater in West Coast of Peninsular Malaysia

The development of groundwater harvesting in Malaysia are induced by the population growth and opening of new areas for housing and industrial activity. Most of the developments are located on a metasedimentary rocks layer with a very low porosity and permeability. A study completed in 2011, investigated the availability and the quality of groundwater in this area (Sapari et al., 2011).

Inspection was conducted at 66 existing tube wells in Selangor, Melaka, Kedah and Negeri Sembilan. For industrials and drinking water supply, the tube wells were constructed by private companies. The location of the wells is mainly at construction areas, manufacturing, residential, school and agricultural areas. The deepest tube well recorded was at a depth of 200 meters while the average depth was found to be around 146 meters.

In general, the groundwater can be classified as fresh water as 74% of the wells produced water with an average of 100 to 150 mg/L total dissolved solids (TDS). The hardness level in the groundwater were moderate with an average of 80.28 mg/L. 27 out of 66 wells recorded hardness level below 61 mg/L. The maximum TDS and hardness recorded were 200 mg/L and 337 mg/L which were 80% and 32% lower than drinking water quality standard accordingly.

The study reported that the iron concentration was in the range of from undetectable to as high as 14.8 mg/L. 54 tube wells out of 66, discovered containing iron exceeding the Malaysia Drinking Water Standard. 36 tube wells recorded significant iron content with an average of 2.39 mg/L. There was no manganese content reported in the study. Due to the characteristics of metasedimentary rock containing mineral such as pyrite (FeS_2), the occurrence of iron in high concentration are natural.

Groundwater at metasedimentary rocks in the West Coast of Peninsular Malaysia are capable of supplying water at the average of 381 m^3 daily. The availability has contributed to the development of industrial activities in the area. Continuous extraction should be supported by an application of treatment mechanism in avoidance of long term exposure of heavy metals towards human living as the areas are associated with industrial activities, as recommended by the report.

Case Study 3: Groundwater in Jenderam Hilir, Selangor

Study on the quality of groundwater in Jenderam Hilir, Selangor was conducted by National Hydraulic Research Malaysia (NAHRIM) in 2011. The concentration of Fe from 8 wells are between 14 to 39 mg/L which exceeds drinking water standard, i.e 0.3mg/L. Analysis made by the NAHRIM found that the content of arsenic in groundwater is very high above drinking water standards compared with mercury, copper, zinc, chromium and lead. Six of the wells in Jenderam Hilir contain high arsenic level which exceeds drinking water standard of 0.1mg / L. Arsenic levels in the groundwater increases as the direct result of the use of uncontrolled pesticides and herbicides for agricultural activity.

Besides, analysis on microbiological species has been done in this study to comply drinking water standard requirement. Two of the samples were collected from upstream and downstream of Sungai Langat and another one from tube well. Based on the analysis, Giardia cyst was present in Sungai Langat with concentration of 0.1-2.9 cysts/l. In contrast, there is no Giardia cyst in tube well. In addition, total coliforms and E. coli were not detected in groundwater samples.

Groundwater Treatment Technology

Approach in the groundwater purification was conducted by either chemical, physical or biological treatments. The treatment mechanisms vary from Fu and Wang, 2011; Ojo et al., 2012. Three pillars in sustainable assessment of developing technologies in groundwater remediation are economic, environmental and is permissible in its social aspect (An et al., 2016). Furthermore, pollutants concentration, component of wastewater, removal or treatment effectiveness, capital investment and operational cost, plant flexibility, skills, chemical or substances required availability and environmental impact all plays important roles in determining the selection of treatment method.

Groundwater contamination occurrences easily scattered, involving large volume of storage. Conventional treatment mechanisms are incapable of purifying heavily polluted groundwater. Fundamental in chemical treatment are decreasing toxicity and mobility by converting contaminants such as heavy meals into an inactive and stable form (Hashim et al., 2011). Meanwhile, physico-chemical treatment technologies includes adsorption, filtration and permeable reactive barriers (PRB). Aeration and rapid sand filtration are commonly found in conventional groundwater treatment mechanism as the methods are economical, chemical free and able to produce biologically stable drinking water (Gude et al., 2017).

The interaction of contaminants with certain plants and micro-organism are the fundamental in the biological remediation mechanism (Hashim et al., 2011). The removal of heavy metal in groundwater in biological treatment is one such example. This occurrs through mechanism such as adsorption, oxidation and reduction reactions.

Review on Groundwater Remediation

As groundwater is one of the water sources to human, the quality of groundwater become a great interest nowadays. However, groundwater can also be affected and be contaminated from various ways such as waste dumps, tailing facilities, agricultural activities and leachate from the landfill (US Office of Water, 1990). Therefore, numerous different technologies for the remediation of groundwater has been applied for the treatment of contaminated groundwater. Basically, the groundwater remediation can be classified into three (3) different classes which are i. Chemical treatment technologies i. Biological/biochemical/biosorptive treatment technologies and iii. Physico-chemical treatment technologies (Hashim et al., 2011).

It is hard to treat contaminated groundwater using the conventional types of remediation because the contaminants are usually dispersed in plumes overlarge area and deep below the surface. Therefore, the chemical remediation technologies came to light and become the best choice. The toxicity or mobility of metal contaminants are decreased by chemical by converting them to inactive condition. Some of the example of chemical treatment technologies that can be applied are oxidation, reduction and also neutralization (Evanko & Dzombak, 1997; Hashim et al., 2011). Meanwhile, the physic-chemical treatment depends on the physical processes/activities and usually it involves the combination of two or more processes in order to decontaminated the pollutants. On the other hand, the biological treatment process uses or apply the natural biological processes which allow plants or other micro-organisms to work and remediate the polluted groundwater. Some of the most applied biological treatment technologies are adsorption, oxidation and reduction reactions (Means & Hinchee, 1994). Table 6 below listed the efficiency of different technologies for the remediation of heavy metals in groundwater and Table 7 below show the estimated annual cost for different treatments.

OZONE IN GROUNDWATER-UPDATE TABLE

Ozone Chemistry

Ozone (O_3) which is a molecule composed of three oxygen atoms is a very unstable gas. Ozone is a gas that exist in room temperature and is highly toxic and corrosive when exposed to the atmosphere. The powerful oxidizing agent with a redox potential of 2.07V, reacts with two oxidation pathways which includes direct reaction and indirect reaction as shown in Figure 1. Direct reaction is predominant slow reaction with pollutants compounded in water and indirect reaction is a fast reactions of free radicals that is produced by ozone decomposition of hydroxyl ions (Niazi, Kalbasi, & Bahramian, 2017).

Table 6. The efficiency of different treatment in heavy metals removal from groundwater

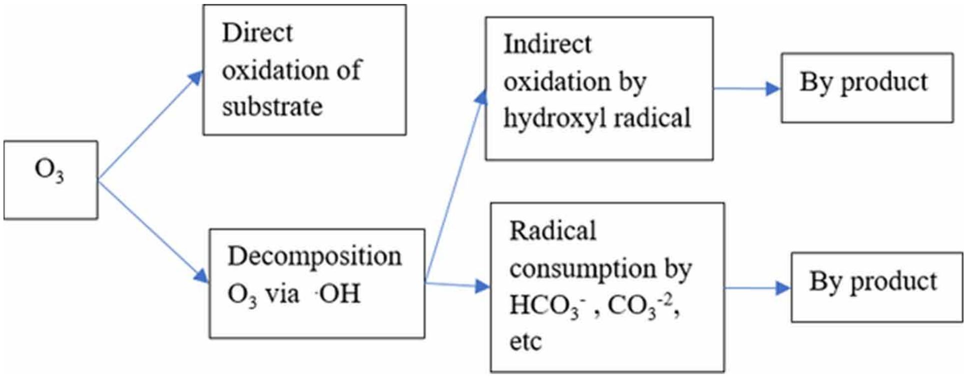
Treatment Methods	Target Removal	Removal %	References
Adsorption			
Material types: Modified activated alumina Iron-based adsorbents ((PPy)/Fe3O4) Calcium-based adsorbents (Quick Lime) Bauxite adsorbent Bio adsorbents Bio adsorbents	F	92.6 97 80.6 94.2 83.77 92.3	Bansiwal et al., (2010) Emamjomeh et al., (2011) Islam and Patel, (2007) Sujana and Anand, (2011) Alagumuthu et al., (2011) Patil et al., (2016)
Iron-doped Activated Carbon (AC) Activated Alumina (AA) Layered Double Hydroxide (LDH) Natural and Modified Zeolites and Clays	As	94 95 87.5 77	Fierro et al., (2009) Pillewan et al., (2011) Grover et al., (2009) Doušová et al., (2011)
High quality limestones	Mn	72	Akbar et al. (2015)
	Fe	99	
Metakaolin based geopolymer	Zn	≥97	Kara et al. (2017)
	Ni		
Zeolite 4A	Ni Cd Mn	≥90	Nwafulugo et al. (2014)
Filtration			
Filtration media: Gabon manganese ore Auto-activated silica sand Clean silica sand	Fe	approximately 100%	Jez-Walkowiak et al., (2017)
Filtration media: Gabon manganese ore Auto-activated silica sand Clean silica sand	Mn	60 100 40	
Filtration	Fe(II)	99.3	Sim et al., (2001)
Filtration	Fe	99.4	Wang et al.2013
Filtration	Fe	99.8	Devi et al. (2014)
Biofiltration	Mn	91	Granger et al. (2014)
Ammonia stripping	NH_3	95.4	Raboni et al., (2013)
Pre-treatment using KMnO4 + filtered through a fixed bed of bone char	Fe	99.9	Rim-Rukeh, (2014)
Flow-Through Bioreactor	Perchlorate	98	Deshusses and Frankenberger, (2000)
Ozonation	Fe	96	El Araby et al. (2009)
	Mn	83	
Iron leaching	Fe	75.4	Du et al. (2011)
Biosorption	Mn^{+2}	39.9	Fadel et al., (2015)
In-situ approaches using ferrous sulphate heptahydrate ($FeSO_4$)	As	77	Pi et al., 2017
in-situ remediation using mixothrophic denitrification process	NO3	85	Li et al., 2017
biological arsenic removal filter (ARF)	Mn	≥50	Shafiquzzaman, 2017
	Fe	≥90	
sequencing batch reactors (SBR)	Cr(VI)	≥95	Mamais et al. (2016)

Table 7. Estimated annual cost for different treatments

Potential groundwater contaminant	EPA maximum contaminant level value	Treatment	Approximate treatment cost per well ($)*
As	10lg/L–0.01 mg/L	Oxidation/Filtration, activated alumina, anion exchange: prior to RO	800–3,000
Bacteria	0	Disinfection	≥150
Cu	1.3 mg/L	Activated carbon, alumina, ion exchangeresins: prior to RO	80–3,000
F	4 mg/L	Activated alumina, distillation, electrodialysis: prior to RO	800–3,000
Fe	300 lg/L–0.3 mg/L	Shock chlorination	≤3,000
Pb	15 ppb–0.015 mg/L	Activated alumina or carbon, ion exchange: prior to RO	80–3,000
Mn	50 ppb–0.05 mg/L	Shock chlorination	≤3,000
Hg	2 ppb	Inorganic: distillation; Organic: granular activated carbon	800–4,000
CH_4	10 mg/L	Well vents	100–4,000
MTBE	20–40 ppb	Air stripping	3,000–4,000
NO^{2-}	10 ppm	Ion exchange, electrodialysis: prior to RO	≥800
NO^{3-}	1 ppm	Ion exchange, electrodialysis: prior to RO	≥800
Ra	5–228 picocuries/L	Cation exchange, distillation: prior to RO	≥800
Rn	10,000 pico curies/L	Granular activated carbon; Aeration	3,000–6,000
Na	20 mg/L	Distillation: prior to RO	≥800
SO^{4-}	250 ppm	Ion exchange; RO	≤3,000
H_2S	No limit set	Shock chlorination; Oxidation/Filtration	≤4,000

*All costs are in 2009 US dollars (Plappally and V, 2012)

Figure 1. Oxidation reaction of ozonation process



Ozone Treatment Method

Application of Ozone in Groundwater

Application of ozone can be grouped into three categories which are disinfectants or biocides, classical oxidants to remove organic pollutants, and pre/post-treatment agents to aid in other unit operations (coagulation, flocculation, sedimentation, biological oxidation, carbon adsorption, etc.).

In pre-oxidation process, functions of ozone constitutes:

1. Removal of iron and manganese
2. Oxidation of organic compounds

In pre-oxidation process, low dosage of ozone within short time was introduced and the rapid reaction occurs in the first phase when ozone is passed to the water sample to be treated.

For main oxidation, the uses of ozone are for:

1. Disinfection of bacteria
2. Inactivation of viruses
3. Removal of DOC after integrating with filtration process
4. Oxidation of organic compounds, e.g. phenols, detergents, pesticides or other hardly biodegraded

In the last decade, ozonation has been introduced in more water treatment plants as a replacement of primary chlorination. This is implemented to control side effect of chlorination. Ozone can be used not only for disinfection, but also to oxidize organic matter as it is a strong oxidant. Ozone is used for treating water that has been contaminated by pesticide or anthropogenic matters. When synthesised with UV and H_2O_2 treatment, ozonation can increase the rate of oxidation process. This advanced oxidation process (AOP) seems to be an effective method to remove emerging contaminants such as pharmaceuticals, endocrine disruptors, new disinfection by products and others.

To increase efficiency of particle removal ozone can also be added prior to coagulation. This process is called microflocculation. However, the impact of this pre-ozonation depends on several factors such as water hardness and DOC concentration. For moderate to high DOC water, the coagulant dose depends on DOC. natural organic matter (NOM) will be converted into smaller compounds such as oxalic acid by ozonation and this affects the coagulation process. Therefore, microflocculation will not occur for water with moderate and high DOC. For low DOC waters, coagulant dose depends on the particles and adsorbed organic matters. Ozonation can react with adsorbed DOC thus altering the amount and conformation of adsorbed organic matters. Microflocculation might occur in DOC water. It can be concluded that pre-ozonation is effective for water with low DOC but it can give negative impact form water with high DOC.

Application of ozonation can synthesize both disinfection and removal of NOM. During ozonation, NOM evolve to BOM which can be eliminate in bio-filter. Up to 50% of NOM can be removed, depending on empty bed contact time (EBCT), temperature, type and form of BOM. Therefore, using bio filter will restraint the regeneration of bacteria in water distribution network and reduce formation of disinfection by product.

Removal of Iron (Fe) and Manganese (Mn)

Fe and Mn are metallic elements found in the Earth'sEarth's crust. Soluble of Fe (II) and Mn (II) from groundwater are not dangerous to human health, if both metals concentration does not exceed recommended level of drinking water. According to WHO, the acceptable limit of drinking water for both Fe and is 0.3 and 0.1 mg/L respectively. The presence of Fe and Mn caused by natural processes in soil and rock geochemistry that contributes high concentration of Fe and Mn in groundwater. Excessive Fe and Mn concentrations in drinking water can result in aesthetic problem such as:

1. Unpleasant metallic taste of water
2. Rusty colour and turbidity of water
3. Taste and odour problem due to iron bacteria growth in pipe distribution networks
4. Staining of kitchen, bathroom fittings and laundry

Ion exchange, membrane process, biological filtration, oxidation by aeration followed by separation and integrated chemical oxidation and separation process are a few examples of method to remove Fe and Mn in water. This chapter highlights on application of ozonation to remove soluble Fe and Mn from groundwater.

During oxidation process, Fe and Mn form insoluble and can be removed easily through coagulation or filtration processes. Ozone is one of the effective oxidizing agent which is capable to oxidize Fe and Mn in groundwater. Ozone oxidise Fe^{2+} as shown in equation (1).

The oxidation reaction equation of ozone is as shown below:

$$2Fe^{2+} \xrightarrow{O_3 \to O_2} 2Fe^{3+} \xrightarrow{H_2O} Fe\left(OH\right)_3 \downarrow \qquad (1)$$

The reaction mechanism is as follows:

$$Fe^{2+} + O_3 \to Fe^{3+} + O_3 \qquad (2)$$

$$O_3^- \leftrightarrow O^- + O_2 \qquad (3)$$

$$O^- + H_2O \to OH_\bullet + OH^- \qquad (4)$$

$$OH_\bullet + Fe^{2+} \to OH^- + Fe^{3+} \qquad (5)$$

$$OH_\bullet + O_3 \to H_2O_\bullet + O_2 \qquad (6)$$

The direct reaction of Fe^{2+} with O_3 is possible, which reaction in equation (3) in not always dominant.

$$O_3^- + Fe^{2+} + H_2O \rightarrow O_2 + Fe^{3+} + 2OH^- \tag{7}$$

The removal of manganese requires more oxidant and is expensive due to more oxidation state compared to iron which only two oxidation states (+2 and +3). Fe can remove at lower ozone dosage however more dosage is required for manganese removal. Excessive ozone dosage that was supplied in groundwater sample may not increase the removal rate of manganese, however it may produce pinkish water due to oxidation of manganese to permanganate.

The oxidation reaction of Mn using ozonation process as shown in equation (8).

$$2Mn^{2+} \xrightarrow{O_3 \rightarrow O_2} 2Mn^{4+} \xrightarrow{H_2O} MnO_2 \downarrow \tag{8}$$

Ozonation is a process of oxidizing soluble metals into insoluble compounds. As shown in equation (7), soluble of Fe (Fe^{2+}) was oxidized into ferric iron (Fe^{3+}) and slowly hydrolysed to form particulate compound of ferric hydroxide ($Fe(OH)_3$). While Mn^{2+} was oxidized to Mn^{+4} and convert into MnO_2 which requires more energy in oxidation process. The removal of particulate compounds of $Fe(OH)_3$ and MnO_2 were very effective by continuous integrated with sedimentation, coagulation and filtration process. This statement is agreed by Akbar et al. (2017).

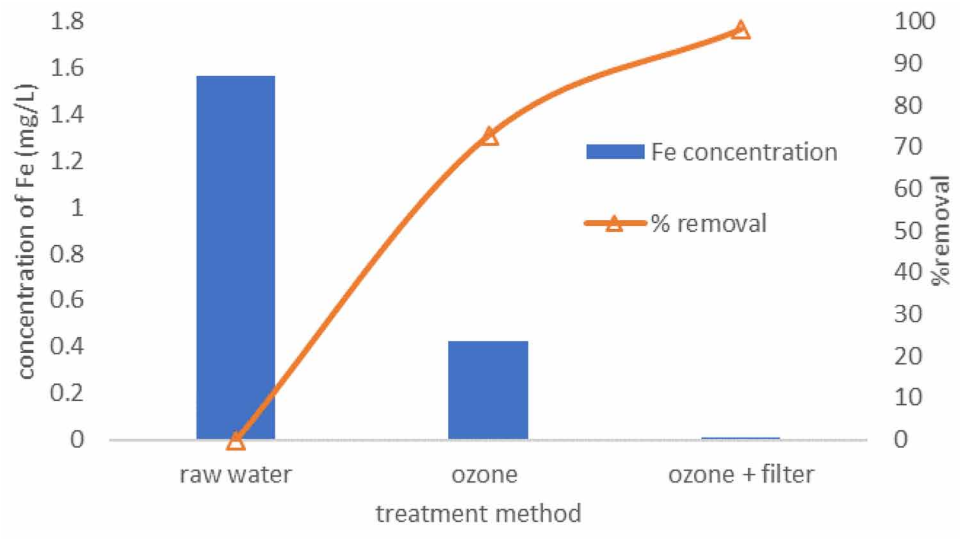
Ozone reacts to oxidize soluble Fe and Mn into insoluble Fe and Mn. Fe was oxidized first, followed by Mn when the both Fe and Mn present together in groundwater in the absence of organic matter. However, when organic matter is present in groundwater, ozone oxidizes organic matter before Fe and Mn. Thus, high ozone dose is required to oxidize Fe and Mn, Organic matter needs to remove at an early stage by different treatment before oxidizing Fe and Mn to enhance the effectiveness of ozone treatment.

In their study, the groundwater sample was collected from University Science of Malaysia (USM) borehole with initial Fe concentration of 1.56 mg/L. In order to determine the removal of both Fe and Mn in groundwater, a hybrid treatment of ozonation with limestone adsorption was proposed. The result shows that this hybrid treatment was highly efficient in removing Fe up to 99.5% and produced very low Fe concentrations in the effluent. However, single treatment of ozone may remove only 72% of Fe with final Fe concentration of 0.43 mg/L which exceeds the permissible limit of drinking water. The detail results on the treatment performance as shown in Figure 2.

Removal of Fe was enhanced by a hybrid treatment resulting in a final Fe concentration that far exceeds the limit of drinking water standard set. They used limestone in removing Fe due to the ability of this media in removing metals such as Fe, Mn, Cd, Ni, Zn, Cd and Al from water and waste water (Aziz, Adlan, & Ariffin, 2008;H. A. Aziz et al., 2001;Labastida et al., 2013).

Besides, analysis result on the chemical properties on limestone using XRF shows that limestone contained 97.93% $CaCO_3$, 0.87% MgO, and 1.2% other elements (Akbar et al., 2015). High quality limestone that contains high $CaCO_3$ may increase pH of water sample and thus precipitate to metal carbonate (Aziz & Smith, 1992). Based on study done by (Akbar et al., 2015), both adsorption of Fe and Mn onto limestone fitted with Langmuir isotherm model rather than Freundlich model which showed that it allowed monolayer adsorption to occur between metals contaminated groundwater and limestone adsorbent. The reaction rate of ozone oxidizes Fe and Mn to Fe^{3+} and Mn^{4+} and thus formed siderite

Figure 2. Comparison of Fe removal for various treatment method
(Akbar et al., 2015)



($FeCO_3$) and rodochrosite ($MnCO_3$) when the ozonated water sample are passed through limestone filter system. Siderite ($FeCO_3$) and rodochrosite ($MnCO_3$) are converted into bicarbonate forms when the CO_2 is present in water. The conversion goes through the reaction as shown in equation (9) and (10).

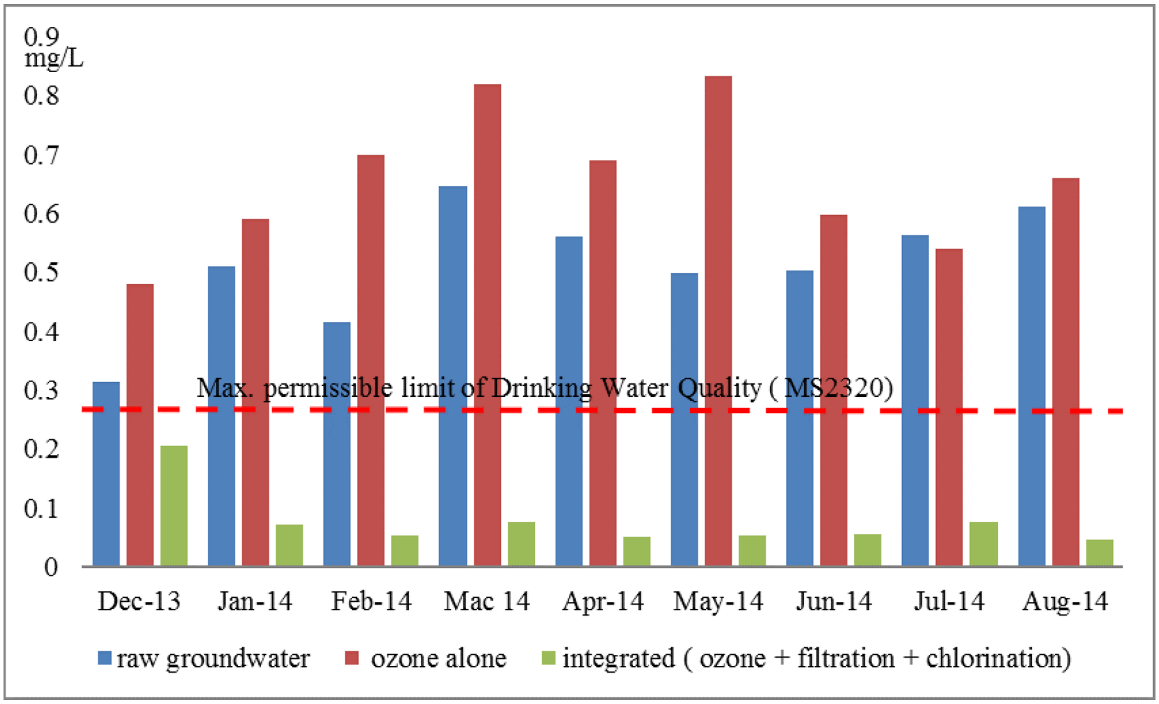
$$FeCO_3 + CO_2 + H_2O \rightarrow Fe\left(HCO_3\right)_2 \tag{9}$$

$$MnCO_3 + CO_2 + H_2O \rightarrow Mn\left(HCO_3\right)_2 \tag{10}$$

Besides, application on hybrid treatment of ozonation with anthracite as filter media was proposed by Air Kelantan Sdn Bhd in Pintu Geng Water Treatment Plant, Kelantan to improve the taste, colour, organic, inorganic and Fe problems present in groundwater. The utilization of groundwater in Kota Bharu as drinking water started in 1935 which the production demand was estimated to be 165 million L/ day (Suratman 2010)., This integrated treatment showed effective removal of Fe from borehole located at surrounding area of this water treatment plant based on desktop and monitoring studies that has been done by Akbar et al. (2015) starting from December 2013 to August 2014. It is as shown in Figure 3.

Previous literature found that anthracite has low volatile content which is effective to remove phosphorus (Ouyang et al., 2013). This statement agrees with Zhang et al. (2015), investigated the potential of modified anthracite was removed for more than 95% of both total phosphate (TP), total dissolved phosphorus (TDP) and phosphate respectively. Studies that has been done by Jiang et al. (2014) reported that optimum anthracite dosage is 85.87 mg/kg for phosphorus removal from aqueous solution. Thus, application of integrated ozonation with anthracite adsorption in Pintu Geng WTP performed well compared to single ozonation process resulted on high quality of drinking water was supplied to consumers at the surrounding of Kota Bharu, Kelantan.

Figure 3. Treatment efficiency of Fe removal from groundwater sources at Pintu Geng Water Treatment Plant, Kelantan
(Akbar et al., 2015)



Ozone is an effective oxidizing agent that requires a short time to complete the treatment. The presence of organic matter though, inhibits the removal of Fe and Mn in groundwater. The amount of ozone dosage needs to be increased and requires longer contact time between 20 to 30 minutes for removal of Fe and Mn from groundwater. Organic matter may change the direct and indirect ozone reaction and compete with both metals in oxidation process. Oxidation of complexed iron depending on the pH and concentration of organic matter in groundwater. According to El Araby et al. (2009), the result indicates that % removal of Mn^{2+} increased from 45% to 89% when pH increases from pH 5 to pH 12 respectively. This result was supported by Sevimli and Sarikaya (2002) which stated that ozone is more reactive hydroxyl radical and decomposition of ozone becomes faster in alkaline condition rather than in acidic condition (Sevimli & Sarikaya, 2002).

Another study using simulated groundwater showed that at same ozone dosage (1.25 mg/L), Fe^{2+} was removed 90% higher than 15% of Mn^{2+} due to faster oxidation of Fe^{2+} than Mn^{2+} (El Araby et al., 2009). When the ozone concentration increases to 3 mg/L, Fe and Mn were removed up to 96% and 83%. More oxidizing agent is required to oxidize Mn^{2+} into MnO_2 compared to oxidising Fe^{2+} into $Fe(OH)_3$. When the ozone concentration increases to 3.5 mg/L, Mn^{2+} is over oxidized to higher valency dissolve state that produce pinkish water containing MnO_4. The removal of Mn was decreased to 62% due to over ozonation and will resolubilize Mn again. The solubility of Mn corresponds to stoichiometry theory of 2.2 mg O_3/mg Mn^{+2}. However, there is no significant effect of Fe removal.

Oxidation of Organic Matter

The presence of organic in raw water becomes a serious problem to human health when it uses water as a drinking water. To comply with drinking water standard, the ozone application in removing organic content is a very effective alternative. Ozonation is an advanced oxidation process that is widely used in drinking water treatment due to its efficacy in removing organic compounds such as dissolved organic matter (DOM), biological organic matter (BOM) and emerging pollutants in water and wastewater. Shown in Table 6, ozone is very effective when combined to some extent in water treatment process as previous literature found that. Meanwhile, comparison between single ozonation treatment with integrated treatment is presented in Table 7. Previous literature proved that the high potential removal occurs in integrated treatments as opposed to ozone alone. Integrated treatment of ozonation with adsorption as shown in Table 8 improved degradation of organic matter and decrease ozone concentration for the treatment.

The combination process of O_3/SSF as the pre-treatment for groundwater recharge was applied in a demonstration plant in Beijing, China. This integrated treatment can be applied in shallow groundwater for more than 2 years. The large organic molecule can be broken down into small molecule by ozone and

Table 8. Various types of integrated treatment for organic matter removal (Shahanis, 2017)

Oxidation Process	Method	pollutant	Findings	Author
Ozone	Ozonation + Slow Sand Filtration	DOC	DOC was removed from 7.2 mg/L to 4.7mg/L	Hübner et al. (2012)
Ozone	Combination Ozonation / Slow Sand Filtration (SSF)/ Nanofiltration (NF)	DOM	Ozonation Leading to Breakdown Of The Large Organic Molecules	Linlin et al., (2011)
Ozone	Ozonation and Adsorption	Micro-pollutants	O_3 + Granular Activated Carbon (GAC) remove 79% and >72% Micropollutant respectively	Hernández-Leal, Temmink, Zeeman, & Buisman, (2011)

Table 9. Comparison performance between ozone alone and integrated treatment (Akbar et al., 2015)

Method	Water matric	Target contaminant	ozone alone	ozone + adsorption	Author
O_3 & Adsorption (GAC)	Textile wastewater	TOC		TOC (37%)	Konsowa, Ossman, Chen, & Crittenden, (2010)
O_3 & Adsorption (AC)	wastewater	*p*-Nitrophenol		COD (91%)	Gu, Zhang, & Lei (2008)
O_3 & Adsorption (GAC)	Stabilized landfill leachate	COD NH_3-N	COD (35%) NH_3-N (50%)	COD (86%) NH_3-N (92%)	Kurniawan, Lo, & Chan, (2006)
O_3 & biological filtration (AC)	Wastewater treatment plant effluent	DOC Trace organic chemical (TrOC)		DOC (50%) TrOC (>90%)	Reungoat et al. (2012)
O_3 & adsorption (GAC)	wastewater	phenolic	The worst for phenol degradation	The best for phenol degradation	Pratarn, Pornsiri, Thanit, Tawatchai, & Wiwut (2011)
O_3 & adsorption (GAC)	Food processing secondary effluent	COD TOC	19g O_3/g TOC	8.2–10.7 g O_3/g TOC	Alvarez, Pocostales, & Beltrán, (2011)

it can accelerate the biodegradation of DOM in SSF. Meanwhile, a large fraction of DOC can be removed through SSF. According to (Linlin et al., 2011), no significant removal of DOC when pre ozonation is introduced to the system but however it can reduce SUVA from 2.2 ± 0.2 to 0.8 ± 0.3 L $mg^{-1}m^{-1}$. Ozonation followed by SSF as bioreactor, remove DOC from 6.4 ± 1.3 to 2.6 ± 0.8 $mg^{-1}m^{-1}$. The removal of DOM is due to biodegradation process. In addition, the application of NF to the integrated with O_3 and SSF improve the treatment efficiency which can reduce DOC to 0.7 ± 0.3 $mg^{-1}m^{-1}$. NF is also efficient in removing humic acid -like and fluvic acid-like.

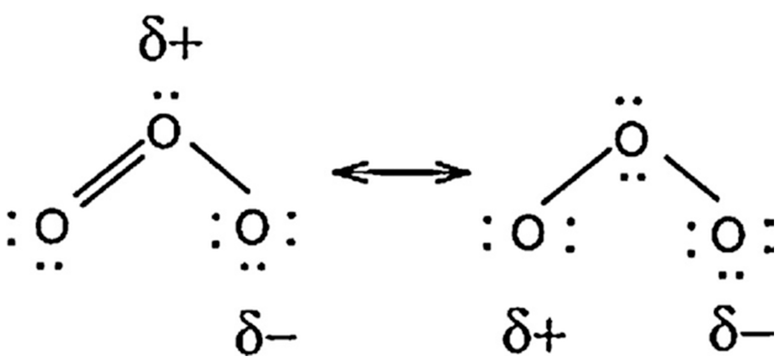
The effect of water matrix and ozonation on natural organic matter fractionation was studied by Agbaba et al. (2015). The removal of DOC and THMFP depends on several factors such as applied ozone dose, the character of NOM, pH and water alkalinity that influence the decomposition of ozone into hydroxyl radical. For groundwater with low alkalinity, low DOC concentration and high pH, the removal of DOC and THMFP were very effective due to the reactions with other radical maybe involved rather than the reaction with ozone that will improve the oxidation of NOM. Because it is highly unstable rapid decomposition of ozone molecules occur at higher pH. The half-life time of O_3 starts from few second to a few minutes depending on the pH of the water sample. According to Shahidi, Roy, & Azzouz (2015), the half-life time of ozone varies from 15 to 25 minutes when the pH varies from neutral to alkaline condition (pH 7 to pH 10). The reactivity of ozone appears when two resonance structures are formed which would explain the different chemical reactions such as cycloaditional, electrophilic and nucleophilic attacks as shown in Figure 4.

The hydroxide ion starts to decompose the ozone molecules in the form of OH. free radicals. In alkaline condition, the decomposition of ozone into radicals may increase with low reactivity as shown in equations (11) and (12) below.

$$O_3 + OH^- \longrightarrow HO_2^- + O_2 \tag{11}$$

$$O_3 + HO_2^- \longrightarrow OH\bullet + O_2 + O_2^- \tag{12}$$

Figure 4. Ozone charge transition between two resonance structures



OH radicals have a higher redox potential of 2.33V with rate of attack of 10^6 -10^9 faster than O_3 with redox potential of 2.07V (Shahidi et al., 2015).

They concluded that ozone is a function as oxidized hydrophobic NOM fraction that increases residual hydrophilic content, which is very reactive to THM formation compared to hydrophobic fraction.

Colour Removal

Coloured groundwater caused by the presence of organic matter such as humic and pulvic acid affects the quality of drinking water through excess colour content in the groundwater. High level of colour in groundwater became a concern over some production wells and thus required some treatment to reduce the colour content. By using chemical oxidation such as ozonation, nanofiltration and reverse osmosis, colour can be removed efficiently. This advanced treatment can improve the quality of groundwater especially chemical and microbiological aspect.

Based on studies done by Tan and Johnson, (2001), ozone oxidation was very effective in removing colour from groundwater. In their study, colour was removed from 120 to 10 colour units which far below than drinking water standard of 15 colour units. During the pumping process, coloured groundwater that contain strong hydrogen sulphide odor is pumped to the surface. The sulphide odor may remove rapidly when ozone oxidation was introduced to the raw groundwater through oxidation process of hydrogen sulphide. Besides, integrated treatment of ozonation with pressurized biological active filtration (PBAF) effectively removed AOC from coloured groundwater, increase the stability of microbiology treated water by ozonation process and minimize the biological regrowth for water distribution system.

Single treatment of ozonation is less effective in treating coloured groundwater. According to Asaithambi, Sajjadi, Abdul Aziz, and Daud, (2017), a hybrid advanced oxidation processes (HAOPs) have been conducted for wastewater. In their study, it was observed that a combination of O_3 and Sonolysis (US) based AOP showed good removal of colour in industrial and wastewater. This treatment can quickly degrade all organic and inorganic pollutant present in water and wastewater. The result indicated the removal of colour may only be 25% and 15% using ozonation and sonication process alone while it may increase up to 100% removal by using a combination of O_3/ US/Fe^{2+}/H_2O_2. The very low production of OH. radicals due to both of single processes only rather than hybrid treatment is the main cause of the difference in colour removal rate. In hybrid treatment, O_3/ US/Fe^{2+}/$H_2O_2{\cdot}OH$ are generated through the reaction between O_3 and $Fe_2{}^+$/H_2O_2 while sonication process may produce H radicals and hydrogen atoms.

Besides that, Amaral-silva, Martins, Castro-Silva, and Quinta-Ferreira (2016) studied on the application of ozonation and perozonation to improve biodegradability of landfill leachate. The result showed that the colour removal increased from 85% to 95% when the ozone dose varied from 5 to 20 mgO_3 whereas the optimum colour removal attained is 95% at 15 mgO_3 of ozone dosage.

Disinfection of Microorganism

In order to assure the water quality are being accepted to the drinking water standard, monitoring of total coliform and E-Coli concentration in groundwater is very important. For drinking water purposes, the presence of these parameters renders the water unsuitable to be used as drinking water. Thus, disinfection process should be done to inactivate or remove the pathogenic and non-pathogenic bacteria in water that can be used as drinking water. In drinking water treatment, there are some disinfectant agent that had been used such as free chlorine, combined chlorine, ozone, chlorine dioxide and UV light.

There are several mechanisms that apply to disinfection process by ozone such as cell wall destruction, cell permeability alteration and inhibition of enzyme activity. Ozone causes direct oxidation and destruction of cell walls, thus resulting in cell lysis and death. Cell permeability alteration allows nitrogen, phosphorous, and other nutrients to flow out. When ozone gas is introduced as disinfectant, it can break the carbon–nitrogen bond, causing nitrogen to escape and subsequently cause the leakage of cellular constituents. In addition, application of ozone as disinfectant alters the bacterial structure classified as damage to the surface of the membrane cell and cell structure (Verma, Gupta, & Gupta, 2016). This causes the bacterial cells to collapse and become very small in size with the range of nm. Ozone oxidizing the cell wall component of the bacteria which causes inactivation of the whole cell is the main reason for this condition.

Besides, there are several factors that influence disinfection process such as contact time, temperature and concentration of disinfectant. According to (Park, Choi, Lee, Kweon, & Song, 2016), the removal efficiency of total coliform was very low when a little dose of ozone gas is introduced even in a long time. In contrast, the increase in the total coliform removal exceeds 90% occurs when the dose applied exceeds 1.6 mg O_3/L in a short time of 0.5 min. The destruction of cells is the result of low dose of ozone whereas further higher doses leads to cell lysis and reduce the size of the cells reduced (Verma et al., 2016).

Xu, Janex, Savoye, Cockx, and Lazarova (2002) mentioned that design in ozonation process for disinfection of faecal coliform in water treatment not only based on the residual ozone or Ct factor but it also relies on mass transfer so no long-contact-time chamber is required. In addition, the quality of the effluent form ozonation process influence the effectiveness of disinfection (Paraskeva & Graham, 2002).

Different pathogenic bacteria require different ozone doses to ensure they are killed in water. Verma et al., (2016) conducted their research to determine the optimum ozone dosage for complete removal of pathogen for secondary treated effluent. The effluent of the treatment needs to achieve WHO standard for irrigation and agricultural purposes. In their study, five types of microbial species (Escherichia coli, Enterobacter, Klebsiella, Serratia/Hafnia, and Citrobacter) need to be removed using ozone oxidizing agent. The result shows that, E-Coli was fully destroyed at ozone dosage of 21 mg/L and followed by Citrobacter. Due to its high sensitivity to ozone, E-Coli are easy to destroy. While Serratia/Hafnia was difficult to destroy due to the lipopolysaccharide (LPS) content in the outer membrane and able to survive in various conditions (aerobic & anaerobic). This microbial species needs more ozone dosage to complete disinfection process. All strains were destroyed when ozone dose increased to 36mg/L. and the total killing rate was more that 99% for microorganism concentration up to 105 CFU/100 mL in secondary treated effluent. This study summarized that ozone is fastest as disinfectant and an alternative to chlorine for groundwater treatment.

CONCLUSION

Groundwater is an important source of fresh water that can be used as drinking water supply which constitutes high quality of water compared to surface water. The majority of population in Europe, Asia Pacific, Latin America, Australia, United States and Kelantan, Malaysia depends on groundwater for drinking water purposes. However, widespread contaminated groundwater is due to human activities that do not preserve the groundwater. When unwanted pollutant such as organic, inorganic and other constituents organic infiltrate into groundwater, pollution occurs. Sanitary systems, wastewater treatment plants, agricultural activities, uncontrolled hazardous waste, and atmospheric contaminants are some examples of the source of pollutants. These pollutants can make their own way down into groundwater through these aforementioned sources.

Chemical precipitation, ozonation, ion exchange, adsorption, membrane filter, coagulation and flocculation, flotation and electrochemical treatment are several application methods for groundwater treatments. Among these treatment methods, ozonation process is getting attention for water treatment process because of its effectiveness in removing various organic and inorganic matter in the water. Ozone has many roles as it can oxidize heavy metals such as Fe and Mn, oxidize organic compound such as phenols, detergents, pesticides or other hardly biodegraded, destroying pathogens and non- pathogen organisms and removing taste, colour and odor that are present in groundwater. Ozone reacts with unsaturated bonds in organic compound to form unstable ozonides, which breakdown to aldehydes and ketones. The efficiency of oxidation process is due to its ability to form hydroxyl radicals for non-selective oxidation.

Although the use of ozone is expensive than chlorine and generate disinfectant by-products that are possibly carcinogenic, it is a very strong oxidizing agent with short reaction time in the treatment. Additional post-treatment will help reduce the formation of disinfectant by-products. A combination of ozone processes and other treatments such as filtration, coagulation, flocculation, adsorption and biological oxidation improving the effectiveness of water treatment rather than single treatment of ozonation, as based on previous studies. This integrated treatment enhances the removal efficiency of contaminated groundwater. It can improve the final water quality to achieve permissible limit of drinking water quality standard. Moreover, the treatment can minimize oxidizing chemical to the final water effluent, reduce more organic compound and overcome the problem of the formation of by-products. Therefore, ozonation process is appropriate to be used as pre-treatment for groundwater.

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Chapter 10

An Overview of Treatment of Antibiotics Using Advanced Oxidation Process

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ABSTRACT

Antibiotics present in the environment are originated from pharmaceutical manufacturing processes or through wastes such as urine and feces. As antibiotics remain recalcitrant and persist in the treated water, consumption of treated water containing antibiotics raises a concern in the development of antibiotic resistance bacteria which would be later released to the environment. It might result in a vicious cycle which new antibiotics needs to be developed and dosage has to increase. Advanced oxidation processes (AOP) have been studied to effectively degrade antibiotics. During this process, hydroxyl radicals are formed to degrade organic compounds. Different APO are available in the literature such as photo-Fenton, Fenton, ozonation, sonolysis (UV), ultrasound combined with ozone, TiO2/direct photolysis, UV/H2O2, UV/ TiO2, UV/IGBT. To treat the high level of concentration of antibiotics, retention time of AOPs needs to be extended or/and OH● radicals need to be produced in a higher concentration for a complete mineralization.

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INTRODUCTION

Over the last 45 years, most of the major industrialized countries have instituted controls on the treatment and the disposal of hazardous wastes. Legislation was placed upon the procedures of hazardous wastes disposal without causing any environmental hazards. In most cases, waste producers are responsible for the direct cost of treatment and disposal, whereas the disposal of household waste is usually funded from general taxation revenue (Stokoe, 1986).

Hazardous waste is a by-product of industrialization - a process which has gathered pace in Asia during the last decade. A method must be found to control hazardous wastes and for their disposal by appropriate facilities in Asian countries in order to avoid some of the environmental effects that have in the past resulted from the uncontrolled disposal of hazardous waste in the older industries societies. However, the solutions appropriate in Asia need not be the same as those that have applied in Europe and North America, where the industrial framework, infrastructure, environment and climate are quite different.

And moreover because of financial constraint on treating the effluent to a high standard and lenient environmental regulation on the effluent disposal limit, limit the Asian industries to adopt the latest technologies in treating the hazardous waste. During antibiotic production the compound still remain in the effluent and also it persist in domestic wastewater when the humans consume for their health care. However this is mostly neglected in consideration while designing the wastewater treatment plant in Asian countries. Since this type of hazardous waste will not be degraded by conventional wastewater treatment plant advanced oxidation process is required.

With the increase in emphasis on higher technology industries in Hong Kong, hazardous waste production has become more significant and the range of wastes produced more varied. Regulations to control the transportation, treatment and disposal of hazardous wastes have been drafted and outline proposals for a hazardous waste treatment centre have been developed. The regulations will assign responsibility to specialist contractors rather than waste producers, for adopting professional standards in the management of hazardous wastes (Stokoe, 1986). These contractors will be controlled by licenses. The licenses are meant to govern the standards of operation of the contractors. Codes of practice are being introduced, setting out appropriate standards for all stages of the management of hazardous waste. The transportation of hazardous waste will be controlled by a trip-ticket system enabling a close check on individual loads of waste in transit between waste producer and disposal site. The hazardous waste treatment centre will include facilities for the treatment of inorganic aqueous based wastes and oily wastes, hazardous waste incineration and the recovery of waste oils and solvents. Public notices in overseas technical journals produced a large response from companies interested in building and operating the plant on behalf of the Government during 1988 (Stokoe, 1986). The control, treatment and disposal of hazardous waste is a justifiable objective in itself and provides other environmental benefits as well. The control of toxic wastes presently discharged directly to sewer, will reduce the incidence of disruption of sewage works and increase the options available for sludge disposal.

Among the hazardous wastes, attention is withdrawn on the use of antibiotics. Despite their vital importance in our daily life, antibiotics have been known to raise concern as a persistent water pollutant in the environment. The occurrence of antibiotics in the aquatic systems has biological impacts on the aquatic life and human health. The use of antibiotic chemical in the pharmaceutical products has reached an estimation from 100,000 to 200,00 tons per year (Kummerer, 2003). The purposes of antibiotics are to treat diseases in human and to promote growth in the agriculture (Hollis, A. and Ahmed, 2013). Antibiotics are made to interfere with the cell walls of bacterial organisms. Since their purpose is to 'destroy' cell walls of bacteria, they are complex in structure and are able to pass through our biological system (stomach) without being broken down into fragments to be able to achieve their task of reaching the alien organisms (harmful bacteria) in the bodies. As a result, the antibiotics are still mostly intact after being excreted from the human metabolism, (Martinez, 2008).

Conventional processes in the wastewater treatment plants (WWTP) are unable to degrade the recalcitrant components in antibiotics. Although antibiotics-contained water is safe for human consumption after treatment, bacteria become resistant to the antibiotics and the human immune system becomes weak. Consequently, to tackle with bacterial infection and diseases, formation and using stronger antibiotics are the option (Halling-Sorensen et al., 1998). It is not a simple practice to formulate new antibiotics due to the time constrain, research facilities, production and commercialisation. Furthermore, treated wastewater eventually ends up into the rivers or seas when they are not re-used for other purposes such as irrigation or for industrial purposes. The antibiotic-containing wastewater comes into contact with pathogens present in waters generally. Water streams are the natural habitats of pathogens. In a long term, studies have shown that residual antibiotics may cause microorganisms to develop antibiotic-resistant pathogens (Bailón-Pérez, García-Campaña, Cruces-Blanco, & del Olmo Iruela, 2008).

Since the conventional wastewater treatment processes do not fully remove recalcitrant pharmaceutics, an approach of the additional advanced treatment technology is required. There are different advanced technologies which have been studied recently for the purpose of disintegrating non-biodegradable products. Those technologies are chemical oxidation using ozone and ozone/hydrogen peroxide (Ternes et al., 2002; Zwiener, 2000), activated carbon as sorption processes (Hartig, Ernst, & Jekel, 2001; Ternes et al., 2002) and membrane filtration such as nanofiltration and reverse osmosis (Petrovic, 2003). Limitations of the treatment processes such as membrane filtration and sorption drive the increasing interest toward exploring and optimising advanced chemical oxidation process (AOP). Here is a list of advanced chemical oxidation processes (Zwiener, 2000).

- Ozone/ Hydrogen peroxide, O_3/H_2O_2
- Ozone/Ultraviolet, O_3/UV
- Ozone/Hydrogen peroxide/Ultraviolet, O_3/ H_2O_2/UV
- Hydrogen peroxide/Ultraviolet, H_2O_2/UV
- Fenton, Fe^{2+}/H_2O_2
- Photo/electron Fenton
- Chelating agent assisted Fenton/photo-Fenton
- Heterogeneous photo-oxidation using titanium dioxide, TiO_2/hv
- γ-radiolysis and sonolysis.

Advanced oxidation processes (AOP) are based on oxidation and reduction. Oxidation is the transfer of one or more electrons from a reductant (an electron donor) to an oxidant (an electron acceptor), which has a higher affinity for electrons. This transfer of electron results in a chemical transformation of both the reductant and oxidant. Consequently, some chemical species are produced and have an odd number of valence electrons known as radicals, which are highly unstable and reactive because one of the electrons is unpaired (Zwiener, 2000).

The oxidation reactions that produce radicals tend to be followed by some additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed. The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The end products of the complete oxidation (i.e., mineralization) of organic compounds such as methyl tert-butyl ether (MTBE) or benzene are carbon dioxide (CO2) and water (H_2O).

AOP involve two stages of oxidation, i.e.1. the formation of strong oxidants (e.g., hydroxyl radicals) and 2. the reaction of these oxidants with organic contaminants in water. However, the term ‘advanced oxidation processes’ refers specifically to some processes in which the oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. In the water treatment applications, AOP usually refer to a specific subset of processes that involve O_3, H_2O_2, and/or UV light. However, AOP could be used to refer to a more general group of processes that involve TiO_2 catalysis, cavitation, E-beam irradiation, and Fenton’s reaction. All of these processes can produce hydroxyl radicals, which can react with and destroy a wide range of organic contaminants, including MTBE. Although a number of the processes may have other mechanisms for destroying organic contaminants, the effectiveness of an AOP is generally proportional to its ability to generate hydroxyl radicals.

The performance of these AOPs can be measured in terms of water quality measurements by comparing the initial value and the final values. There are various analytical ways that are used to measure the degree of water purity. Table 1 shows details of some analytical terms for water characterisation and their functions.

To achieve the target performance level of interest, the advance oxidation processes can be simple or requires a combination with other technology. The selection of the process is based on some of the following criteria.

- Degradation efficiencies in terms of COD, BOD, DOC & TOC.

Table 1. Classification of water quality indicators and their respective functions

Water Quality Indicators	Functions
Chemical oxygen demand, COD (mg/L)	The amount of oxygen required to oxidize an organic compound to carbon dioxide, ammonia, and water By knowing the amount of oxygen used to oxidise, the initial amount of components which are oxidised can be determined.
Bio-chemical oxygen demand (BOD)	The amount of dissolved oxygen required by aerobic biological microorganisms to break down organic material present in a water sample at a certain temperature over a specific amount of time.
Total organic carbon (TOC)	The amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality or cleanliness of pharmaceutical manufacturing equipment
Dissolved organic compounds (DOC)	The amount of organic compounds that have been dissolved in a water sample.
Total suspended solids (TSS)	The amount of particles found in terms of dry-weight when a water sample is filtered.
Total dissolved solids (TDS)	The amount of particles which are dissolved in a water sample at specific temperature.
Turbidity	The transparency (cloudiness) of water is measured by turbidity.
pH	A scale used to measure the acidity or alkalinity of water by the number of H_3O^+ present in the water.
Alkanity/ VFA	Alkalinity is the quantitative ability of an aqueous solution to neutralise an acid.
Electrical conductivity, (mS/cm)	The number of electrons which can pass through as electricity in a solution determining the number of ions present in a water sample.
Water hardness (mmol/L)	Amount of minerals (calcium and magnesium ions) found in water.

- Operating ambient conditions such as pressure, temperature and pH.
- Possible implementation in wastewater treatment plant.

The present study focused on the (1) different methods of the oxidation processes, particularly methods that are employed in the wastewater treatment plants, (2) reviews of some studies in the antibiotics and their degradation processes, (3) employed methods to determine a degradation pathway.

ANTIBIOTIC SOURCES

Many point sources from which antibiotics are present in water flow across to reach environmental water streams. Two main sources of antibiotics are found in the environment. First, it is from the excretion through urine and faeces. Second, it is from the pharmaceutical manufacturing industries where an amount of antibiotics is present in the effluent (Magureanu, Mandache, & Parvulescu, 2015).

Recently, the newest concern of recycling wastewater is the presence of chemicals such as antibiotics, endocrine disrupters compounds, and personal health care products. Endocrine disrupters, which interfere with the body's natural ability to produce, release, transport, metabolize, bind and eliminate hormones in the body, have been observed in wastewater discharges in the water bodies all over the world. For example, the steroid 17b-estadiol is an important hormone in fish experiments conducted has indicated possible reproduction consequences (Schoenfuss, Martinovic, & Sorensen, 2001).

Substantial quantities of pharmaceuticals are used in human and veterinary medicine. They are often not metabolised by the body after administration. Depending upon their excretion rate, they are released into the effluent and reach sewage treatment plant. If they are not degraded, they could enter the environment, where little is known about their fate and effects. They usually have two characteristics, which declare them as environmental hostile: they are stable and biologically effective (Carballa et al., 2004). For these reasons optimisation of production processes and effective end-of pipe treatment is necessary to avoid broad contamination of receiving environment due to the pharmaceutical industry.

Several studies have observed antibiotic agents in the aquatic environment, including groundwater, surface water, and wastewater treatment plant (WWTP) effluent (Heberer, Schmidt-Baumler, & Stan, 1998; Hirsch, Ternes, Haaberer, & Kratz, 1998). Sources of antibiotic agents to the environment include effluent from WWTPs, leachate from landfills, discharge from septic tanks, runoff from veterinary medicine and growth promoters in livestock, and the application of manure and sludge containing antibiotics. Despite knowing the sources and pathways of pharmaceuticals into the environment, actual concentrations and availability are unknown.

Another concern of pharmaceuticals in the environment is the development of antibiotic resistance of bacteria due to the presence of antibiotics in wastewater. In fact, several studies have identified antibiotic resistance in bacteria at WWTPs and in WWTP effluents (Bell, 1978; Malik & Ahmad, 1994; Misra, Kumar, & Singh, 1979; Radtke & Gist, 1989; Stelzer, Ziegert, & Schneider, 1985). Antibiotic resistances can be identified in bacteria by a traditional agar dilution method or by surveying for beta-lactamase activity using acidometric tests or chromogenic cephalosporing tests (Handal & Olsen, 2000). The acidometric test is less expensive than the chromogenic cephalosporin tests, but the latter test is more sensitive. Materials to perform both tests are commercially available. Susceptibility tests may be used to detect the presence of beta-lactamases using the double-disk diffusion test, isoelectric focusing and the E-test. Antibiotic resistance is of great concern in that pathogens may develop resistances to antibiotics when exposed at the WWTP. Antibiotic resistant bacteria would then be released to the environment where a host may be infected. To overcome the resistance developed by the bacteria, new antibiotics may need to be developed or doses may have to increase, resulting in a vicious cycle.

Domestic Waste

Excretion was pointed to be one of the main sources of contamination in the water resource. Since the antibiotics are not fully metabolised in the human anatomical systems, a natural excretion of the complex antibiotics in the water is inevitable (Magureanu et al., 2015).

Irresponsible consumption and disposal of antibiotics cause the water contamination. It is known that prescription given by physicians on antibiotics are not completely followed by patients. Normally, when on antibiotics, a course of one week or more, is given to patients. By the end of the third or fourth day of the prescribed course, the patient starts to feel better. Some patients chose not to continue their course due to this reason. It is a generally very bad practise since physicians prescribe medication based on their knowledge and according to regulations provided by health authorities, depending on the country. The remaining antibiotics which should have been consumed are simply thrown to waste because antibiotics cannot be re-used for any other reasons. This is an unwise practise from the antibiotic consumers. Disposing the pharmaceutical products, which contains the antibiotics, in the waste unintentionally causes a contamination in the water. From the waste, the antibiotic will eventually reach the household sewage and end up in the rivers and lakes as the general water streams. The United States reported that tetracyclines have been detected at the level of 0.11 μg/L in the surface waters and at 0.52 μg/L and 0.17 μg/L in the effluent of the sewage treatment plants (J. Jeong, Song, Cooper, Jing, & Greaves, 2010).

Pharmaceutical Industries

Pharmaceuticals have been identified in the environment for several decades (Kummerer, 2001). However, the fates of pharmaceutical agents are unknown in many cases. In order to understand the potential impacts of antibiotic agents in the aquatic environment at trace concentrations, the fate of the pharmaceuticals needs to be investigated. Specifically, information needs to be collected regarding the emission, occurrence, fate and effects of pharmaceuticals in the environment. The occurrence of antibiotics in the world water streams is caused from the pharmaceutical industries, especially antibiotic manufacturing (Magureanu et al., 2015). The antibiotic component present in process streams is also present in the effluent discharged from the industries (Nithyanandam & Saravanane, 2013). Several authors have studied the implementation of the advanced oxidation processes as pre-treatment in the wastewater treatment plant (Ikehata, Jodeiri Naghashkar, & El-Din Gamal, 2006). According to the Malaysian Drug Authority (DCA), more than 235 drug companies, e.g. Hovid Berhad Pharmaniaga Manufacturing Berhad and CCM Duopharma Biotech Sdn Bhd, are manufacturers of generics, especially antibiotics among many others (injectable, painkillers, health supplements). Therefore, the contamination of antibiotics in the water is a problem to resolve.

The improperly domestic disposal and presence of antibiotics in the effluents from the pharmaceutical manufacturing activities increasingly accumulate antibiotics in the wastewater. Thus, it leads to a greater volume of the effluent being released. The effluent waste streams as a point source of antibiotic end up in the general waters such as lakes and streams in the environment.

ADVANCED OXIDATION PROCESSES

Advanced oxidation processes are based on the generation of hydroxyl radicals, which are known as species with a very strong oxidising power. Table 2. shows the oxidising power of some common oxidants, and the hydroxyl radical stands in the second place after fluorine.

Hence, the hydroxyl radicals can be oxidising almost all organic compounds and the end product are in carbon dioxide (CO2) and inorganic materials. The reaction rate of the hydroxyl radicals is in the range from 106 M-1s-1 to 109 M-1s-1 (Jin, Peldszus, & Huck, 2015). Hydroxyl radicals are proved to be among the best species used during advanced oxidation processes.

Advanced oxidation process was investigated for reducing the overall organic content which is measured by chemical oxygen demand (COD) of the wastewater from an industrial facility that produced cleaners and floor care products (Bergendahl, Hubard, & Grasso, 2003). The wastewater contained up to 5% surfactants, solvents, and chelating agents. The COD of the wastewater from the facility needed to be reduced in concentration before discharge to the local public treatment facility. Figure 1 shows the beneficial outcomes which are obtained upon the use of AOPs in waste water treatment plants.

Advanced oxidation can also be used to destroy specific pollutants that remain in wastewater after other treatment steps. Fenton's oxidation was used to decrease the concentration of organic contaminants in water (Bergendahl & O'Shaughnessy, 2004). Experiments with a pilot-scale system were carried out and obtained a successful degradation of many of the contaminants present with Fenton's oxidation, an effective advanced oxidation reaction. Many of the contaminants present in this wastewater were significantly decreased in concentration (i.e. m- and p-xylenes), although some were not (i.e. 1, 1, 1- trichloroethane). Overall, there was an 81.8% reduction in organic contaminant mass in the water following Fenton's oxidation process (Bergendahl & O'Shaughnessy, 2004). Fenton's oxidation has also been found to be very effective for mineralizing methyl tert-butyl ether (MTBE) in water.

The hydroxyl radicals produced by AOPs are also effective for treating and conditioning sludge produced from wastewater processes as they destroy cell walls of microorganisms. The cell material becomes solubilized with advanced oxidation, and amenable for further oxidation or other treatment.

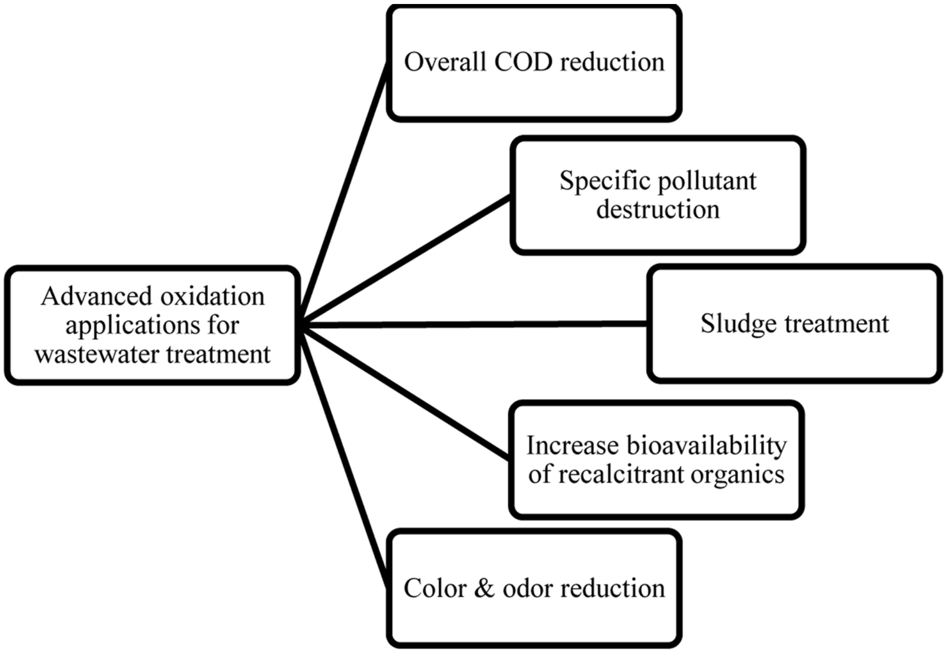
A full-scale activated sludge system was investigated to treat 120,000 gallon/day municipal wastewater (Yasui, Nakamura, Sakuma, Iwasaki, & Sakai, 1996). Part of the recycled sludge in the system was subjected to ozonation. The wastewater treatment system was run for up to 10 months, with no excess sludge disposed – It was sludge less system. New efforts have focused on integrating advanced oxidation with other technologies. Molecular sieve zeolites have great capacity to adsorb organic contaminants from

Table 2. Oxidation potential against standard hydrogen electrode of some relevant oxidants

No.	Oxidant	Oxidant E^0 [V]	No.	Oxidant	Oxidant E^0 [V]
1	Fluorine	3.03	7	Permanganate	1.68
2	Hydroxyl radical	2.80	8	Chlorodioxide	1.57
3	Singlet oxygen	2.42	9	Hydrochloric acid	1.45
4	Ozone	2.42	10	Chlorine	1.36
5	Hydrogen Peroxide	1.78	11	Bromine	1.09
6	Perhydroxyl radical	1.70	12	Iodine	0.54

Source: (Wols & Hofman-Caris, 2012)

Figure 1. Application of advanced oxidation process for wastewater (WW) treatment



water. Yet these contaminants are merely transferred to the solid phase. However, advanced oxidation can destroy these adsorbed contaminants and regenerate the sorbent. Preliminary experiments where silicalite, after repeated adsorption cycles with chloroform in water, becomes saturated and unable to sorb any more contaminant (after the eighth cycle). But after advanced oxidation, the silicalite regains its original sorption capacity (after the ninth cycle) (Yasui et al., 1996).

Among all the pharmaceutical drugs that cause contamination problems in the environment, antibiotics take an important place due to their high consumption rates in both veterinary and human medicine (Balcioglu & Otker, 2002; Kummerer, 2001). Antibiotics generally have low biodegradability since they are biocidal substances and the degradation of these substances cannot be accomplished in the natural environment or biological treatment plants. Consequently, the antibiotics on the surface and ground water were detected in the concentration range of µg/l and ng/l, respectively (Wollenberger, Halling-Sorensen, & Kusk, 2000). Toxic effects of low concentrations of antibiotics on aquatic organisms have been investigated in the mg/l range (Kummerer, 2003; Wollenberger et al., 2000).

Despite the presence and chronic toxic effects of antibiotics in the aquatic environment, few studies reported in the literature have dealt with the treatment of these substances (Adams, Scanlan, & Secrist, 1994; Balcioglu & Otker, 2002, 2003). It was found that conventional biological treatment systems were not effective in the removal of antibiotics (Ingerslev & Halling-Sorensen, 2000; Kummerer, Hartmann, & Meyer, 1997). Therefore, it is clear that chemical oxidation technologies are necessary for the removal of this kind of pollutants.

Chlorinated aromatic compounds are toxic chemicals that have been introduced into the environment as herbicides and fungicides. These compounds are generally chemically resistant, causing their removal from contaminated waters to be a difficult task. In this respect, photo-oxidation reactions provide a promising solution to this problem as these reactions can mineralize most of the chlorinated aromatic and aliphatic compounds (Benoit-Guyod, Bruckner, & Benoit-Guyod, 1994; Burrows et al., 1998; Lang, Brodilova, & Lunak, 1996; Legrini, Oliveros, & Braun, 1993). The primary products of photo initiated reactions depend on the wavelength of the incident radiation because it determines which component of the system absorbs radiation, which excited state will be populated and therefore, which step initiates the reaction.

Chlorinated aromatic compounds can be excited directly using wavelengths shorter than 300 nm. For example, compounds such as chlorophenols and 4-chlorophenoxyacetic acid (CPA) are transformed by oxidative removal of the side chain, by replacement of the chlorine by hydroxy or hydrogen, and by condensation reactions (Burrows et al., 1998; Crosby & Wong, 1973) . When hydrogen peroxide or ozone is present, UV irradiation produces hydroxyl radicals in high quantum yields (Legrini et al., 1993; J. L. Lopez et al., 2000).

Dissociation of H_2O_2 into two OH• radicals can also be photosensitized by the excited states of an aromatic substrate (Lang et al., 1996). The hydroxyl radicals are highly reactive and bring about the effective degradation of nearly all organic compounds (Legrini et al., 1993; J. L. Lopez et al., 2000; Lun^ak & Sedlak, 1992). It is pertinent to mention that photo degradation of a primary compound can lead to various products that may be even more toxic (Zertal, Sehili, & Boule, 2001). In this case, mineralization into carbon dioxide and inorganic ions are required. An effective way of enhancing photo degradation of various organic compounds is photo catalysis. Numerous water pollutants have been treated by heterogeneous photo-catalysis in titanium dioxide and zinc oxide suspensions (Djebbar & Sehili, 1998; Legrini et al., 1993; Modestov, Glezer, Marjasis, & Lev, 1997; Serpone et al., 2000).

Oxidative Degradation of AOX and COD

AOX (absorbable organic halogen) is an important parameter for the characterization of wastewaters with regard to their biodegradability. AOX is defined as the sum of all halogeno-organic compounds which can be adsorbed by activated carbon. As a large number of these compounds show a significant toxicity on humans and bacteria, sewage water legislation in Germany provides very strict regulations for the discharge of AOX - Containing wastewaters. AOX containing wastewaters often entail financial problems for specific industrial branches. AOX may be removed by reverse-osmosis, air stripping or adsorption by activated carbon.

Unfortunately, all these methods involve a further disposal. The rates of AOX degradation through a biological treatment are in most cases are too low. In recent years, in contrast to the non-destructive methods, so-called “advanced oxidation processes” (AOPs) have been proposed for the degradation of toxic pollutants. These methods are based on the combination of classical oxidants such as H_2O_2 with UV radiation or a catalyst. In these processes, hydroxyl radicals are generated causing an elimination of chloride from halogeno-organic compounds (Legrini et al., 1993). This has been observed by the degradation of many model compounds such as chlorophenols.

In this way both AOX and the toxicity of the wastewater are reduced. The application of several AOPs has also been tested in some pilot-plant studies. In spite of the enormous physical, chemical and technical knowledge about AOPs, experts still disagree about the most efficient method for dealing with a specific wastewater problem.

Different Oxidation Process Methods Employed for Degradation of Antibiotics

The performance of oxidation processes, i.e. ozonation, Fenton process, Photo-Fenton process, UV, sonolysis and Fenton-like methods are reviewed and compared in Table 3. The most occurring antibiotics found in the water stream were chosen.

Table 3. Comparison of different advanced oxidation processes (AOP) used to degrade antibiotics

Antibiotic	Method of degradation	Cost	Description	Removal efficiency (%)			References
				COD	TOC	Targeted compounds	
Amoxicillin (AMX)	Photo-Fenton (Fe/ H_2O_2 coupled with solar simulator)	Medium	● Total mineralisation after 5 minutes of irradiation ● Total removal of AMX using $FeSO_4$ ● TOC removal by 73% using $FeSO_4$ ● TOC removal by 81% using FeO_X	-	-	100	(Trovó, Pupo Nogueira, Agüera, Fernandez-Alba, & Malato, 2011)
	Fenton	Low	● Total mineralisation occurred in 2 minutes ● OD increased from 0 to 0.37 within 10 minutes ● COD reduction by 81.4% ● DOC reduction by 53.4% ● Increase in nitrate concentration from 0.3 to 10 mg/L in 60 minutes ● Increase in NH_3 concentration from 8 to 13 mg/L in 60 minutes Process can be implemented in WWTP.	81.4	-	-	(Elmolla & Chaudhuri, 2009)
	Ozonation	High	Ozonation performed in a semi continuous stirred gas-liquid reactor at 25℃ ● TOC removal by 90% within 4 minutes at pH 5.5 ● Hydrolysis of AMX resulted into 2Amino2-(p-hydroxyphenyl)	-	90	-	(Andreozzi, Canterino, Marotta, & Paxeus, 2005)
			400mg/L AMX used. ● COD reduced by 86% ● TOC reduced by 52% ● BOD increased from zero to 60mg/L at pH 11.5	86	52	-	(Dogruel & S., 2004)

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Table 3. Continued

Antibiotic	Method of degradation	Cost	Description	Removal efficiency (%)			References
				COD	TOC	Targeted compounds	
	Photolysis	Medium	Integrated photo catalytic adsorbents (IPA) prepared from TiO_2 and natural zeolite were used to degrade AMX. ● Complete removal of AMX and its thermal degradants after 240 minutes of irradiation ● Results showed that best efficiency is using TiO_2 P25 peroxide which degrade by 80% within 45minutes followed by TiO_2 achieving a removal of 50% within 45 minutes.	-	-	100	(Kanakaraju, Kockler, Moti, Glass, & Oelgemoller, 2015)
Penicillin G β-Lactam class	Ozonation	High	Semi-batch reactor used to carry out experiment. ● COD reduction by 50% at pH 12 ● TOC removal by 52% at pH 12 ● Higher pH works best for ozonation. ● Recommend an addition of H_2O_2 for better performance.	50	52	-	(Arslan-Alaton & Caglayan, 2005)
	Photo-Fenton Sonolysis (UV)	Medium	Studies were carried out for wastewater effluent. Optimization of 2 processes: photo-Fenton and sonolysis. ● Optimum condition of 20mM H_2O_2 and 1mM Fe^{2+} at pH 3.5, complete mineralisation in 30 minutes ● Optimum condition for sonolysis is 35kHz at pH 3, complete mineralisation in 70minutes Fenton process preferred to the sonolysis method as it is more efficient.	-	-	100	(Saghafinia, Emadian, & Vossoughi, 2011)

continued on following page

Table 3. Continued

Antibiotic	Method of degradation	Cost	Description	Removal efficiency (%)			References
				COD	TOC	Targeted compounds	
Sulfamethoxazole (SMX) Sulfonamide class	Ozonation	High	The catalytic activity and selectivity of montmorillonite exchanged with Na^+, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} cations were comparatively investigated in the ozonation of SMX ● Total removal of COD within 60 seconds on addition of catalyst to ozone. ● Intermediates of Muconic acid, Maleic acid, Glyoxal and Oxalic acid were identified. Reaction kinematics was determined for each intermediate.	100	-	-	(Shahidi et al., 2015)
	Ultrasound combined with ozone	High	Ultrasound alone gives low SMX removal. Ozone alone without any catalyst gives a degradation of 70% within 5 minutes. ● TOC removal by 90% within 5 minutes by combining ultrasound and ozone Reaction kinetics was calculated for each pH Reaction pathways are proposed by finding intermediates by HPLC, GC-MS.	-	90	-	(Guo et al., 2015)
	Photo-Fenton	Medium	Comparison of efficiency between hydrolysis and photo-Fenton. ● Chlorine ions decrease the efficiency of experiment as Cl react with Fe to form FeCl and providing less Fe to reduce the antibiotic. ● Increase of DOC removal to 75% efficiency on addition of H_2O_2. ● Total removal of SMX using 30 mg L^{-1} of H_2O_2	-	-	100	(Trovó et al., 2011)

continued on following page

Table 3. Continued

Antibiotic	Method of degradation	Cost	Description	Removal efficiency (%)			References
				COD	TOC	Targeted compounds	
Tetracycline	TiO_2/direct photolysis	Medium	50mg/L of tetracycline was used. ● Complete conversion of tetracycline in 2 hours ● TOC removal by 90% in 6 hours.	-	90	100	(Di Fabio et al., 2003)
			Author was able to present a kinetic model of experiment reaction rates.	-	-	-	(Addamo et al., 2005)
Ceftriaxone β-Lactam class	Ozonation O_3/H_2O_2	High	pH affects the experiment for ozonation ● COD removal by 53% at pH 3 ● COD removal by 74% at pH 7 ● COD removal by 82% at pH 11 ● Increase in BOD/COD ratio from zero to 0.10 COD reduced by 90% at a pH of 7 with O_3/H_2O_2 Reaction kinetics could not be determined.	82	-	-	(Akmehmet Balcıoğlu & Ötker, 2003)
Norfloxacin	Fenton Photo-Fenton UV/H_2O_2 UV/ TiO_2 UV/IGBT	Medium	● COD reduction by 95% ● TOC reduction by 93% Optimum conditions: pH 3, Fe concentration of 30 ppm and H_2O_2 concentration 150mg/L. Photo-Fenton method is more efficient than UV alone, Fenton process, UV/H_2O_2, UV/TiO_2 and UV/IGBT	95	93	-	(Shankaraiah, Poodari, Bhagawan, Himabindu, & Vidyavathi, 2016)
Oxacilin β-Lactam class	TiO_2 photocatalysis Sonochemical treatment Photo-Fenton	Medium	● 90% of mineralisation by TiO_2 photocatalysis ● Pollutant removed after 120 minutes of degradation by sonochemical methods ● 100% of mineralisation of pollutant by Photo-Fenton method. Several degradation pathways were proposed.	-	-	100	(Serna-Galvis, Silva-Agredo, Giraldo, Florez, & Palma-Torres, 2016)

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Table 3. Continued

Antibiotic	Method of degradation	Cost	Description	Removal efficiency (%)			References
				COD	TOC	Targeted compounds	
Gemifloxacin	Photochemical Oxidation	Medium	● 40 to 60% degradation by photochemical oxidation ● 65 to 85% degradation of gemifloxacin by peroxide with UV process ● 38 to 65% degradation by Fenton and 68 to 97% degradation by photo-Fenton oxidation process	-	-	97	(Shankaraiah et al., 2018)
Ciprofloxacin	Modified Photo Fenton process	Medium	● 100% removal efficiency of ciprofloxacin in 40 min for higher dose H_2O_2 concentration of 100 mmol/L ● 60% TOC removal using modified photo-Fenton process	-	60	100	(Mondal, Saha & Sinha, 2018)
Ciprofloxacin	Electrooxidation-ozonation	High	● COD removal efficiency of 90.3% in Electrooxidation-ozonation process (EOOP) ● Electrooxidation process (EOP) could remove only 70% of Ciprofloxacin	90.3	-	-	Rahmani et al., 2018
Tinidazole	UVC and simulated solar radiation	High	● % of Tinidazole degradation (120 min) by solar is 97-100 ● % of Tinidazole degradation (120 min) by UVC is 93-100	-	-	100	Velo-Gala et al., 2017

FENTON OXIDATION PROCESS IN ANTIBIOTIC TREATMENT

Fenton chemistry, later known as Fenton reaction, is an oxidation of organic materials by the mixture of iron (II) ions (Fe^{2+}) with hydrogen peroxide (H_2O_2). The efficiency of the Fenton process depends on the concentration of H_2O_2, Fe^{2+}/H_2O_2 ratio, pH, temperature and reaction time (Elmolla & Chaudhuri, 2009). The initial concentration of the pollutant also has an influence on the efficiency of the process. There are two reaction pathways, in which the reaction takes place, (1) a radical pathway production and (2) a non-radical pathway (Barbusinsk, 2009).

Mechanism of Fenton in the radical pathway: Fenton reagent is a reddish-brown solution that can be produced by mixing an amount of ferrous (II) sulphate ($FeSO_4$) and hydrogen peroxide. Upon the addition of hydrogen peroxide to the FeSO4 salt, many bubbles and heat immediately release because the reaction is highly exothermic and vigorous (Elmolla & Chaudhuri, 2009). Eq (1) is the general reaction between ferrous sulphate and hydrogen peroxide together with sulphuric acid. Sulphuric acid is used in the reaction to decrease the pH of the solution. On a normal basis, there is a generation of iron (III) sulphate and water. However, without the addition of sulphuric acid, a chain of reactions occurs as described from Equations (2) to (6) (Barbusinsk, 2009).

$$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O \text{ Eq} \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \; K_{22} = 40 - 80 \text{ Lmol}^{-1} \text{ s}^{-1} \text{ Eq} \tag{2}$$

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \; K_{23} = 9.1 \text{ x } 10^{-7} \text{ Lmol}^{-1} \text{ s}^{-1} \text{ Eq} \tag{3}$$

$$Fe^{3+} + \bullet HO_2 \rightarrow Fe^{2+} + H^+ + O_2 \; K_{24} = 2.5\text{-}5 \text{ x } 108 \text{ Lmol}^{-1} \text{ s}^{-1} \text{ Eq} \tag{4}$$

$$Fe^{2+} + \bullet HO_2 \rightarrow Fe^{3+} + HO_2^- \; K_{25} = 0.72 - 1.5 \text{ x } 106 \text{ Lmol}^{-1}\text{s}^{-1} \text{ Eq} \tag{5}$$

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \; K_{26} = 0.33 - 2.1 \text{ x } 106 \text{ Lmol}^{-1}\text{s}^{-1} \text{ Eq} \tag{6}$$

The initial step is given in Eq (2). The termination reaction is given in Eq (5) and Eq (6). The generation of radicals happens at step Eq (3).

Bench-scale experiments were conducted to evaluate the potential for reducing the COD of this wastewater with Fenton's reagent. The results of the experiments showed that Fenton's reagent was very successful, reducing the COD more than 96%. It was also found in these experiments that the reactions were exothermic (3.748 ± 0.332 J of heat were released per mg/L COD removed). This heat could be captured for useful purposes in the facility (Bergendahl & O'Shaughnessy, 2004).

Several studies have demonstrated that the best oxidation efficiency was achieved when neither H_2O_2 nor Fe^{2+} is overdosed, so that the maximum amount of OH● radicals is available for the oxidation of organics (Torrdes, Perez, Mansilla, & Peral, 2003). Many authors suggested H_2O_2/Fe^{2+} mass ratio to be optimal at 1 to 10, but it must be optimised for particular wastewater to minimize scavenging effects (Torrdes et al., 2003). For pharmaceutical wastewaters, usually Fe^{2+}/H_2O_2 mass ratio from 1/2 to 1/10 is found to be the most effective one (San Sebastian, Fernandez, Segura, & Ferrer, 2003).

The Fenton reaction has a short reaction time among all advanced oxidation processes and it has other important advantages (Gotvajn & Zagorc-Koncan, 2005). Iron and H_2O_2 are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easily to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters, as well as pharmaceutical wastewaters (A. Lopez, Pagano, Volpe, & Di Pinto, 2004; San Sebastian et al., 2003; Torrdes et al., 2003).

Each AOP has its own performance in terms of the degradation degree of the recalcitrant compounds. Some methods such as ozonation were proved to be very efficient by reaching mineralization of the pharmaceutical products i.e. no presence of organic component after degradation. However, from the 'implementation' point of view, it requires more equipment and procedures to install a pre-treatment process in the wastewater treatment plants.

Fenton has a high efficiency in the reduction of COD and TOC, varying from 95% to 100% (total mineralization) within 5 minutes of the reaction. The rate of reaction is high with k (rate constant) values of 63 L mol-1 s-1. However, as reaction progressed, there was a regeneration from Fe(III) to Fe(II), which caused the reaction rate to be slower (Serna-Galvis et al., 2016).

If the reaction rate for a particular by-product is slower, it may be the rate limiting step in the complete mineralization of the target compound and the by-product will accumulate. Ideally, AOP systems are designed to completely mineralize the organic contaminants of concern to CO2 and H2O. However, this may require more energy and higher chemical dosages. Consequently, it may result in being cost prohibitive in some certain applications.

The conditions for Fenton process are suitable for operation. The conditions are at ambient conditions which are atmospheric pressure of 1 atm and at ambient temperature of 25°C. pH adjustment is required from 2 to 3. Various researchers operated their Fenton processes at pH 3. In the optimization of Fenton for the antibiotics such as amoxicillin, ampicillin and cloxacillin, the authors stated that the optimum conditions are COD/H_2O_2/Fe^{2+} molar ratio of 1:3:0.30 and pH 3 (Elmolla & Chaudhuri, 2009).

Iron species can influence the efficiency of degradation in the study of different species of iron (FeOx and FeSO4). FeOx favours oxidation more than FeSO4 as per some findings. However, the use of FeOx exhibited the presence of oxalate, which is toxic to neonates. Thus, the use of FeOx is rejected (Trovó et al., 2011). The use of Ferrous (II) sulphate is maintained to carry out the experiment.

An increase in the fragments of organics material scavenges for the hydroxyl radicals. It is suggested that, to scavenge all the radicals in the treated sample to mineralisation, the required amount of hydrogen peroxide highly depends on the initial COD. Thus, higher concentrations of the Fenton reagent at 0.3 M and 0.4 M showed a better result than that at 0.1 M and 0.2 M (Nithyanandam & Saravanane, 2013).

From the industrial implementation point of view, it is important to know the initial concentration at which the effluent is being oxidised. There is obviously a variation in COD level of effluent from industries. Thus, a control strategy should be considered when applying Fenton process in WWTPs. For example, feedback control strategies which measure the initial COD of the effluent before injecting hydrogen peroxide.

There is evidence that the mechanism of the Fenton reaction is considerably more complicated. The reaction time necessary for the Fenton method is extremely low and depends on H_2O_2 concentration and temperature. Within 5 min a near complete destruction of COD could be observed.

An advantage of the Fenton treatment is the low reaction time which is only about 5% in comparison to the other methods. Capital and operating costs for application of Fenton's reagent can be expected to be low compared to the other AOPs. Iron and hydrogen peroxide are cheap and easily available.

The Fenton method shows the shortest reaction time. If a given wastewater problem requires the degradation of large amounts of COD (> 5 000 mg/l) this kind of treatment will be most appropriate. The other methods involve very long reaction times. Fenton treatment, however, appears to be technically very complicated, as the pH should be near 2 during the reaction, and the dissolved iron has to be precipitated as Fe(OH), by neutralization at the end of the process. Hence, pH adjustment methods should be studied furthermore. The precipitation of Fe(OH) can be filtered out after oxidation treatment of waste water.

Atrazine Degradation by Anodic Fenton Treatment

The growing concern about pesticides and their degradation products in natural waters is reflected in the significant monitoring studies undertaken by the United States Geological Survey (USGS) through the National Water Quality Assessment (NAWQA) Program and the Midwest Pesticide Study (MWPS) (Sandy, Grady, Jr, Meininger, & Boe, 2001) . In these studies, conducted from 1993 to 1995 and 1991 to 1994, respectively, thousands of sample wells and springs were used across the US to generate data for a range of compounds in rural and urban groundwater.

Atrazine stood out as a compound of concern. Although 98% of all detections for seven herbicides of interest (atrazine, cyanazine, simazine, alachlor, metolachlor, prometon and acetochlor) were <1 mg/L, atrazine was the only herbicide found to exceed the US Environmental Protection Agency (EPA) water quality criterion for drinking water of 3 mg/L. Atrazine has also had the highest application rates for this group of herbicides for the 30-year period 1964–1994 (Barhash, Thelin, Koplin, & Gilliom, 1999).

Ciba Crop Protection conducted a monitoring study specifically for atrazine and its seven major triazine degradation products, desethylatrazine (DEA), deisopropylatrazine (DIA), diaminochlorotriazine or desethyldeisopropylatrazine (DEIA), hydroxyatrazine (HA), desethylhydroxyatrazine (DEHA), deisopropylatrazine sites across 19 states were based on high use areas, previous histories of atrazine detection, and the need to cover a range of geographic areas in the US (Blau, Holden, Johnson, & Cheung, 1998). Eight wells of the 1505 contained atrazine concentrations in excess of the 3.0 mg/L or 3.0 ppb maximum contaminant level (MCL).

Many community water systems in the Corn Belt are considered to be in violation of the revised Safe Drinking Water Act with respect to atrazine. Both atrazine and its metabolite DEA have been included in the EPA Draft Drinking Water Contaminant List (EPA, 1997). Total triazine load in midwestern streams was investigated for monitoring for atrazine and four degradation products, DEA, DIA, DEIA and HA (Lerch, Blanchard, & Thurman, 1998). High maximum concentrations of atrazine were found in both northern Missouri streams (136 mg/L) and Midwest streams (50.4 mg/L).

Atrazine has recently been a compound of interest for a variety of chemical oxidation techniques. Atrazine was degraded to ammeline using a combined ozone/hydrogen peroxide treatment (Nelieu, Kerhoas, & Einhorn, 2000). A conventional ozonation and the combined ozone/peroxide treatment was used to degrade low concentrations of atrazine (Acero, Stemmler, & Von Gunten, 2000). An irradiated iron/oxalate treatment system was applied to low concentrations of atrazine (Balmer & Sulzberger, 1999). A photo- Fenton degradation of atrazine was study (Huston & Pignatello, 1999), while a classic Fenton approach and combined Chemical and biological degradation was applied (Arnold, Hickey, & Harris, 1995; Arnold, Hickey, Harris, & Talaat, 1998). These studies had various advantages and disadvantages, but there is still a need for a method that can be used in situ and that can Conveniently detoxify reasonably high concentrations of pesticide wastewater (>100 mM).

A STUDY ON THE RELATIONSHIP BETWEEN BIODEGRADABILITY ENHANCEMENT AND OXIDATION OF 1,4-DIOXANE USING OZONE AND HYDROGEN PEROXIDE

4-Dioxane (dioxane) is a cyclic ether as a water pollutant which has major impacts on human health and the environment. It is used widely in industry as a solvent for many organic and inorganic compounds (Sandy et al., 2001). Dioxane is also produced as a by-product in many industrial processes such as ethylene glycol, ethylene oxide, and polyethylene tetraphthalate manufacturing factories (Anaizy & Akgerman, 2000; Sandy et al., 2001). 1,4- Dioxane is a known carcinogen to animals and a suspected carcinogen to human, and hence, is classified as a hazardous compound and a priority pollutant (Stefan & Bolton, 1998). If not removed from industrial wastewater effluent, 1, 4- dioxane occurs as a xenobiotic constituent of groundwater and drinking water (Adams et al., 1994).

Conventional water treatment techniques are limited in their effectiveness for the treatment of 1, 4-dioxane-contaminated water. Since dioxane is very hydrophilic and water soluble and has a very low vapor pressure (with a Henry's law constant of 9.05×10-6 atm.m3/mol at 25°C), carbon adsorption and air stripping are not feasible and cost effective. Also, distillation is not a feasible option under normal circumstances because of dioxane's boiling point (bp=101°C) which makes the separation and removal process extremely energy intensive. Despite the fact that dioxane biodegradation was achieved through bio-augmentation and the use of enriched microbial cultures, conventional biological processes cannot oxidize this compound effectively due to its high resistance to biotransformation. Also, biological processes may be subject to upset with respect to the conversion of dioxane (Adams et al., 1994).

A typical advanced oxidation technologies (AOTs) involves a combination of ozone and hydrogen peroxide (O_3/H_2O_2) which is particularly promising for recalcitrant materials due to its capability to produce high levels of hydroxyl radical (OH•), a strong oxidant. This process has been applied to several toxic nonbiodegradable compounds such as methyl-tert-butyl ether, atrazine, and alachlor and has resulted in significant pollutant removal efficiencies.

Several studies examined O_3/H_2O_2 process for the removal of 1, 4-dioxane in aqueous solutions. All these studies showed that O_3/H_2O_2 could remove 1, 4-dioxane to low ppb levels. The impact of OH• scavengers was investigated and observed that dioxane removal was negatively affected by the presence of humic acids in the solution (Kosaka, Yamada, Matsui, & Shishida, 2000). In addition, Adams et al. showed that O_3/H_2O_2 process could be used as a pre-treatment process to enhance biodegradability of dioxane contaminated water (McGrane, 1997).

Although all these studies indicated that AOTs could be used to enhance biodegradability of dioxane contaminated water, no systematic study focused on the kinetics of 1,4-dioxane oxidation and its relationship to biodegradability enhancement. The oxidation kinetics and its relation to biodegradability enhancement are important information that are integral to potential success of AOTs in large scale water treatment and purification applications.

PHOTOCHEMICAL DEGRADATION OF HYDROPHILIC XENOBIOTICS IN THE UV/H_2O_2 PROCESS

Natural waters are often contaminated with hydrophilic xenobiotics such as amino-poly-carboxylates and aromatic sulfonates (Rossknecht, 1991). Amino-poly-carboxylates and aromatic sulfonates were classified as the most important hydrophilic xenobiotics in the aquatic system (Brauch, 1991). These substances are widely used in industrial and domestic processes. Because of their biological resistance, these substances pass through the conventional wastewater treatment processes and appear in natural waters which were used as raw waters. The development of techniques to eliminate these substances in drinking water treatment is, therefore, important. Problems arise, however, from their poor degradability by classical oxidation methods using ozone or chlorine (Lang et al., 1996; Schullerer & Brauch, 1989).

Their hydrophilic character leads also to a low efficiency of activated carbon filtration (Johannsen, Gross, Gaukel, Sontheimer, & Frimmel, 1994; Schullerer & Brauch, 1989). Photo- chemical oxidation, a powerful degradation method for the treatment of contaminated raw water, seems to be a promising tool for the elimination of this problematic class of micropollutants (Hessler, Gorenflo, & Frimmel, 1993; Legrini et al., 1993; Yon Sonnag, 1993).

Basically, there are two prominent techniques of UV irradiation in water treatment: irradiation in the absence of an oxidant for the disinfection of water (Wolfe, 1990; Yon Sonnag, 1993) and irradiation in combination with an oxidant (e.g. H_2O_2) for the removal and/or detoxification of pollutants. If UV radiation is used for the disinfection of water, chemical reactions with organic matter are not envisaged, because of an increase in microbial regrowth potential or the formation of trihalogenated methanes after chlorination (Sorensen & Frimmel, 1995).

The removal of micropollutants in the UV/H_2O_2 process is based on the photolysis of H_2O_2, which leads to reactive OH● radicals. The OH● radicals are known as strong oxidants and oxidize organic matter like pesticides with a high efficiency (Beltrain, Ovejero, & Acedo, 1993; Ho, 1986). Hydrophilic xenobiotics can be eliminated effectively in the UV/H_2O_2 process as well.

Data are available for the degradation of amino-poly-carboxylates, EDTA and NTA and aromatic sulfonates in waters (Sorensen, Sagawe, & Frimmel, 1996).

Nitrate as a major compound of many natural waters is known to interact with UV light with the formation of OH● radicals. This is of significant interest to know in which way nitrate influences the photochemical degradation of organic micropollutants (Yon Sonnag, 1993). Nitrate absorbs light in the UV range and acts as an inner filter for the UV light (Hessler et al., 1993). However, because nitrate can form OH● radicals when irradiated, it might also be able to increase the degradation rate of the photolytic processes.

ADVANCED OXIDATION OF THE PHARMACEUTICAL DRUG

In recent years pharmaceutical drugs have emerged as a novel class of water contaminants for which public and scientific concern is increasing steadily because of the potential impact on human health and the environment even at trace levels. Huge amounts of these chemicals in terms of thousands of tons are annually used for therapeutic purposes or in animal farming in each European country, and may be excreted both unmetabolized and as active metabolites. Improper disposal or industrial waste may also contribute to their occurrence in aquatic environments, due in part to ineffective degradation in sewage treatment plants.

A typical case is (2-[20, 60-dichlorophenyl) amino] phenyl acetic acid) (diclofenac, 1), a popular non-steroidal anti-inflammatory drug widely used to treat inflammatory and painful diseases of rheumatic and nonrheumatic origin which has been detected in many municipal sewage treatment plant (STP) effluents. Although it is susceptible to photo degradation by complex mechanisms depending on environmental conditions, its presence has been documented in river and lake waters. Preliminary investigations concerning diclofenac impact on aquatic life indicated some adverse effects on rainbow routs exposed to water concentrations of 1.0 mgL-1 for 28 days. Although no conclusive data is available about the possible environmental effect of diclofenac in surface waters, an evaluation of the suitability of currently available processes for removal of organic pollutants from STP effluents seemed appropriate.

Recently, some investigations on the removal of diclofenac from contaminated and drinking waters by means of advanced oxidation processes (O_3, O_3/H_2O_2 and photo–Fenton), have appeared; however, neither detailed kinetic assessments nor intermediate/product analysis during the degradation pathways were provided.

It is reported that the oxidation behaviour of diclofenac to ozone and UV/H_2O_2, two widely used oxidizing systems with established effectiveness and a high level of technical development for industrial application. Specific aims of the study were to investigate the kinetics of the processes and to assess the nature of the main intermediates along the route to mineralization. This latter aspect is of particular relevance, since potentially toxic species may be produced by incomplete degradation of organic pollutants and their assessment is an absolute requirement should the method be applied for water remediation.

PHOTOCHEMICAL ELIMINATION OF PHENOLS AND COD IN INDUSTRIAL WASTEWATERS

Photochemical methods including photolysis and photo-catalysis, are attractive environmental remediation technologies for organic pollutant degradation and final mineralization in aquatic and air environment, and have been researched widely for many years. The photo-Fenton reaction (e.g. $UV/H_2O_2/Fe^{2+}$) is a primary area of photolysis and has been studied in detail. It promises a significant pathway for the treatment of wastewater contaminated by various organic compounds (Takahashi, Nakal, Satoh, & Katoh, 1994). Heterogeneous photo catalysis, using various semiconductor photo catalysts such as titanium dioxide, zinc oxide, and ferric oxide, is also a feasible method for the detoxification of water containing various organic and inorganic pollutants, such as halogen organics, insecticides, surfactants and heavy metals.

Homogeneous photolysis methods, compared with photo catalysis, do not demand a separation procedure of solid catalyst after treatment. For effective treatment, photolysis requires short wavelengths of strong energy UV light and other chemical oxidants such as hydrogen peroxide and ozone. However, photo catalysis can use long wavelengths of less energy near UV and visible light, such as sunlight for effective elimination of pollutants.

Fixing photo catalyst on a supporter avoids the need for a separation process of slurry catalyst from water, but this process has much less photo catalytic activity (2.6 times slower) than suspending systems. Combining homogeneous photolysis and photo catalysis methods can enhance the efficiency of treatment due to the association role of the two methods via promoting the light utilization rate of different wavelength of lamps or sunlight on H_2O_2 and photo catalyst. A combined system can be photo catalyst together with strong energy UV light, or together with H_2O_2/Fe^{2+}. These systems can photo catalyse and photolyze toxic substrates directly or indirectly.

Some studies have been reported on the combination of photolysis and photo catalysis for wastewater treatment. In natural environment, phenol derivatives are toxic and refractory pollutants. They are present extensively in the wastewater of oil refining, pharmacy, electroplating, papermaking, coking and iron-smelting industry etc. (Alvares, Daper, & Parsons, 2001; Halling-Sorensen et al., 1998; Scott & Ollis, 1995). Some industrial wastewaters have various substituted phenols and non-biodegradable compounds. The typical chemical composition of some industrial wastewaters is shown in Table 4.

The treatment of phenol containing wastewater to a harmless level of 0.5 ppm is a difficult process for many chemical and biological methods because of its high solubility and stability. There are many reports on photolysis and photo catalysis for treatments of phenol containing wastewaters. Most photo catalytic treatment processes of phenol containing wastewaters use slurry TiO2 as photo catalyst because until now it is the most efficient and non-toxic photo catalyst, but in practical application there is a problem how to separate the slurry from wastewater for industrial application. Some researchers examined the photo activity of other materials such as ZnO, CdS, and Fe, O etc. which also showed activity on various pollutants

Ferric compounds, especially tri-iron tetra-oxide, have been surveyed as a photo catalyst. Because it has magnetic properties, the suspending powder can be recollected from the wastewater by magnetic methods. Related ores as alternatives to the pure compounds are very interesting in economical point of view. Magnetite as a ferric photo catalyst is a good choice because its main component contains magnetic hi-iron tetroxide. With respect to aluminium oxide as a photo catalyst it is interesting to look to the possibilities of using its ores of bauxite and kaolin as photo catalysts. The effect of combining photolysis (employing strong energy UV light) and photo catalysis (using magnetite and dialuminium trioxide as photo catalysts) was investigated on the treatment possibilities of various types of industrial wastewaters (Nithyanandam & Saravanane, 2013).

REVIEW OF ANTIBIOTICS AND THEIR REACTION DURING AOP

Many antibiotics have been studied for the past 15 years, since the concern of the antibiotic resistant bacteria have been overlapping subject matters. The antibiotics from different sub-classes namely, β-Lactam antibiotics, Macrolide (non-β-lactam) antibiotics, Quinolone antibiotics and Sulfanoamide antibiotics have been reviewed by various authors in the field of the advanced oxidation processes. Table 5 shows a list of classified antibiotics that have been studied due to their repetitive occurrences in the analysis.

As can be seen in Table 5, for each study, a specific antibiotic was chosen to be degraded by one or two methods. The common methods of degradation are Fenton and ozonation. As the literature progresses, a few number of studies have been made on 'Cephalosporin' family of antibiotics and hence, their degradation efficiencies and degradation pathways are limited in literature (Ikehata et al., 2006). Similar feedback is reported while carrying the study of treatment of the pharmaceutical sludge. The author found that 7- amino cephaslosporanic acid (7ACA) was the main degradation product in the pharmaceutical

Table 4. The components of some industrial wastewater

Name of wastewater	Phenols (ppm)	COD* (ppm)	Colour and compounds present	pH
Phenolic resin	400	~	Pink, resin, formaldehyde, Cu^{2+}, HCl	1
Petroleum refining	50	500	No colour	7
Naphthenic acid	12	1300	No colour	6
Shale dry distillation	200	16,000	Dark brown, cyanide, hydrocarbons, etc.	8

sludge (Deshpande, Baheti, & Chatterjee, 2004). A sludge contained a variety of pharmaceutical products including antibiotics, anticonvulsant, antidepressant. 7ACA, which is a major intermediate during the quantitative analysis, raised attention of groups of cephalosporins. The production pathway of 7ACA by enzymatic means and by means of chemical degradation of cephalosporin C confirms that 7ACA is an intermediate for the antibiotics belonging to cephalosporin family (Deshpande et al., 2004).

Furthermore, Keisuke Ikehata et al. specifically emphasised on the missing information of the degradation pathway of Ceftriaxone, the 3rd generation class of antibiotic from the Cephalosporin family. Hence, more literature is converged on the studies carried out on Ceftriaxone (Ikehata et al., 2006)

Ceftriaxone Antibiotic

Ceftriaxone is a β-lactam semi-synthetic antibiotic. It is from the third-generation cephalosporin antibiotic and is able to kill bacterial activity in organisms. β-lactam antibiotics have a tendency to undergo rapid ring opening by hydrolysis which results in a poor antimicrobial activity. Ceftriaxone is distributed in the form of its disodium salt. Figure 2 shows the skeletal structure of ceftriaxone, displaying the different bonds which make the compound recalcitrant in water.

Table 5. List of most occurring antibiotics that have been studied by AOP

Class	Sub Class	Name of pharmaceuticals	Method used	References
Antibiotic	β-Lactam	Amoxicillin, Cefradine	Photo-Fenton Fenton	(Elmolla & Chaudhuri, 2009)
		Ceftriaxone, Penicillin VK	Ozonation O_3/H_2O_2	(Akmehmet Balcıoğlu & Ötker, 2003)
		Penicillin G,	Ozonation	(Arslan-Alaton & Caglayan, 2005)
	Macrolide	Azithromycin, Clarithromycin	Fenton Fenton-like Electro-Fenton	(Mahdieh, Yazdanbakhsh, & Amir, 2013)
		Erythromycin	Ozonation	(Luiz et al., 2010)
		Lincomycin, Roxithromycin,	Ozonation	(Liu, Jiang, Nanaboina, & Korshin, 2011)
	Quinolone	Ofloxacin	Solar Fenton Solar TiO_2	(Michael, Hapeshi, Michael, & Fatta-Kassinos, 2010)
		Enrofloxacin	Ozonation	(Liu et al., 2011)
	Sulfonamide	Sulfamethoxazole	Electron Beam Ozone UV	(T. Kim et al., 2012)
		Sulfadiazine, Sulfadimethoxine, Sulfamerazine, Sulfathizole	TiO_2	(Petrovic, Radjenovic, & Barcelo, 2011)
		Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfamerazine	Free hydroxyl radical	(Mezyk, Neubauer, Cooper, & Peller, 2007)

The use of ceftriaxone antibiotic is popular in the world. Many places such as the United States and China have reported the presence of ceftriaxone in their waters. Similarly, Malaysia also has reported the persistent reoccurrence of ceftriaxone in the waters (Karunakaran et al., 2012). Karunakaran et al. reported that a prevalence of ceftriaxone resistance and the associated genes were determined in 149 non-duplicate non-typhoidal Salmonella isolated in 2008 -2009 from patients in hospital in Kuala Lumpur, Malaysia. The resistance keeps on increasing from 2.7% in 2008 to 4.0% in 2009. It is recommended that monitoring should be made in the health field because the resistance creates limitations in therapeutic options (Karunakaran et al., 2012). Table 6 represents some information of the ceftriaxone antibiotic.

DEGRADATION PATHWAY

Beside the general indicators of water quality (COD, BOD, TOC, DOC, TSS), it is important to identify the degradation intermediates and final products by following the evolution of the reaction during the treatment. This will help to optimise the treatment.

The advanced performing technologies such as Mass Spectrometry, Fourier Transform Infrared Spectroscopy (FTIR), Liquid Chromatography Mass Spectrometry (LC-MS), High Performance Liquid Chromatography (HPLC), Gas Chromatography Mass Spectrometry (GC-MS) are preferred among others to identify fragments of compounds based on their retention time and mass. Table 7 shows a comparison of different identification technologies used to retrace the compounds present after degradation of certain antibiotics with some respective identified intermediates.

Figure 2. Skeletal structure of Ceftriaxone antibiotic

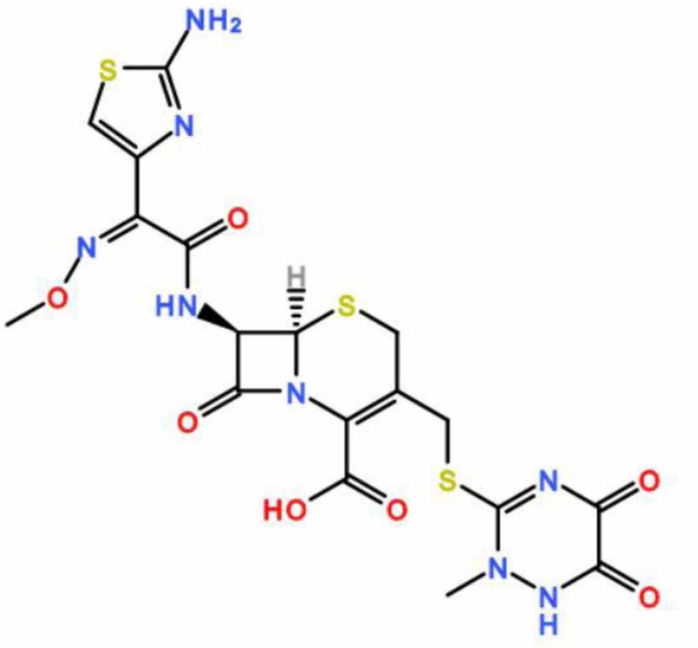

Table 6. Summary of Ceftriaxone antibiotic details

Attributes	Details
Name	Ceftriaxone
Brand names	Rocephin, Epicephin, Arixon, Elcefrin
Chemical formula	$C_{18}H_{18}N_8O_7S_3$
Molecular weight	554.58 g/mol
CAS Registry	73384-59-5
Antibiotic class	Third-Generation Cephalosporin
Antimicrobial Spectrum	Staphylococcus aureus (methicillin susceptible), Coagulase negative Staphylococci, Streptococcus pneumoniae (penicillin susceptible), Streptococcus spp., Haemophilus influenzae, Moraxella catarrhalis, Neisseria meningitides, Neisseria gonorrhoeae, Enterobacteriaceae, E. coli
Mechanism of action	Cephalosporins exert bactericidal activity by interfering with bacterial cell wall synthesis and inhibiting cross-linking of the peptidoglycan. The cephalosporins play a role in the activation of bacterial cell autolysins which may contribute to bacterial cell lysis.
Pregnancy Risk Factor	B

Mass Spectrometry is widely used in the literature. Some authors suggested the use of GC-MS or most preferably LC-MS. Since water is not convenient to be found in GC-MS, using LC-MS is another option. However, to use HPLC, the compounds of interest must be identified and pre-ordered to verify the presence of the particular components to be identified. Ceftriaxone as an antibiotic not reviewed in terms of degradation, HPLC does not seem to be the first choice for the qualitative analysis.

Degradation of Pentachlorophenol by Ozonation and Biodegradability of Intermediates

Pentachlorophenol (PCP), a highly chlorinated hydrocarbon, has been widely used as a wood preservative and biocide. It is prevalent in the environment and found in over one-fifth of the contaminated sites on the National Priorities List. Owing to its acute and chronic toxic and carcinogenic nature, PCP is on the US EPAs list of Priority Pollutants and subject to a stringent maximum contaminant level (MCL) of 0.001 mg/L set for drinking water. Even more toxic compounds such as polychlorinated dibenzodioxins and dibenzofurans are possible combustion products of PCP.

Both biological and chemical remediation were used for PCP. Among scores of chemicals tested, PCP ranked among the most toxic and recalcitrant compounds to activated sludge. Advanced oxidation processes (AOPs) such as Fenton reagent, ozone, ozone/UV, ozone/ultrasound, and UV/H_2O_2 were found useful for treating chloro-phenols and chloro-benzenes (Benoit-Guyod et al., 1994). Reaction products were identified as oxalic acid, formaldehyde, and acetone. Hydroxylation and hydroxylation with dechlorination steps based on OH●˙ radical was employed to affect the degradation of chlorophenols and PCP.

Studies on PCP degradation by ozonation have primarily focused on kinetics. The kinetics of ozonation of PCP was studied in aqueous solutions and reported as second-order reaction of O_3 with PCP with rate constants varying from 104 to107 m-1 s-1 depending on pH (Kuo & Huang, 1995) . The reaction of O_3 with PCP was also studied and found this direct reaction to be second-order free radicals' involvement (J. Y. Kim & Moon, 2000). The kinetics and mechanism of PCP degradation with ultrasound irradiation

Table 7. Methods employed to identify intermediate compounds after degradation process of some antibiotics

Antibiotic	Degradation method	Intermediates identified	Description	References
Trimethoprim (TMP)	Electro-Fenton	Aromatic products Carboxylic acid	HPLC and GC-MS were used to identify intermediates. Evolution of the reactions monitored at different time intervals by measuring the molecular weight of each new formation. The action of hydroxyl radicals on aromatic intermediates is easier than on carboxylic acids.	(Mansour et al., 2015)
Ciprofloxacin	Ferrous-activated persulfate	N/A	Use of MS technology. 3 major degradation pathways were identified with a confirmation of the intermediates.	(Ji, Ferronato, Salvador, Yang, & Chovelon, 2014)
Tetracycline	γ-radiolysis	Phenolic product	HPLC and GC-MS technology used to identify species. Aromatic rings form a resonance-stabilised carbon-centred radical followed by elimination of hydroperoxyl radical.	(Joonseon Jeong, Song, Cooper, Jung, & Greaves, 2010)
Ampicillin	UV irradiation	Carbonyl group identified	Mass spectrometry (MS) analysis used. Aromatic ring was targeted for attack by hydroxyl radical. Successful degradation of β-lactam antibiotic increases the bio-availability of the treated solution beneficial for activated sludge in WWTP.	(He, Mezyk, Michael, Fatta-Kassinos, & Dionysiou, 2014)
Oxacillin (OXA)	Photocatalysis	N/A	HPLC and MS technology used to identify the present species. ● β-lactam ring is a highly reactive site because carbonyl-nitrogen bond is labile. ● Thioether group has a high nucleophilic character. ● Aromatic ring experiences electrophilic substitutions. ● Oxazolyl substituent enhances the amide activity.	(Serna-Galvis et al., 2016)

and ozonation, in which the thermolytic decomposition of O_3 in the presence of ultrasound irradiation effectively produced two OH● radicals per O_3 molecule (Weavers, Malmstadt, & Hoffmann, 2000). They found the formation of tetrachloro-o-benzoquinone intermediate originating from initial hydroxyl radical attack of PCP at the ortho position.

Degradation of PCP using AOPs that involve O_3 can be via direct reaction with O_3, via secondary free radicals (e.g., OH●) from O_3 hydrolysis, or via both concurrently. While past studies have primarily focused on the kinetics of PCP degradation, relatively few have been undertaken to provide mechanistic details and identification of intermediates and products for PCP degradation by O_3. This work has examined the degradation pathway of PCP under ozonation and evaluated the biodegradability of intermediates over progressive stages of ozonation. An underlying focus has been to examine the viability of using an integrated system utilizing ozonation followed by biological treatment for the treatment of PCP and possibly other highly toxic polychlorinated aromatics.

CONCLUSION

Antibiotic compound (C18 or above) could be degraded to C3 molecules. However, for complete mineralisation retention time of advanced oxidation process need to be extended or/and OH● need to be produced in a higher concentration. Advanced Oxidation Process is a prominent method which can be implemented in wastewater treatment plants for complete mineralization of xenobiotic compounds such as antibiotic. Degradation pathway of the pharmaceutical chemicals can be obtained from GC-MS or LC-MS with the support of FTIR analysis later confirms the presence of functional group.

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KEY TERMS AND DEFINITIONS

Antibiotics: Drugs used in medical treatments of bacterial infection by either killing or inhibiting the growth of bacteria.

Ceftriaxone: A type of antibiotics, called β-lactam, which is semi-synthesized as the third-generation cephalosporin antibiotic.

Degradation Pathway: A condition or process to degrade antibiotics.

Fenton Process: An oxidation of organic materials by a mixture of iron (II) ions with hydrogen peroxide.

Hydrogen Peroxide: An inorganic chemical with a chemical formula (H_2O_2), used in Fenton process.

Oxidation: The transfer of one or more electrons from an electron donor (reductant) to an electron accepter (oxidant), which has a higher affinity for electrons.

Ozonation: An infusion of ozone gas (O_3) into water as a technique used in wastewater treatment to oxidize water pollutants.

Radical: A chemical specie having an odd number of valence electron and highly reactive.

Wastewater Treatment: A general term referring to methods/technique to treat wastewater at the water treatment plant by removing impurities and pollutants in the used water for the purpose of water reuse.

Chapter 11

Comparative Study of Advance Oxidation Processes for Treatment of Pesticide Wastewater

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ABSTRACT

This study compared the amount of catalyst and energy efficiency required for operation of five advanced oxidation processes (Fenton, UV photo-Fenton, solar photo-Fenton, UV/TiO2/H2O2, and FeGAC/H2O2) for degradation of the pesticides chlorpyrifos cypermethrin and chlorothalonil wastewater. Under optimum operating conditions, degradation in terms of COD and TOC removal and biodegradability (BOD5/COD ratio) index (BI) were observed to be (1) Fenton – 69.03% (COD), 55.61% (TOC), and 0.35 (BI); (2) UV photo-Fenton – 78.56% (COD), 63.76% (TOC), and 0.38 (BI); (3) solar photo-Fenton – 74.19% (COD), 58.32% (TOC), and 0.36 (BI); (4) UV/TiO2/H2O2 – 53.62% (COD), 21.54% (TOC), and 0.26 (BI); and (5) FeGAC/H2O2 – 96.19% (COD), 85.60% (TOC), and 0.40 (BI). The cost was $39.9/kg TOC (Fenton), $34.1/kg TOC (UV photo-Fenton), $30.1/kg TOC (solar photo-Fenton), $239/kg TOC (UV/TiO2/H2O2), and $0.74/kg TOC (FeGAC/H2O2). The FeGAC/H2O2 process was found to be most efficient and cost effective for pretreatment of the pesticide wastewater for biological treatment.

INTRODUCTION

There is a very high interest in the surface water usage and protection in Malaysia. This is because it provides about 98% of the water needs of various communities in the country (Azhar, 2000). Therefore, contamination could be very dangerous as it would cause a critical health risk to the entire population. The Department of Environment (DOE), under the Ministry of Natural Resources & Environment,

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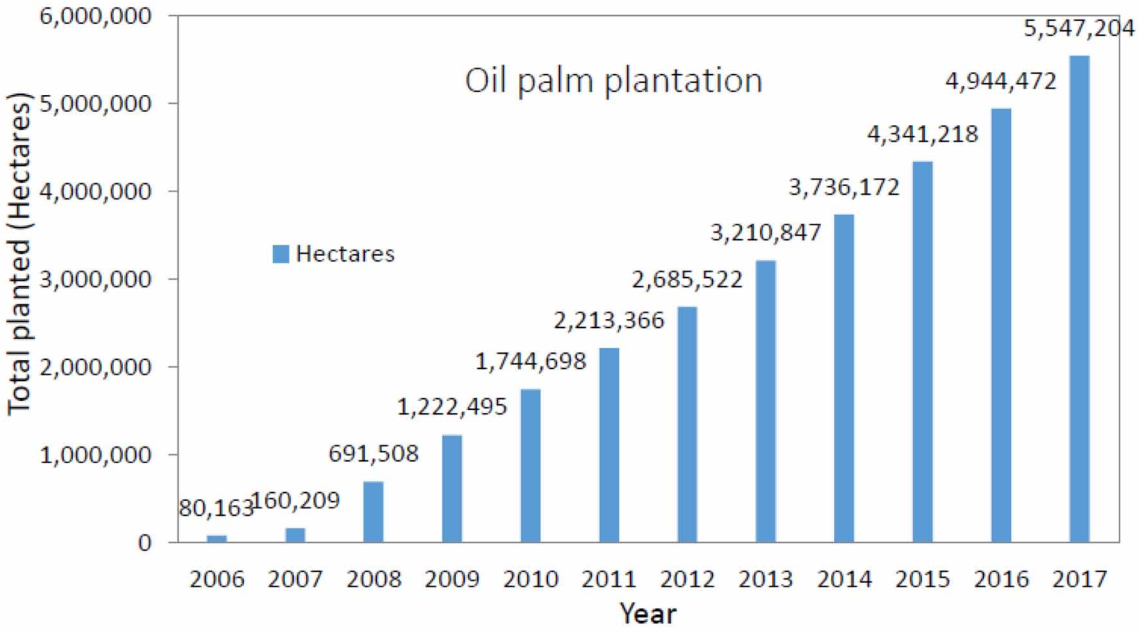
Malaysia is charged to monitor river water quality annually. However, pesticide contamination and its concentration in rivers are not documented in the water quality reports (DOE, 1998 and 2010; National Water Quality Index of Malaysia (DOE, 2017), whereas the pesticide industry is about the top supporting sector for the agricultural industry which brings in high income revenue to the economy. According to Sime Derby updated annual reports, the total land bank covered by their plantation is approximately 1,000,000 hectares. This includes over 602,000 ha planted with oil palm, over 13,400 ha planted with rubber, over 5,600 ha planted with sugar cane and close to 9,000 ha is used as grazing pastures (Sime Darby Annual reports, 2017) as seen in Figure 1. This shows an increase in use of pesticides due to the huge increase in planted hectares from 200 until 2017.

On the one hand, the documented pesticide concentration detected in soil residue, waterways, rivers and crop fields (Abdullah, 2002) calls for strict and improved monitoring and/or alternatives in the eventual wastewater treatment process before discharge into the inland waterways and rivers (Naubi et al., 2016). On the other hand, treatment of the pesticide wastewater requires to be complete in order to degrade active ingredients or the organic bonds of parent compounds used in the formulation and production of the pesticide. In other to accomplish this, the use of economical treatment methods which are sustainable irrespective of the concentration of pesticide wastewater at any given treatment plant is imperative.

Pesticides are grouped into various unique classes including organochlorine, organophosphorus, carbamate, pyrethroid, etc. The organochlorine pesticide (OCPs) is about the most common. It is one of the pesticides categorized as persistent organic pesticide (POP). A revised version of POPs were added to the archive during the Stockholm Convention in year 2009 listed additional pesticides and Malaysia is signatory to this treaty (Qiu & Cai, 2010; Martins et al., 2013; Pariatamby & Kee, 2016). In addition, some pesticides numbering up to 40 and chosen by the Malaysian Ministry of Agriculture are still being

Figure 1. *Oil palm plantation in terms of planted hectares*
(Sime Darby, 2017)



found in the surface waters and basically chlorinated pesticides, namely heptachlor, Aldrin, chlordane, Dieldrin, DDT, endosulfan, heptachlor and HCH isomers. Pesticide residues such as organochlorines can exist in aquatic environment as a result of precipitation, runoff and leaching from nearby agriculture field. Typically, residue mobility is influenced by their chemical characteristics such as strong affinity to particulate matter, low biodegradation and low water solubility (Malhat & Nasr, 2013). In addition, where non-targeted organisms are affected, it could degenerate the ecosystem and every living organism, and reduce water and environmental quality. This is especially in the case of application of endocrine disruptors within the pesticide family or classes (Tomza-Marciniak & Witczak, 2010). However, recent studies hold the opinion that pesticides reduced the number of mosquitoes i.e. larvicides and pathogen transmission to wildlife and humans (Lawler, 2017). In spite of stoppage of globally banned categories of pesticides, the absolute binding of the law on businesses remain ineffective and uncertain. Some studies carried out in the ASEAN (Association of Southeast Asian Nations) region, have identified the impact of pesticides that are banned globally. They also reported their presence in surface water and sediment of rivers including, Han River, South Korea (Kim et al., 2009), Gomti River, India (Malik et al., 2009), Daliao River and Qiantang River, China (Tan et al., 2009; Zhou et al., 2006), as well as in the Mae Klong River and Patani River, Thailand (Houng et al., 2002; Poolpak et al., 2008; Samoh & Ibrahim, 2009), Red and Duong Rivers (Vietnam). Globally banned and restricted pesticides that may affect human health was reported in tap water and surface waters of rivers in Cameron Highlands, Pahang. Endrine ketone, DDE (a derivative of DDT), endosulfan and aldrin were detected in a total of five sampling sites conducted at the Bertam and Terla rivers. Also, the ascertained if it was in portable water supply in Brinchang town. Endosulfan for example, has been banned in Malaysia and around the world, and as pesticide organic pollutant (POP), it is prone to accumulate and could find its way into the food chain and eventually to humans beings. It can travel long distances, but it degrades very slowly in the aquatic matrix. This study investigates the degradation of pesticide wastewater (containing chlorpyrifos, cypermethrin and chlorothalonil) by five AOPs (Fenton, UV photo-Fenton, solar photo-Fenton, ultra violet/titanium dioxide/hydrogen peroxide (UV/TiO_2/H_2O_2) and Fe^{3+} granulated activated carbon/hydrogen peroxide (FeGAC/H_2O_2 processes), and the effect of the operating conditions of each process on the pesticide degradation (COD and TOC removal) and biodegradability (BOD_5/COD ratio) improvement. In addition, their individual effective cost analysis were carried out. This is an attempt to explore possible treatment alternatives that may be adopted. Choice of the selected pesticide was based on their use in cultivation of important economic crops and their solubility in water which allows for their propagation in the aquatic environment possible.

BACKGROUNG OF THE STUDY

Surface water is one of the most important resources for human sustenance and with increase in agricultural activities a corresponding increase in the pollution of catchment areas including rivers and inland waterways is expected. This will occur as increasing demand for agro-fuels, vegetable oil and food would spur rapid expansion of palm oil plantations, rice and fruit production. To meet this demand, thousands of square kilometres of mainly rainforest and agricultural land will be ploughed for planting new seedlings and the use of pesticides in these plantations cannot be underestimated.

The past decades have witnessed a considerable increase in agricultural produce around the globe. Pesticides have undoubtedly played a major role in driving this growth as have other agricultural related technological innovations. However, the increasing use of pesticides has a concomitant impact on the environment (May et al., 2017). Pesticides include herbicides, insecticides, nematicides, fungicides and soil fumigants, and represent a diverse group of inorganic and organic chemicals (Skevas et al., 2012). The use of pesticides in Malaysian agricultural sector has rapidly grown from 1960s till date. Before the 1960s, pesticides were mostly consumed by agricultural farms in industrialized nations. But with increasing agricultural awareness in the mid-1960s, developing country exports have included pesticide industry products (Lutz et al., 1998). Annual pesticide consumption in different countries in the Asian region shows that Malaysia is placed second after China, and India comes third in ranking as seen in Figure 2 (Abhilash & Singh, 2009).

Wastewater discharged from the production of pesticide has high organic and inorganic constituents and it could be poisonous and cancerous. In some cases, it is refractory to conventional treatment methods and requires an effective treatment prior to discharge (Li et al., 2009). Some pesticides are normally resistant to chemical and/or photochemical degradation under typical environmental conditions (Burrows et al., 2002; Oller et al., 2011). The major sources of pollution by pesticides includes during its application in agricultural practice (0 ~10 µg/L) (Water Science and Technology Directorate Environment Canada, 2011), (Figure 3), drainage water from intensive agriculture field, including water from washing and rinsing pesticides containers and application equipment (10~100 mg/L) for wet lands, and effluent from agricultural industries and pesticide formulation and manufacturing plants (10 ~ 1000 mg/L) (Chiron et al., 1997; Malato et al., 2000; Ballesteros et al., 2009).

Figure 2. Consumption of pesticide in different countries in Asia region
(Abhilash and Sing, 2009).

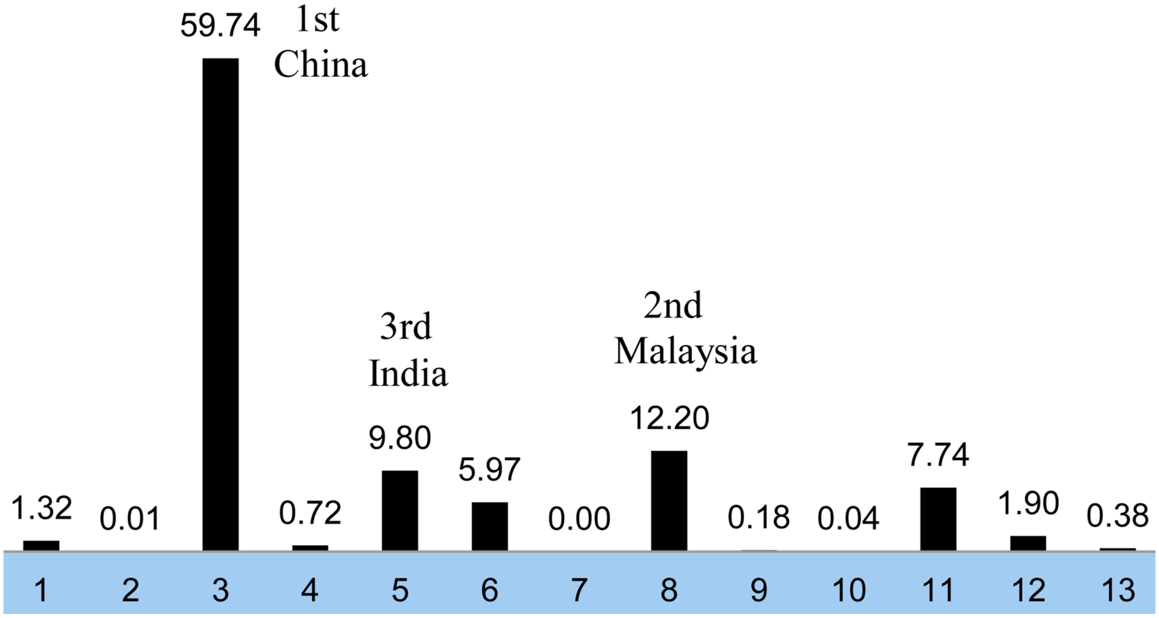


Figure 3. Application of herbicides on row crops

Potential health risks due to pesticides have been observed in studies such as in toxicology and epidemiology and includes; genetic malformations, cancer and damage of the immune system, neurodevelopmental disorders, (Kaltenhäuser, et al., 2017; Skinner et al., 1997; Bassil et al., 2007; McKinlay et al., 2008). For as low as less than 500 mg/L pesticide concentration in wastewater or surface water could be dangerous to humans (Malato et al., 2002). It has been shown that in many water and wastewater streams, oxygen-depleting substances including pesticides affect the macro invertebrate community significantly and cause a change towards the species (Bunzel et al., 2013). Further, pesticides are quite toxic to be immediately mineralized or degraded by the individual microorganisms (Schafer & Waite, 2002), and the efficiency of any applied treatment may also be heavily dependent on the chemical nature of the pesticide (Chang et al., 2008; Yu, 2002; Mahalakshmi et al., 2007; Zhu et al., 2004; Calza et al., 2004; Sakellarides et al., 2003). Some pesticide compounds *per se* have little or no toxicity, but the compounds they could degenerate into during fermentation or after degradation are highly toxic and more harmful than its parent active ingredient or compound (Saien & Khezrianjoo, 2008).

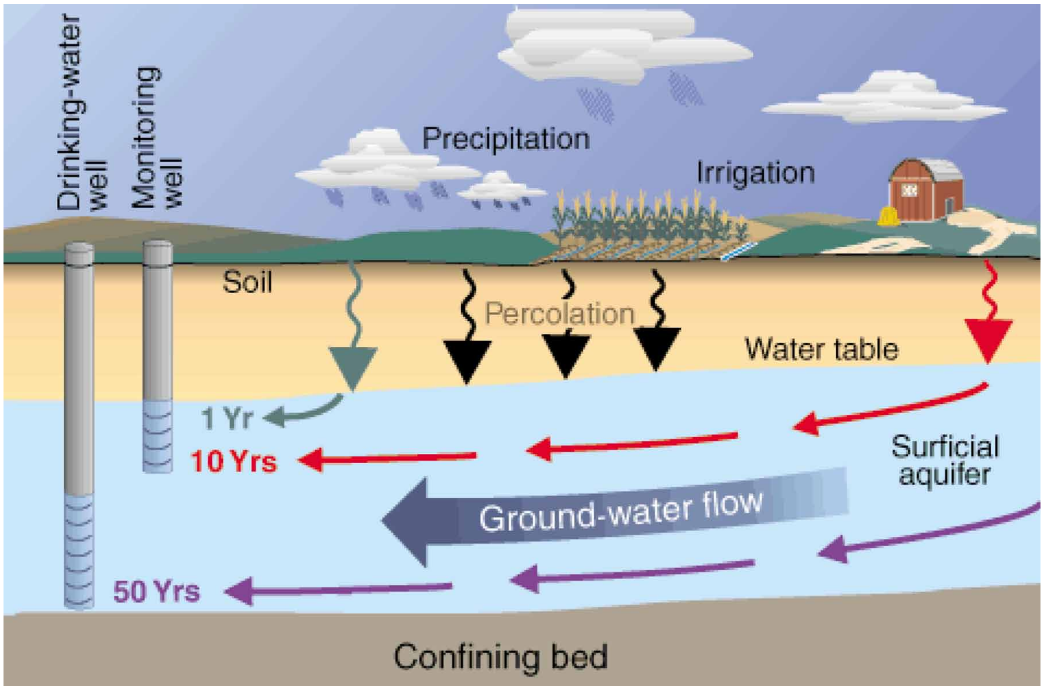
Pesticides are categorized as emerging contaminants and maybe classified as persistent organic pollutants (POPs). They have been continuously detected in natural water and inland waterways in Malaysia. At low concentrations, it is a serious concern to the authorities, public and to all those involved in potable water production and wastewater treatment. Pesticides have been reportedly detected in Krian river basin Perak, Penang marine fish, Tanjong Karang Selangor river, major river systems in Malaysia, Sabah and Bernam river sediments (Abdullah, 1995). A study found traces of organophosphorus and organochlorine pesticides in river water (Cheah, 1996). Another study conducted in Selangor river, detected organochlorine pesticides and organophosphate pesticides (chlorpyrifos and diazinon) (Leong et al., 2007). Recovery of alkylphenols and pesticides in rivers (Selangor state) were between 50 and 120% (Tan & Mustafa, 2004). Pesticides chlorothalonil and methamidophos was observed to cause a negative effect on the peripheral and central nervous system of 80 farmers (IPOPs, 2005; Kimura et al., 2005). Dioxins are also reported to form when pesticides are exposed to sunlight during sunlight and their potential health risk make them to be classified by world health organization as POPs. These dioxins when they enter the human body have a half-life of 7 to 11 years (Holt et al., 2012). Some rivers have generally been found to decline annually in their water quality (Naubi et al., 2016). The relevance of monitoring these pesticides presence in surface water and in other water resources have continued to be emphasized (Prabhakaran et al., 2017).

Pesticide wastewater may contain biodegradable and non-biodegradable substances originating from the starting materials used in its production, intermediates and by-products formed during production process and/or from the active ingredient. These formations are also favoured under alkaline conditions and high temperatures (150-600°C), even at lower temperature in the presence of catalysts such as aluminium salts, iron, copper, Fe (III)-montmorillonite clay or radicals as well as during irradiation with ultraviolet (UV) light (Holt et al., 2012). Pesticide may reach the aquatic matrix (waterways and aquifer systems) through mobile or point sources. Examples of activities whether mobile or point source includes agriculture, horticulture, forestry, chemical industry and domestic activities (Reichenberger et al., 2007). This poses a persistent threat as it may cause deterioration of the flora, fauna and the aquatic matrix on which human existence depends (Gentz, 2009). Sewage sludge is reported to be contaminated with a wide array of xenobiotics (organic pollutants) that may have negative impact on soil organisms. In three various locations in Johor Barhu state of Malaysia, organochlorine pesticides (52 – 159 mg/L) were found in sewage sludge (Ahmad et al., 2004). Organic contaminants in sludge can ultimately enter the food chain through application to agricultural land.

Pesticide formulation and production companies exist in large numbers in Malaysia. However, some companies visited during this study, practice continuous recycle of their wastewater for reuse in their production process because of the high pesticide concentration and cost required for treatment of the wastewater. Removal of pesticide compounds by wastewater treatment plant has not been effective due to their recalcitrant nature and high organic and inorganic concentration of the pesticides compounds (Malato et al., 2002). Some other companies reportedly treat the pesticide wastewater using biological processes only and hence the obvious detection of pesticide active ingredients in inland waterways and rivers as a result of incomplete degradation of the pesticide by the conventional wastewater treatment process. It cannot be ruled out that some of these pesticides may include those from agricultural field run off. Although the environmental problems related to sewage and industrial effluents are being addressed by the introduction of integrated treatment systems such as the proposed central toxic waste plant, immediate and possible future treatment technologies and environmental management strategies require careful study. Thereafter formulation of policies that will meet economic and environmental sustainability can be proposed for consideration. Also, the development of appropriate treatment systems to meet future solutions will have to include waste minimization by the introduction of environmentally sound technology as an integral part, as well as reuse of effluents, recycling and by-products of treatment systems (Abdullah, 1995; Naubi et al., 2016; Prabhakaran et al., 2017). Else, the government's effort towards achieving the status of an industrialized nation by the year 2020 without assurance of the quality of the Malaysian aquatic environment will be uncertain. Therefore, it is paramount to seek alternative treatment methods for complete degradation of pesticide active ingredients in the wastewater generated during production processes before discharge into surface water.

The Malaysian effluent discharge standard stipulates that pesticide active ingredients must be non-detected in treated pesticide wastewater to be discharged into surface water. Available literature confirms the presence of pesticide active ingredients in the aquatic environment. Aside that, about 50% of discharge into surface water is from wastewater treatment plants (DOE, 2010). This makes it pertinent to completely treat the pesticide wastewater before discharge. Pesticide wastewater can also contaminate ground water if care is not taken (Figure 4). It is thought that the soil acts as a protective filter that stopped pesticides from reaching groundwater, however, studies have now shown that this is not the case. As a result of runoff from field crop applications, seepage from polluted surface water, leaks, spills and ac-

Figure 4. Pesticides reaching water-bearing aquifers below ground from applications at gardens or crop fields
(U.S. Geological Survey, 2016).



cidental discharge and poor disposal habits or re-injection of waste materials into wells during drilling, pesticides can get to aquifers whether in low or high-water table areas (U.S. Geological Survey, 2016).

Biological processes are usually applied for treatment of wastewater as they are cost effective and more importantly environmental friendly. Never the less, non-biodegradable organics including pesticides are powerful enough to kill the micro-organism that maybe available in a typical activated sludge process. Due to this occurrence, advanced oxidation process (AOP) are prerequisite to enhance the biodegradability of the pesticide wastewater before application of the biological treatment. Several treatments have been reported for the selected pesticides in this study, however, they have targeted pesticide removal by other methods such as ozone (Wu et al., 2007), wet lands (Xiaoqiuang et al., 2008; Hua et al., 2009), nitrogen spurge and bimetallic ion (Ghauch & Tuquan, 2008), *bacillus cereus* and sentinel species (Sherrard et al., 2004; Zhang et al., 2009a) and electrochemical oxidation (Samet et al., 2010a and 2010b). It is vital to assess AOP treatment of a pesticide wastewater containing pesticide active ingredients and at the same time evaluate the operating cost of each process (Zapata et al., 2009; Oller et al., 2011).

Amongst the different approaches to pesticide degradation, AOP is known to be very effective in treatment of non-biodegradable wastewater (Farré et al., 2008) as against reverse osmosis which retains the contaminants in elevated concentration in the membrane reactor (Einav et al., 2002). The adsorption and stripping processes transfers pollutants from one phase to another without actual destruction and the ozone precursors could pollute the air adversely (Sauer et al., 2002). The biological treatment is limited to biodegradable wastewater which is non-toxic to biological cultures and this makes it to require pre-treatment by AOP to improve the biodegradability of wastewater. There is a need to proffer low-cost and effective treatment for pesticide wastewater in order to attain discharge standards required by local authorities.

PESTICIDE AND ITS CLASSIFICATION

The employment of chemicals to control weeds started in 1932 with the first pesticide being 4-6-dinitro-o-creosol. This continued after the Second World War based on the needs to produce synthetic chemicals for crop protection and to increase world food production. Subsequently, commercialization of 2, 4 dichlorophenoxiacetic (2,4-D) in 1945 and 4-chloro-2-methlphenoxiacetic acids (MPCA) in 1946 (Cobb and Kirkwood, 2000), ureas in 1950, triazines in 1955 and the bipyridiniums in 1960 and the use of pesticides became usual in a few other countries (Van Rensen, 1989). Any substance intended for the prevention or destruction of pest on the field and affecting negatively the harvest or the various stages of food handling (production, processing, storage, transport or marketing) of wood, commodities and or administered to animals for increased products is referred to as a pesticide (FAO, 2002). A pest is considered as an organism in direct competition with humans for a valued resource. They also have the potential of reducing both quality and quantity of marketable agricultural produce (Baugher & Singha, 2003). The classification of organisms according to their official scientific status, by class, order, family, similar habits and biology or the related species or with a few striking exceptions is the most basic approach commonly used for classification of pesticides (Hill, 2002).

The classification by World Health Organization (WHO) distinguishes between the more and the less hazardous forms of each pesticide is based on the toxicity of the formulation or composition of the active ingredients. The classification is usually based on the acute oral and dermal toxicity to rat. These are standard procedures in toxicology. The LD_{50} value is a statistical estimate of the amount in milligram of toxicant per kg of bodyweight needed to kill 50% of the test animal population. Table 1 presents the recommended criteria for classification from the original World Health Assembly proposal. WHO now uses the acute toxicity hazard categories from the Globally Harmonized System (GHS) for the classification and labelling of chemicals and was adopted by the United Nations in 2002. This change is consistent with the 1975 World Health Assembly resolution which envisaged that the WHO classification would be further developed with time in consultation with countries, international agencies and regional bodies. The GHS meets this requirement as a classification system with global acceptance following extensive international consultation (WHO, 2010).

The classification given in Table 1 is of active ingredients, and only forms the starting point for the final classification of an actual formulation. It is by far preferable that the final classification of a formulation should be based on toxicity data obtained on that formulation by the manufacturer. The criteria set out in the classification are normally applied to first-hand data. The classification of pesticide (WHO, 2010) in Table 1 is shown with examples in Table 2. Another pesticide classification according to its implications is presented in Table 3 (Foo and Hameed, 2010) while Table 4 shows the characteristics of selected pesticides for this study. Figure 5 presents a pictorial view of the typical pesticide cycle which the daily application in fields may be subjected to. Various pesticides and their characteristic properties and active ingredients will respond differently in the environment in terms of degradation. Hence, treatment of generated wastewater is recommended in every case. Although in several countires around the globe, monitoring and reporting of pollution by pestiicde application is poor, efforts must be made to include it in water quality assessment. Difficulty in moniroing could be as a result of non availablity of financial support, facilities and laboratories, personnel and chemical reagents required (University of Reading ECIFM, 2006). These and more are areas government authorities are encouraged to improve their strenghts in order to have strong monitoring policy of surface water.

PESTICIDE IN AQUATIC ENVIRONMENT AND ITS RESISTANCE

The presence of pesticide compounds in the aquatic environment has been widely reported especially in water resources such as in surface water (Bottoni et al., 2013; Varca, 2012), groundwater (Stuart et al., 2012) and potable water (Bottoni et al., 2013). The presence of organochlorine pesticides have also been reported in edible marine biota within the coastal region (Santhi et al., 2012), in breast milk (Zhou et al., 2012), plant samples in a crude oil producing region (Sojinu et al., 2012) and in surface sediments (Lu et al., 2012). When pesticides are applied on a field, they become mobile in the environment and several factors therein affect them in the process. Thus, they do not remain at their target site, but often move and enter the aquatic environment through transfer to air, soil, food and surface and ground water (Islam & Tanaka, 2004; Cessna 2009). Figure 6 shows a simplified method for various routes pesticide enter surface and ground water and how pesticide may change and remain in the atmosphere.

Pesticide resistance is the ability of a particular type of organism to survive exposure to a pesticide that would normally kill an individual of that species. Pesticide resistance may probably increase when a pesticide with a single mode of action is used repeatedly without any other control measures (Uri, 1997). This could also happen as a result of selection caused by a changing environment (Hillesheim et

Figure 5. The pesticide cycle

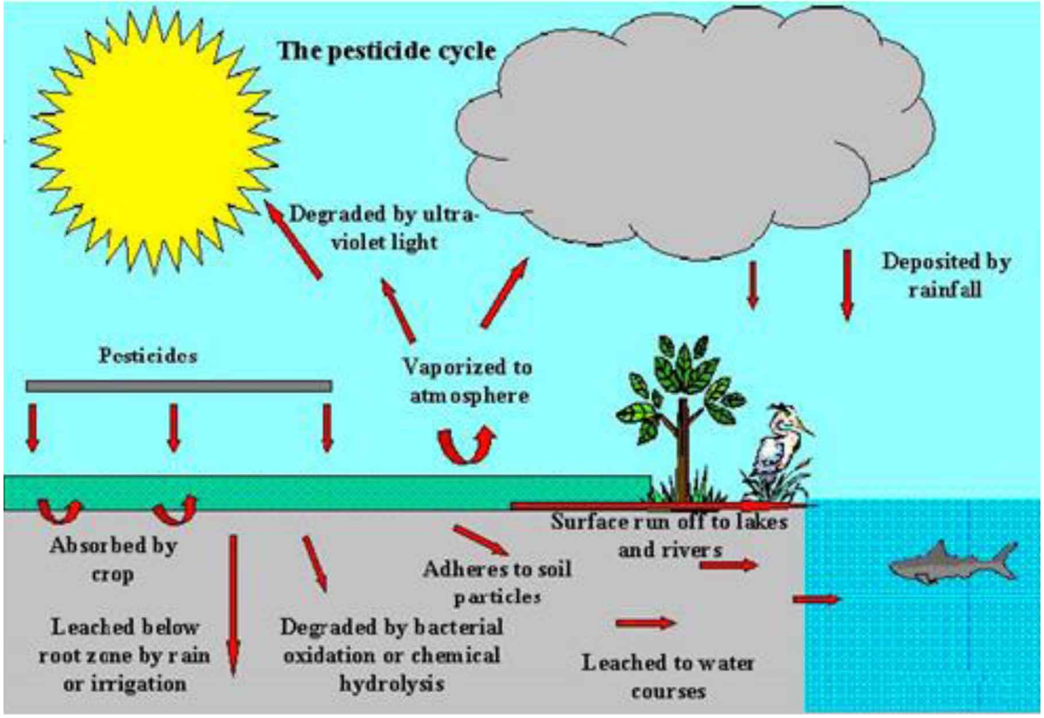


Table 1. Revised criteria for classification of pesticides

Class	LD_{50} for the rat (mg/kg body weight)	
	Oral	**Dermal**
Extremely Hazardous (1A)	<5	<50
Highly Hazardous (1B)	5-50	50-200
Moderately Hazardous (II)	50-2000	200-2000
Slightly Hazardous (III)	Over 2000	Over 2000
Unlikely to Present Acute Hazard in Normal use (IV)	5000 or higher	5000 or higher

(WHO, 2010)

Table 2. Pesticide classification with examples

Class	Common name	Chemical type
Extremely Hazardous (1A)	Phorate Phosphamidon	Organophosphate Organophosphate
Highly Hazardous (1B)	Profenofos & Cypermethrin Carbofuran	Combination pesticide Carbamate
Moderately Hazardous (II)	DDT Cypermethrin Chlorpyrifos Carbaryl Quinalphos	Organochlorine Pyrethroid Organophosphate Carbamate Organophosphate
Slightly Hazardous (III)	Acephate Azamethiphos	Organophosphate Organophosphate
Unlikely to Present Acute Hazard in Normal use (IV)	Carbendazim Atrazine Chlorothalonil	Carbamate Triazine N/A

(WHO, 2010)

al., 1996). Pesticide resistance at a population level, as opposed to just a few individual pests within a species, can occur after repeated exposure to a single type of pesticide (Figure 7). This is because only the resistant organisms are left to reproduce with other resistant organisms. When a resistant population occurs, the pesticide is no longer useful for managing that specific pest and other management options must be sought (Uri, 1997). Thus, knowledge of the resistance mechanism is essential in developing a suitable resistance management strategy. This is important to prevent or eliminate resistance when it occurs. Several resistance management strategy, such as reduced penetration of the active ingredient so as to reduce uptake thereby changing the behaviour of the target species and modification of the metabolism (and/or detoxification) process are known (Hillesheim et al., 1996). There are reported cases of pesticides resistance in both household (Brewer & Tremble, 1994) and field applications (Mahmoud et al., 1986).

Table 3. Classification of pesticides by implication

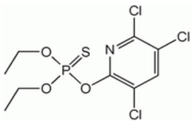
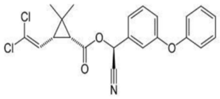
Type	Implication
Algaecides	Control algae in bodies of water, including swimming pools.
Antimicrobials	Kill microorganisms that produce disease.
Attractants	Attract specific pests using natural insect chemicals called pheromones that confuse the mating behavior of insects.
Avicides	Control pest birds.
Bio-pesticides	Naturally occurring substances with pesticidal properties
Defoliants	Cause foliage to drop from a plant, typically to aid in harvesting process
Desicccants	Aid in drying process of plants or insects, usually for laboratory purposes
Fumigants	Produce vapors or gases to control air or soil-borne insects and diseases
Fungicides	Destroy fungi that infect people, plants, and animals.
Herbicides	Control noxious weeds and other vegetation that are growing or completing with a desired species
Insect Growth Regulators (IGRs)	Accelerate or retard the rate of growth of insects Control or eliminate insects that affect people, plants, and animals.
Insecticides	Kill mites that live on plants, livestock, and people.
Miticide (Acaricides)	Kill snails and slugs.
Molluscicides	Kill nematodes, which are microscopic wormlike organisms that live
Nematicide	in the soil and cause damage to food crops.
Ovicides	Control insect eggs through the application of low-sulphur petroleum oils to plants and animals
Piscicides	Control pest fish
Plant Growth Regulators (PGRs)	Accelerate or retard the rate of growth of plant
Predacides	Control vertebrate pests.
Repellents	Repel pests such as mosquitoes, flies, ticks, and fleas.
Rodenticides	Control mice, rats, and other rodents.

(Foo & Hameed, 2010)

FATE OF ENVIRONMENTAL MICROBIOLOGY DUE TO DISCHARGE OF UNTREATED PESTICIDE WASETWATER

The fate of pesticides in the microbial environment is usually expressed in terms of a number of interacting processes which help to estimate their biodegradability, persistence and mobility. This is put together under the transport mechanism, transfer methods and transformation likelihood (Wilkinson et al., 2017; Gavrilescu, 2005). The eventual fate of every pesticide applied on the field or present in untreated wastewater discharged to the environment, are reported to be affected by the physical and chemical properties of the pesticide. Chemical degradation may occur as a result of reactions such as photolysis (photochemical degradation), hydrolysis (reaction with water), oxidation, and reduction (Vela et al., 2017). Biological degradation may also occur as soil microbes consume or degrade pesticides. These microbes are most prevalent in the top several centimeters of soil. The extent of degradation may range from the formation of metabolites to the formation of inorganic decomposition products. In addition, the location of application and its characteristics including the soil and groundwater conditions, weather

Table 4. Characteristics of selected pesticides for study

Common Name Molecular Formula Chemical Family	WHO Class	Toxicological Effect	Ecological and Physical properties
Chlorpyrifos $C_9H_{11}Cl_3NO_3PS$  Organophosphate	II	Toxicity to humans, including carcigenicity reproductive and developmental, neurotoxicity and acute toxicity.	Toxic to aquatic organism Water solubility: (Ave. mg/L) 1.18 Hydrolysis Half-life: (Ave Days) 2,118 Aerobic Soil Half-life: (Ave Days) 30.5 Anaerobic Soil Half-life:(Ave Days) Nil Reactivity: Hydrolyzed by strong alkalis Adsorption Coefficient (Koc): 9,930
Cypermethrin $C_{22}H_{19}Cl_2NO_3$ Pyrethroid 	II	Excessive exposure can cause nausea, headache, muscle weakness, salivation, shortness of breath and seizures	Toxic to fish Water solubility: (Ave. mg/L) 0.2 Hydrolysis Half-life: (Ave Days) 2,118

(WHO, 2010)

Figure 6. Routes for entry of pesticides into the atmosphere, surface, ground waters and mechanisms of pesticide transformation in air, soil and plants

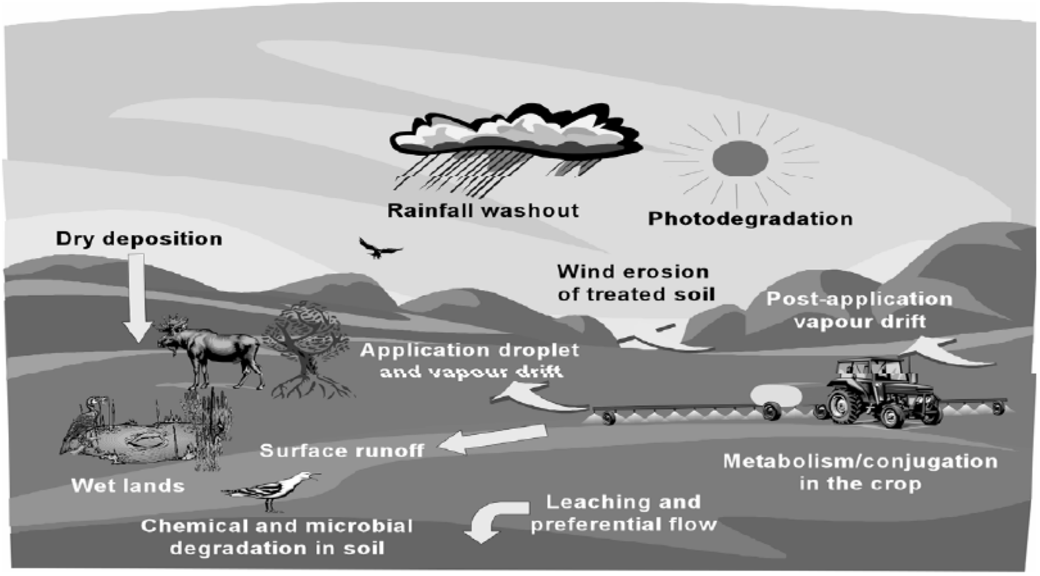
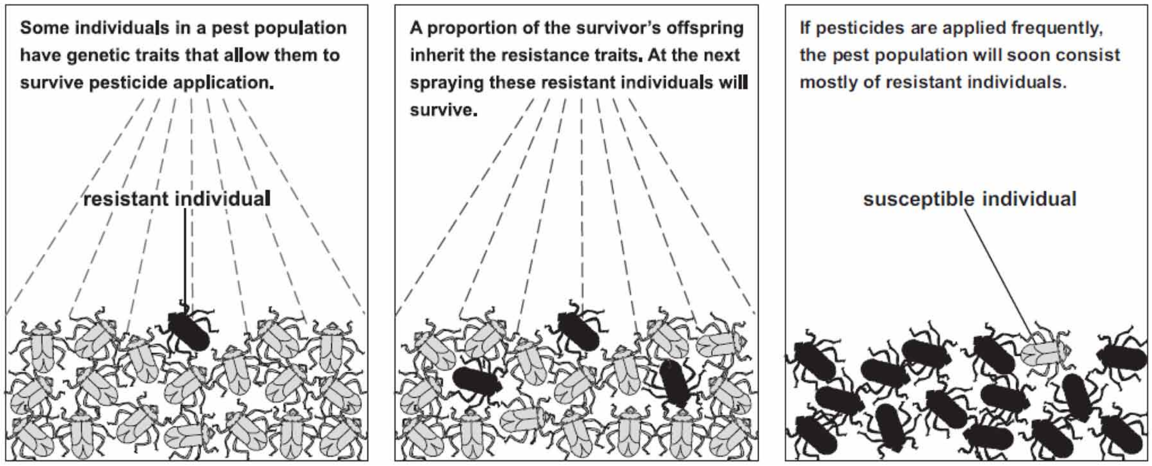


Figure 7. Pesticide development over time as resistant individuals survive to reproduce

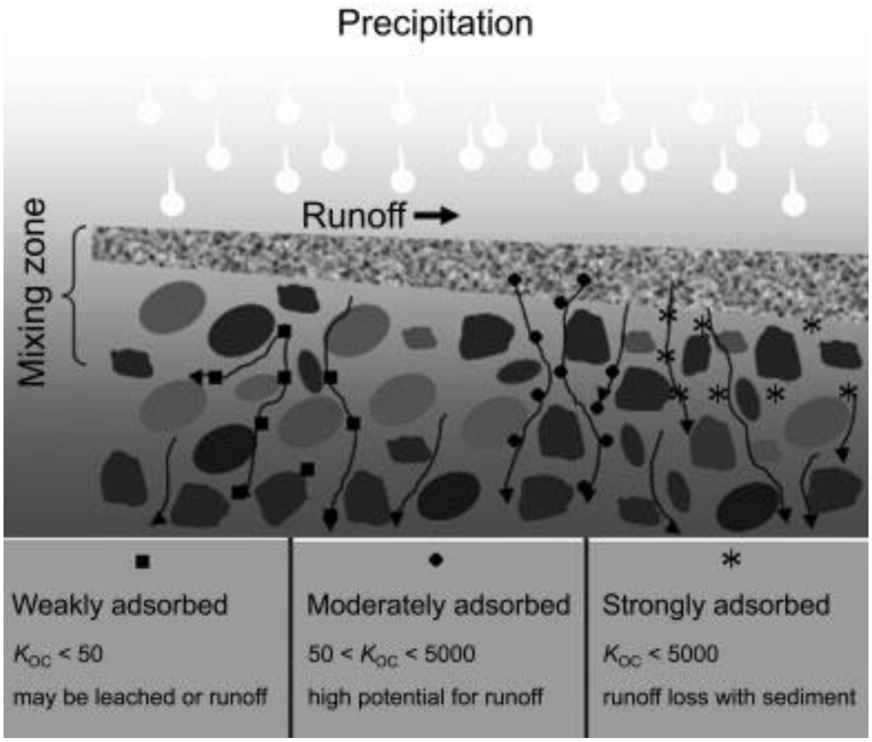


and area climatic conditions, biological population, and method of handling or community practice with respect to application methods may determine how much degradation will occur (Lelander et al., 2015; Gavrilescu, 2005). A pesticide is likely to contaminate groundwater or leach if its sorption coefficient is low, half-life is too long, and its water solubility is quite high. Sorption is commonly evaluated by use of a sorption (partition) coefficient (Koc) based on the organic carbon content of soils. It is a measure of the tendency of pesticides to be attached to soil particles. Higher values (greater than 1000) indicate a pesticide that is very strongly attached to the soil and it is less likely to move unless soil erosion occurs. On the other hand, lower values (less than 300 to 500) indicate pesticides that will move if any flow of water or a high potential to leach or runoff on the surface is observed as seen in Figure 8.

Pesticide persistence is usually estimated with regards to the half-life, and this requires about 50% of a pesticide to be transformed or degraded (National Academy of Sciences USA, 1993). Pesticides with low sorption coefficients have a high probability to leach. Pesticides that have long half-lives may be persistent. The fate and transfer pathways of pesticides applied to croplands are complex. They require some knowledge of a combination of their chemical and physical properties, their transformations (intermediates), and also the physical transport process. Transformations and transport are strongly influenced by specific conditions of the location and community handling practices.

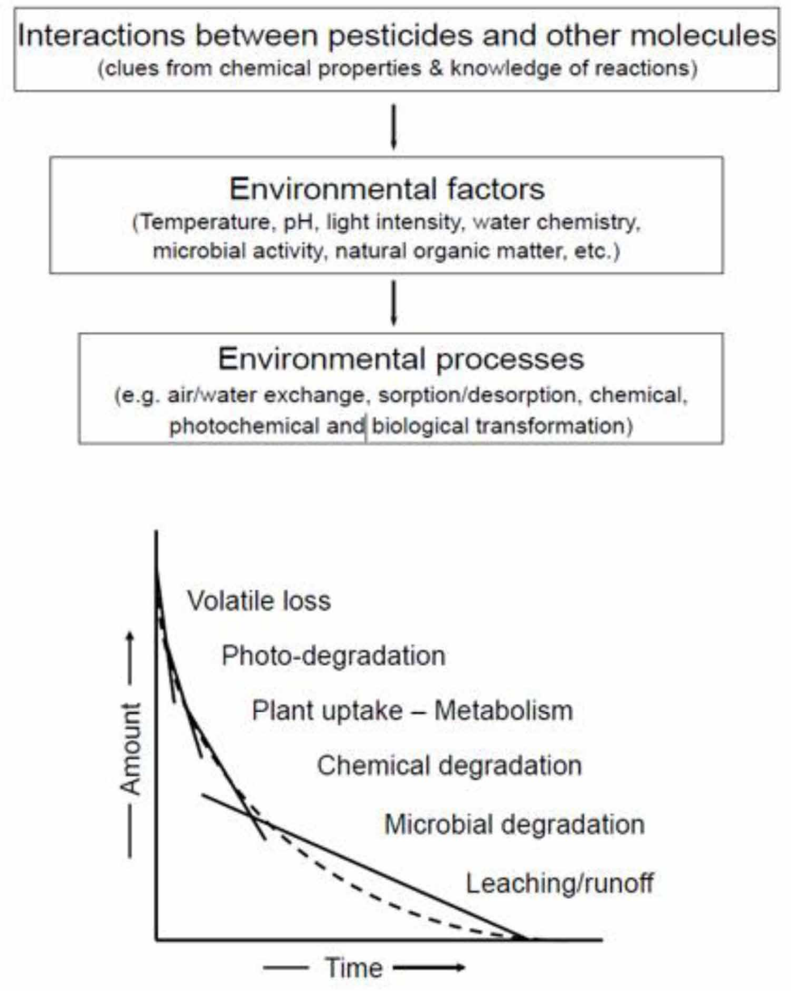
Pesticides applied to cropping systems may be degraded by microbial action and chemical reactions in the soil. Pesticides can also be immobilized through sorption onto soil organic matter and clay minerals. Pesticides may be lost through atmospheric volatilization process. Pesticides that are taken up by pests or crop plants either can be transformed to degradation products (which are often less toxic than the original compound) or, in some cases, can accumulate in plant or animal tissues. A certain portion of the pesticides applied are also removed when the crop is harvested. Pesticides that are not degraded, immobilized, detoxified, or removed with the harvested crop are subject to movement away from the point of application (Brahushi et al., 2017; National Academy of Sciences USA, 1993). The main routes for pesticides to reach the environment are basically through volatilization and possible aerial drift, runoff to surface water bodies (in either dissolved or particulate forms), and notably through leaching into groundwater basins. The fate and transfer pathways of pesticides applied to croplands are complex, requiring some knowledge of their chemical properties, their transformations (breakdown), and the physical

Figure 8. Partition runoff for pesticide runoff



transport process. Transformations and transport are strongly influenced by site-specific conditions and management practices. Pesticides maybe degraded by microbes, chemical reactions, and light or photo degradation. This process may take anywhere from hours or days to years, depending on environmental conditions and the chemical characteristics of the pesticide (Castillo et al., 2016). Microbial degradation is the breakdown of pesticides by microorganisms such as fungi, bacteria, and other soil microorganisms. Soil organic matter, texture, and site characteristics such as moisture, temperature, aeration, and pH are principally known to affect microbial degradation. Microbial activity usually is greatest in warm, moist, well aerated soils with a neutral pH. Microbial breakdown tends to increase when soil temperatures are warm, pH is favourable, oxygen and moisture are sufficient and where there is high yield in the soil fertility. Microbial degradation occurs at a higher rate in the surface soil horizons, particularly in areas with high organic matter. Usually, the rate decreases with depth in the soil, where conditions such as moisture, temperature, and aeration are less favourable for microbial activity (Kerle et al. 2007). Chemical degradation occurs when a pesticide reacts with water, oxygen, or other chemicals in the soil. As soil pH becomes extremely acidic or alkaline, microbial activity usually decreases. However, these conditions may favour rapid chemical degradation. The rate and type of chemical reactions are prone to be influenced by similar conditions explained earlier on (Kerle et al. 2007; Coelho et al., 2017). The intensity of sunlight, length of exposure, and properties of the pesticide affect the rate of photodegradation. A good number of pesticides are susceptible to photodegradation to some extent. Pesticides that are applied to foliage or to the soil surface are more susceptible to photodegradation than pesticides that are incorporated into the soil. Pesticides may break down faster inside plastic-covered greenhouses than inside glass greenhouses, since glass filters out much of the ultraviolet light that degrades pesticides (Kerle et al. 2007; Coelho et al., 2017). The degradation of recalcitrant pesticides occurs slowly under natural conditions, thus efforts are required to be made to enable an improved process especially in wastewater treatment. When pesticide is used on a field, the microbial community structure will have a marked changed, even if the overall microbial activity remains unaffected by the pesticide. Bacterial population may be increased compared to fungal population and vice-versa. Some microorganism may be suppressed and others may proliferate in the open ecological niches. Bacterial biomass could be measured by the analysis of muramic acid and fungal biomass can easily be measured by the ergosterol control (Pal et al., 2006). The fate of pesticides in the microbial environment can have either positive or adverse effect, nevertheless, typical processes they interact with when applied are shown in Figure 9. Thus, risk assessment should include the measure of microbial diversity. Work in this respect is lacking and would require research.

Figure 9. Pesticide fate in the environment



FATE AND RISK OF PESTICIDE APPLICATION ON THE ENVIRONMENT

When pesticides are applied on an agricultural field or park, they become mobile in the environment and several factors affect them in the process. Thus, they do not remain at their target site, but often move and enter the aquatic environment through the following modes of transfer as described in the subsequent sections.

Transfer to Air

Pesticides transfer to air during application to crops and quickly distributes in the air. However, this is dependent on techniques applied, stage of crop and weather outlook (University of California, 2016). About 50% of applied pesticides could be transported outside the crop field by wind in 1-10% (Emans et al., 1992). Where the water-based spraying is used such as boom sprayer, 10% of the pesticide applied remains in the atmosphere (or returns to atmosphere as a result of possibly volitization) (Audsley et al., 1997). This scenario is typical for good weather conditions. The fate of pesticides in the air or atmosphere takes residence time into account. For persistent pesticides with residence time greater than 60 d, the pollutant has time to dilute in the atmosphere with an equivalent volume of dilution at about 10,000m^3/m^2. For shorter residence time, degradation occurs before full mixing in the atmosphere. The residence time of pesticides in the gas phase depends on the degradation constant of OH● radicals. This is estimated by pseudo first-order reaction equation. The pesticide distribution coefficients for aerosol–air are proposed and explained elsewhere. The calculated residence time ranges from a few hours to few days with extreme values up to more than one year (Finizio et al., 1997).

Transfer to Soil

The percentage of pesticide active ingredients reaching the soil is about 85% and 5% remains on the cop leaves and it is added to the 10% loss to the atmosphere This accounts for the direct initial emission to soil (air to soil), the fraction that comes from the air–plant–soil route and what is eventually deposited outside the crop field where it was applied. The pesticide is also reported to be diluted in the soil at 0.1m^3/m^2 (Audsley et al., 1997).

Transfer to Surface and Ground Water

Transportation of pesticides by water can occur through wet deposition, run-off from surfaces, infiltration of water through the ground, ditches, storm sewers, tile lines, drains, rivers, and open water currents. Water can actually behave much like air in terms of transporting pesticides. Water that is moving at a high velocity can carry heavier pesticides, or particles that pesticides may be attached to, than water that is moving slowly. Faster moving water also has the potential to move pesticides farther. Pesticides in open water systems may float on the water, diffuse into the water, or deposit onto the sediments at the bottom of the water body. Pesticides that move from the ground surface through the soil may reach shallow ground water or deeper aquifers (Evangelou, 1998). Contamination in groundwater is usually estimated using a model proposed by Jury et al. (1987). This model is of the assumption that water flows steadily in the soil, and there is an equilibrium distribution of pesticides in the soil which follows a linear adsorption rate and the biodegradation is highly dependent on the depth of the soil as well. There has been models and indicators applied for management of larger-scale field environments, for example, the erosion/productivity impact calculator (EPIC) (Sharpley and Williams, 1990), groundwater loading effects of agricultural management systems (GLEAMS) used to determine the transfer of pesticides to surface water (Leonard et al., 1987), pesticide root zone model (PRZM) (Carsel et al., 1984), and leaching estimation and chemistry model—pesticides (LEACHM-P) (Wagenet & Hutson, 1989). Margni et al. (2002) reported that detailed assumptions, parameters defining the soil properties, hydrological and erosion data are used in the model to calculate the pesticides filtration into surface water. In addition, the principal pesticide parameters used in the various models to calculate the transfer of pesticides to surface and ground water are: the organic carbon sorption coefficient Koc, the residence time in the soil $t_{1/2}$, and the quantity applied. The results also show that a small proportion of pesticides reach the ground water (in most cases the pesticide run-off) and it is less than 10% of the applied dose.

Transfer to Food

Biotechnology has achieved release of genetically modified organisms (GMOs), such as engineered soybean, colza, maize and tomatoes, and did promise a solution to food security needs and nutritional problems (Kush, 2002). These Infact, GMOs are said to be resistant especially to several insect pests, created moulds, natural frost and dry conditions, etc., and may be able to change agricultural industry (Pingali & Traxler, 2002). Upon increasing use of pesticides to meet growing demand, there is a possibility that there would be pesticide residues on the foods being produced. For example, soybean and other plants were modified to be tolerant to gliphosate, a common herbicide used to fight weeds allowing for much higher crop yields. However, because the weeds become increasingly resistant to this herbicide, the use of these GMOs rendered the farmers dependent on the use of more and more gliphosate (Sharpe, 1999). To determine the amount of pesticide residues in food and to look at their relevance compared to exposure via inhalation and drinking water, the residue concentrations are determined from tolerance values. The tolerance value is defined as the maximum pesticide concentration that may be observed in food from a correct application and is commonly used to assess dietary risk (Margni et al., 2002). For chlorothalonil, the average residue concentration after peeling, washing and processing amounted to 5% of the tolerance value. Due to the lack of available information in the literature, it is assumed that the pesticide concentrations in food corresponds to 5% of their respective tolerance values to obtain a first estimate on the magnitude of the transfer of pesticide to food. In addition, pesticide transfer to food potentially represents one of the most important exposure pathways for humans (Margni et al., 2002). A food web study reported that almost half of the edible aquatic animals had higher levels than those recommended for human consumption by the US EPA (Grung et al., 2015).

Pesticides may become airborne during the spraying process and, following application, by volatilization from soil, water and vegetation surfaces. The degree of spray drift is dependent on physical characteristics of spray application – the equipment used, the droplet size and the height above ground at which the spray is applied. Drift is usually expressed as a percentage of the applied dose of active ingredient that is likely to move outside the intended spraying area. If equipment and conditions remain constant for different insecticides, this proportion will remain constant (WHO, 2010). The potentially adverse effects of exposure to pesticides on the general population, and specifically on the more susceptible groups such as infants and children, are a public health concern. Apart from ingestion of foods and drinking water, inhalation of ambient air could be a relevant pathway of exposure to pesticides (Coscolla & Yusa, 2016). In addition to the potential adverse effects of pesticide on humans, they pose a variety of negative effects on the environmental receptors such as water, soil, microorganisms (for both target and non-target organisms) and air contamination (Burger et al., 2008; Mariyono et al., 2008). Poor pesticide application skills has been said to be linked to the following:

- Negative effects on non-target organisms (e.g., reduction of beneficial species populations),
- Water contamination from mobile pesticides or from pesticide drift,
- Air pollution from volatile pesticides,
- Injury on non-target plants from herbicide drift,
- Injury to rotational crops from herbicide residues remained in the field,
- Crop injury due to high application rates and,
- Wrong application timing or unfavourable environmental conditions at and after pesticide application (Reus et al., 2002).

Many of these potential pesticide negative effects on the environment depend on the interactions between the various physicochemical properties (vapour pressure, stability, solubility, pKa) of the pesticide, soil persistence and adsorption and other soil factors (such as pH, organics, inorganics, soil moisture, soil microflora, soil fauna), plant species, toxicity, pesticide dosage, weather conditions prevailing after pesticide application, and how long pesticide persists in the environment and climate of the region may account for various adverse effects on the environment (Reus et al., 2002). Since the above enumerated factors vary from one agricultural field to another and from one planting season to another, the outcome of the effect of one location and the fate of the pesticide maybe different. Thus, carrying out environmental risk assessment, must be based on each location. Pesticide fate maybe initially assessed by the calculation of the predicted environmental concentration (PEC) and the estimated environmental concentration (EEC) (Matthews, 2006). These concentrations are calculated for soil, water, sediment, and air, and their validation is performed by comparison with the data obtained from the three levels of tests (Tier 1 – acute toxicity, Tier 2 – reproduction test and Tier 3 – Field test) (which are normally needed before approval and registration of the pesticide) in order to assess the pesticide toxicity on key non-target organisms. The toxicity exposure ratio (TER) is also calculated to determine whether the risk to the organism is acceptable or not (Hornsby et al., 1993). The TER is calculated from the LC50 or equivalent measure (LD50, NOEC = no observed effect concentration) of the susceptibility of an organism divided by the PEC relevant to the situation in which the organism is living. The risk quotient (predicted exposure concentration to predicted no effect concentration) is the inverse of TER and this is calculated by dividing the PEC with the indicated toxic dose (Matthews, 2006). Considering the negative effects linked with the use of pesticides in agriculture, the need to use a criteria to select pesticides that are cost effective, technically efficient and safe for the operator and the environment recently has become imperative (Hornsby et al., 1993; Reus et al., 2002; Bockstaller et al., 2009). The need to also use particular environmental risk indicators as alternatives to measure pesticide impact even with the related methodological difficulties or as a result of practical reasons such as time and costs has also become a practice (Bockstaller et al., 2009). The said indicators have been proposed and applied by Reus et al. (2002) and Bockstaller et al. (2009) to access potential risks of pesticides for water contamination, soil organisms (mainly earthworms), bees, air emissions, bioaccumulation, and human health. Calculation of the environmental indicators used in the reported studies were based on the pesticide mobility in soil (organic-carbon adsorption coefficient, Koc), toxicity to water (lethal concentration for aquatic organisms, LC50), toxicity to soil organisms (NOEC) and persistence in soil (half-life, DT50). A study reported that new indicators with greater reliability than those already existing are required to predict potential risk of pesticides and as such help to reduce the potential negative effects of pesticides on the environment (Reus et al., 2002).

Environmental risk assessment is a complex and multifaceted task. Although, regional and possibly national guidelines and acts may have been promulgated, there is no globally established system for environmental risk assessment. Performance of environmental risk assessment for outdoor space spraying is important in order to address the following issues (WHO, 2010):

- The absolute risk to non-target organisms for each type of insecticide used;
- The relative risk of different pesticides;
- The number of repeat applications likely to lead to risk to organisms in the environment;
- Current best practice for the application of pesticides to minimize risk.

Where regulatory assessments are needed to be done, basic assessment of the probable pesticide volatilization and redistribution in the environment would be followed by models or measurements that would enable the determination of the likely concentration in air and the movement of the active ingredient through the environment. Deposition or presence of pesticide in the air may also be estimated over time and distance from the applied source to give estimated concentrations in the receiving medium whether it is soil or water. There is no standardization of any models and each has advantages and disadvantages depending on the medium from which volatilization occurs (soil or water) and the conditions of transport (WHO, 2010). Several pesticide risk indicators and models have been developed over the years. However, a recent study has reported a new pesticide risk indicator, the Pesticide Load (PL), which was introduced in Denmark. The PL consists of three sub-indicators for human health, ecotoxicology and environmental fate, respectively. Each of the three sub-indicators of the pesticide load (PL) is estimated and expressed as the PL per unit commercial product (kg, L or tablet). PL for human health (PLHH) is based on the risk phrases on the product label, while PL for ecotoxicology (PLECO) is estimated on the basis of the $LC/LD/EC_{50}$ values of the active ingredients for acute toxicity to mammals, birds, fish, daphnia, algae, aquatic plants, earthworms and bees and NOEC values for chronic toxicity to fish, daphnia and earthworms. PL for environmental fate (PLFATE) was calculated on basis of the half-life in soil (DT50), the bioaccumulation factor (BCF) and the SCI-GROW index. PL does not consider the actual exposure, i.e. it reflects the relative risks associated with the use of pesticides (Kudsk et al., 2018).

PESTICIDE WASTEWATER

Pesticide wastewater resulting from formulation and production facilities and wash water used in the process of removing pesticides from the equipment during cleaning process (John, 1984; Moreira et al., 2012) contains a variety of non-biodegradable constituents with high concentrations of organic contaminants measured as COD and BOD_5. Medium to high conductivity corresponding to low and/or moderate concentrations of dissolved iron, sulphate, polyphenols, chloride, phosphate, bromide, magnesium, lithium, sodium, fluoride, potassium and calcium are some of the constituents of a typical pesticide wastewater (Moreira et al., 2012). However, the composition of pesticide wastewater can vary from one production plant location to another. Due to high concentration, toxicity and composition of pesticide wastewater from manufacturing agrochemicals, its treatment and purification have become one of the biggest challenges (Jin et al., 2010). Therefore the constituents of pesticide wastewater in a production plant should be intermittently analyzed and reported. Some studies reported analysis and characterization of pesticide wastewater with the precursor chemicals, active ingredients and other organic/inorganic and ionic characteristics. A typical pesticide wastewater has been characterized in terms of measured parameters (Chen et al., 2007; Vilar et al., 2012) (Table 5). Safe wastewater discharge standards for Malaysia is shown in Table 6. This is the regulation required to be adhered to by all industries formulating and producing pesticides in the country. The regulatory body is the Department of Environment (DOE), under the Ministry of Natural Resources & Environment, Malaysia. They are charge with the responsibilities to ensure a clean environment, safe, healthy and productive environment for present and future generations, conservation of the country's unique and diverse cultural and natural heritage with effective participation by all sectors of society, and to ensure sustainable lifestyles and patterns of consumption and production. For comparison, some of the South East Asian countries effluent discharge standard are presented on Table 7.

ADVANCED OXIDATION PROCESS

Advanced oxidation process (AOP) is highly effective for degradation/removal of majority of wastewater/water pollutants. The process involves the production of hydroxyl radicals ($OH^{\cdot}$) which are capable of degrading organic contaminants in wastewater (Pera-Titus et al., 2004). As a result of high organic strength such as the COD of pesticide wastewater, chemical pretreatment, being a partial oxidation of the non-biodegradable wastewater in order to produce biodegradable reaction intermediates is required. It is important to mention that, if the chemical pretreatment is for a very short reaction time, the intermediates produced may still be structurally the same and similar to the initial non-biodegradable and/or toxic compounds. However, if the wastewater contains a large quantity of biodegradable compounds, the pre-oxidation would not be needed because it would be a waste of chemicals (Oller et al., 2011).

AOPs are usually operated at near ambient temperature and pressure (Glaze et al., 1987). They can be classified according to the reaction phase (homogeneous or heterogeneous) or depending on the method used to generate non-selective $OH^{\cdot}$ species (chemical, electrochemical, photochemical, sonochemical or radiolytic techniques). Each of them offers different ways for $OH^{\cdot}$ production. Mineralization end products are generally water, carbon dioxide and inorganic ions and in some cases a large residue is generated.

Fenton, UV Photo-Fenton and Solar-Photo-Fenton Processes

Fenton reaction mechanism as described in Reaction (1) (Fenton, 1894). The hydroxyl radicals ($OH^{\cdot}$) is generated by the reaction between hydrogen peroxide and ferrous salts named the Fenton reagent.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \qquad (1)$$

The Fe^{2+} is reduced by the reaction with hydrogen peroxide to form ferrous ion and additional radicals again. The second process is called Fenton-like and it is slower than the initial Fenton reaction. It allows Fe^{2+} regeneration in an effective mechanism as in Reactions (2-3) (Pignatello, 1992). Where iron is added in a small quantity thereby acting as a catalyst while hydrogen peroxide is continuously consumed.

Table 5. Characteristics of pesticide wastewater

Parameter	(Chen et al., 2007b)	(Vilar et al., 2012)
COD (mg/L)	33700 ± 2100	1662-1960
BOD_5 (mg/L)	6100 ±700	1350-1600
BOD_5/COD ratio	0.18 ± 0.2	0.79-0.83
TSS (mg/L)	-	62-82
VSS (mg/L)	-	52-52
TP (mg/L)	2120 ± 130	7.5-23
TKN (mg/L)	3300 ± 230	-
NH_4-N (mg/L)	3080 ± 210	33-41
SO_4^{-2} (mg/L)	2530 ± 160	68 - 107
OP (mg/L)	2040 ± 100	-
Conductivity µmhos/cm	-	739-786
DOC (mg/L)	-	513-696
Turbidity (mg/L)	-	43-188
Total Carbon (mg/L)	-	536-735
pH	1.5-2.5	6.7-7.2
NO_2^- (mg/L)	-	5.3-34
NO_3^- (mg/L)	-	0.002-7.2
N (mg/L)	-	118-114
Fe^{2+} + Fe^{3+} (mg/L)	-	2.0-2.5
PO_4^{3-} (mg/L)	-	7.5-23
F^- (mg/L)	-	0.8-1.9
Br^- (mg/L)	-	1.2-5.4
Cl^- (mg/L)	6370 ± 540	58-92
Li^+ (mg/L)	-	0.1-0.3
Na^+ (mg/L)	-	80-84
K (mg/L)	-	34-37
Mg^{2+} (mg/L)	-	18-39
Ca^{2+} (mg/L)	-	112-128

Table 6. Malaysian industrial effluent discharge standard

Parameter	Effluent Concentration
Chemical oxygen demand (COD)	A: 80 mg/L, B: 200 mg/L
Biochemical oxygen demand (BOD_5)	A: 20 mg/L B: 40 mg/L
Active ingredient (Pesticide specific)	N.D
Total suspended solids (TSS)	A: 50 mg/L B: 100 mg/L
pH	5.5-9.0
N.D = Non-detectable	

Source: Environmental Quality Act 1974, (Industrial effluent) Regulation. Seventh Schedule, Regulation 12, amended 2009 PU (A) 434). There are two standards; Standard A is applicable to discharge into any inland waters within catchment areas listed in the Third Schedule, while Standard B is applicable to any other inland waters or Malaysian water.

Table 7. South East Asian countries industrial effluent discharge standard

Country **Parameters**	**Brunei**	**Cambodia**	**Indonesia**	**Laos**	**Philippines**	**Singapore**	**Thailand**	**Vietnam**
Chemical oxygen demand (COD)	150	50	200	120	60	100	120	100
Biochemical oxygen demand (BOD_5)	30	30	100	30	20	50	20	50
Active ingredient (Pesticide specific)	N.S	N.S	N.S	N.S	N.S	N.D	N.S	N.D
Total suspended solids (TSS)	30	50	50	40	70	50	50	80
pH	6.0 – 9.0	6.0 – 9.0	6.0 – 9.0	6.5 – 8.5	6.0 – 9.0	6.0 – 9.0	5.5 – 9.0	5.5 – 9.0

N.S = Not stated
N.D = Non- detectable

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\cdot} + Fe^{2+} + H^+ \quad (2)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \quad (3)$$

The rate-limiting step is the regeneration of Fe^{2+} reaction (2 and 3). Ferrous ion remains at trace levels with approximately constant Fe^{3+} concentration. Reactions (4-6) shows other important dark reactions involving ferrous ion and hydrogen peroxide

$$Fe^{2+} + HO_2^{\cdot} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (4)$$

$$Fe^{2+} + OH^{\cdot} + Fe^{3+} \rightarrow Fe^{3+} + OH^- \quad (5)$$

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (6)$$

The radical reactions and auto-decomposition of hydrogen peroxide is also involved in the complex process seen in Reactions (7-10). These reactions may occur in multiple steps (Sychev and Isaak, 1995).

$$2\ H_2O_2 \rightarrow 2\ HO_2^{\cdot} + O_2 \quad (7)$$

$$2\ OH^{\cdot} \rightarrow H_2O_2 \quad (8)$$

$$2\ HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (9)$$

$$HO_2 + OH \rightarrow HO_2 + O_2 \tag{10}$$

Degradation of organic contaminants by Fenton process is increased further when UV-visible light with wavelengths lower or greater than 300 nm is applied to a reactor system (Kiwi et al., 1994; Pignatello et al., 1999). Ultra violet (UV) light and solar photo of wavelength 280 nm and greater than 400 nm, respectively could also be used. During this reaction, the photolysis of Fe^{3+} complexes promote regeneration of Fe^{2+} which can further react with more hydrogen peroxide as in Reactions (11-13):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-+} OH^{\cdot} \tag{11}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH^{\cdot} + H^{+} \tag{12}$$

$$H_2O_2 \rightarrow 2OH^{\cdot} \tag{13}$$

This process reduces the production of the iron sludge associated with a typical Fenton process leading to lower iron salt reduction.

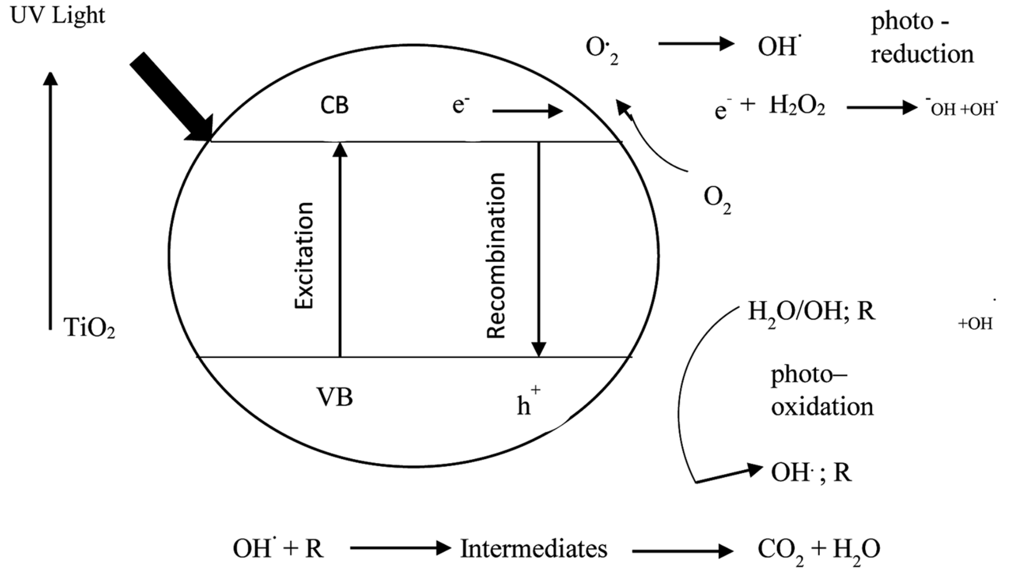
UV Light/Titanium Dioxide/Hydrogen Peroxide Process

The UV light/titanium dioxide/hydrogen peroxide ($UV/TiO_2/H_2O_2$) process is another type of advanced oxidation process. Its mechanism is such that when incident light reaches the semiconductor catalyst (TiO_2), it gets excited to become an electron-donor site (reduction point) and electron-acceptor site (oxidation point) providing a large area for redox reactions. The photocatalyst in this case is titanium dioxide (TiO_2) and its activity typical starts from the point when photons of a certain wavelength are incident upon its surface, and then electrons are promoted from the valence band (VB) and are transferred to the conductance band (CB) as illustrated in Figure 10. This creates positive holes in the valence band, which then reacts with the hydroxylated surface to produce $OH^{\cdot}$ for oxidation reactions to occur (Bhatkhande et al., 2001). The valence band (VB) and conductance band (CB) are the main bands of interests in the photocatalysis process. The energy distance between valence band (VB) and conductance band (CB) is known as the band gap (Lorret et al., 2009).

Mechanism of the Tio_2 Photocatalytic Degradation

The TiO_2 photocatalysis has been known to be a reliable alternative for treatment of wastewater. Wet air oxidation (WAO) and AOP using Fenton reagent and UV/H_2O_2 are competing processes against photocatalysis. WAO accomplishes oxidation at elevated temperatures (150-325°C) and oxygen pressures ($1\text{-}20 \times 10^3$ kN/m^2). In the case of AOP employing an artificial UV light and a semiconductor (such as TiO_2) as photo catalyst in the presence of hydrogen peroxide (oxidant), leads to an increase in the rate of photocatalytic oxidation (Emilio et al., 2002). Irradiating particles with UV light results in the promotion of an electron from the valence band (VB) to the conduction band (CB) of the particle. The outcome of this process is a region of positive charge, a hole (h^+) in the VB and a free electron (e^-) in the CB reaction (14) (Pedroza et al., 2007):

Figure 10. Illustration of TiO_2 photocatalytic degradation process



$$TiO_2 + hv \rightarrow TiO_2\,(e^- + h^+) \tag{14}$$

The holes can react with surface bound hydroxyl groups (OH^-) and adsorb water molecules to form $OH^•$ as in Reactions (15 and 16) (Gupta et al., 2007):

$$OH^- + h^+ \rightarrow OH^• \tag{15}$$

$$H_2O + h^+ \rightarrow OH^• + H^+ \tag{16}$$

Hydroxyl radicals ($OH^•$) are known to be powerful oxidizing agents. They react readily with surface adsorbed organic molecules, either by electron or hydrogen atom abstraction, forming organic radical cations or by additional reactions to unsaturated bonds as seen in Reaction (17) (Sadik et al., 2007). During the photocatalytic process, $OH^•$ reacts with organic compounds and species adsorbed onto, or very close to the semiconductor surface and results in degradation.

$$\text{Organics} + OH^• \rightarrow \text{Degradation Products} \tag{17}$$

Modified Advanced Oxidation Processes

The modified AOPs are more recent alternatives which may be used to replace other existing AOPs. Fenton process application is of great concern because it the most commonly applied AOP. Modified Fenton process has been applied in solving apparent limitations in Fenton process. Modified Fenton process could be in terms of replacement of standard catalysts such as ferrous and/or ferric ions or novel adsorbents, increase in process temperature up to 80-120°C i.e. the so-called catalytic wet hydrogen peroxide oxidation process, or the application of novel highly stable and active heterogeneous catalysts (Fe_2O_3 or Fe supported into SBA-15 mesostructured material, etc. (Goi et al., 2008). Also, the application of iron chelates (typically organic acids) which can promote chemical oxidation of contaminants by formation of iron–chelate complexes amongst others, but aimed at preventing iron precipitation between pH 5 and 7 and minimizing non-specific losses of soluble iron (Kang & Hua, 2005). These chelates are naturally occurring and hence are degradable by microorganism (Watts & Dilly, 1996). The primary advantage of some of these modifications is for the effective generation of $OH^{\cdot}$ at near-neutral pH and reduction of iron sludge production in other cases (Goi et al., 2008). This is important as it will be more practical in the case of treatment of continuous wastewater streams which may require application of acid and subsequent neutralization and this may increase salinity owing to pH conditioning after treatment (Lipczynska-Kochany & Kochany, 2008).

Iron/Granular Activated Carbon/Hydrogen Peroxide Process

The iron/granular activated carbon/hydrogen peroxide ($FeGAC/H_2O_2$) process applied in this study was proposed to circumvent the problem of iron sludge production in Fenton process (Fan et al., 2007). The process is possible through the impregnation method carried out by coating iron oxides on the surface of granular activated carbon (GAC). This has been applied in the decolourization of Acid Black 24 (Fan et al., 2006), removal of fulvic and humic acids in municipal landfill leachate (Fan et al., 2007) and degradation of crystal violet (Chen et al., 2011).

There is insufficient literature to buttress the determination of the equilibrium proportions of ferric species as a function of pH and concentration or less presence of iron-related ionic species with respect to ratio, dosage and time in the $FeGAC/H_2O_2$ process. The species of iron are affected by the synthesis methods and conditions (Jang et al., 2008; Thirunavukkarasu et al., 2003) and at different temperatures the impregnated iron oxide manifested a more crystalline form (Jang et al. 2008). In a study, the initial amount of iron oxides on GAC surface was approximately 38 mg Fe/g GAC and after treatment, the loss of iron oxide was less than 5% (Chen et al., 2011). Acid black decolourization rate of 8.71 mg/min by the $FeGAC/H_2O_2$ process was also reported (Fan et al., 2006).

Activated carbon (AC) is known to decompose hydrogen peroxide. Presumably, the process entails exchange of a surface hydroxyl group with a hydrogen peroxide anion as in Reaction (18) and according to Bansal et al. (1998) as cited in Khalil et al. (2001). The formed surface peroxide is known to have increased its oxidation potential which enables the decomposition of another hydrogen peroxide molecule with the release of oxygen and regeneration of the AC surface as in Reaction (19).

$$AC\text{–}OH + H^{+}\,OOH^{-} \rightarrow AC\text{–}OOH + H_2O \tag{18}$$

$$AC\text{–}OOH + H_2O_2 \rightarrow AC\text{–}OH + H_2O + O_2 \tag{19}$$

Apart from the decomposition reaction, hydrogen peroxide may be activated on the AC surface bringing about the formation of $OH^{\bullet}$. AC is seen to function as an electron-transfer catalyst in the same manner similar to the Haber–Weiss mechanism in a typical Fenton reaction, and having AC and AC^{+}

as the oxidized and reduced catalyst states, respectively as in Reactions (20 and 21) (Kimura and Miyamoto, 1994).

$$AC + H_2O_2 \rightarrow AC^+ + HO^- + OH^\bullet \tag{20}$$

$$AC^+ + H_2O_2 \rightarrow AC + HO_2^\bullet + H^+ \tag{21}$$

In the FeGAC/H_2O_2 process, activated carbon acts as an adsorbent, yet at the same time the presence of ferric iron enables the adsorbent (FeGAC) to interact as a catalyst to degrade adsorbed or dissolved organic matter. The GAC is involved in the catalytic activity due the graphitic structure and functional groups on their surface (Bach and Semiat, 2011). The FeGAC therefore, has high adsorption capacity due to GAC surface. In addition, the oxidation strength of H_2O_2 is enhanced by the catalytic properties of FeGAC in the removal of pesticides from the wastewater. The following reaction mechanisms are suggested in order to account for results obtained in the FeGAC/H_2O_2 process as in Reactions (22- 28) (Bach & Semiat, 2011).

$$AC + Fe^{3+} \rightarrow AC^+ + Fe^{2+} \tag{22}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{23}$$

$$AC^+ + H_2O_2 \rightarrow AC + HOO^\bullet + H^+ \tag{24}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{25}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{26}$$

$$H_2O_2 + OH^\bullet \rightarrow HOO^\bullet + H_2O \tag{27}$$

$$HOO^\bullet + OH^\bullet \rightarrow H_2O + O_2 \tag{28}$$

In many Fenton systems, the rate-limiting constituent in $OH^\bullet$ production is ferrous ions production as in Reaction (23). The formation of ferrous ions in the FeGAC/H_2O_2 system may be explained by the fact that activated carbon (AC) is considered to function as an electron transfer catalyst with AC and AC^+ as the reduced and oxidized catalyst states, respectively (Bach and Semiat, 2011). AC behaves as an electron donor in order to reduce the ferric ions to ferrous ions as in Reaction (22). The competing reaction existing between the formation of ferrous ions as in Reactions (22 and 23) and their consumption are shown in Reactions (24 and 25). The Reactions (26-28) show the ferrous ion regenerated to react with produced $OH^{\bullet}$ and subsequent scavenging of $OH^{\bullet}$ by excess hydrogen peroxide in the system. Other complex reactions also occur in the auto-decomposition of hydrogen peroxide yielding water and oxygen as in Reaction (8). The competition between the decomposition of hydrogen peroxide and the formation of ferrous ions by increasing the FeGAC concentrations is the main key for understanding the mechanism. Thus, FeGAC/H_2O_2 mechanism combined with adsorption is basic for the FeGAC/H_2O_2 process to proceed in degradation of pollutants in wastewater (Fan et al., 2007; Chen et al., 2011).

Merits and Limitations of the Five Processes

Fenton and photo-Fenton processes have been applied in the treatment of wastewater (Vilar et al., 2011). They are promising oxidative processes which utilise reagents that are safe to handle and environmental friendly. Highly complicated apparatus and pressured systems are not required for the implementation of the technology and can be piloted in laboratory before scaling up to an industrial level (Kavitha & Palanivelu, 2004). In terms of cost saving, the degradation efficiency of the oxidation process could be reduced while being accelerated by irradiation of UV light and better still by using a solar light source. Indeed, complete mineralization of the organics can be achieved by the photo-Fenton process (Araña et al., 2001). The major limitation of the process is the comparable higher operating cost associated with the chemical reagents and energy required for the light especially UV compared to conventional biological treatment process. In addition, the required pH adjustment, probable iron sludge generation and additional cost in disposal are some setbacks in using this process (Pignatello et al., 2006).

The main advantages of TiO_2 catalyst are the enhanced photocatalytic oxidation strength i.e. effectively oxidizing a wide range of organic compounds, electronic and optical properties (Lorret et al., 2009), lack of mass transfer limitations, operation at ambient conditions, inexpensive, commercially available, non-toxic in nature and photochemically stable (Pekakis et al., 2006). There maybe no need for post-treatment if the organic pollutants have been decomposed to non-toxic byproducts such as water, mineral acids and carbon dioxide. In addition, the large surface area together with physical properties may be modified by doping, size reduction, or sensitizer, and this has no substantial effect on its photocatalytic activity (Zhang et al., 2009b).

The limitation of the TiO_2 catalyst includes stirring during the reaction and seperation of catalyst from the treated wastewater after each experimental run. It may also require sedimentation, centrifugation and filtration in order to recover highly dispersed and suspended catalyst from the treated wastwater. Apart from the time consumption, this process may become unsustainable and ineffective as the particle size diminishes or suspended and could penetrate fitration materials and clog them eventually. Another demerit is that the TiO_2 threshold or ideal wavelenght corresponds to energy band gap of 3.02 ev which is near ultra-violet (UV) radiation (300 nm). Therefore, utilising this process is limited due to the need for UV or other light excitation source. This limitation is compounded since TiO_2 absorbs only 5% energy solar spectrum, thus more research is required to develop materials (TiO_2 based) which can utilize more of solar light that is active enough to excite the TiO_2 photocatalyst (Han et al., 2009). Therefore, a photocatalytic system that accounts for cost effectiveness through usage of renewable solar energy source which is highly economical compared to UV irradiation which requires electrical power input is paramount (Ghaly et al., 2011).

There are few studies that have reported FeGAC/H_2O_2 application for treatment of wastewater. However, observed limitations of the treatment process are noteworthy. The effect of organics forming complex substrates during oxidation or mineralization by Fenton/modified Fenton treatment. The presence of cupric ions in the H_2O_2/UV process at 254 nm was observed to considerably decrease mineralization of humic acids due to the formation of humic acids-cupric complexes (Liao et al., 2001). This formation was reported to be more difficult to oxidize than the non-complexed form of humic acids. In the study of azo dye degradation, only partial decolourization was achieved (Kusic et al., 2006). According to Kusic et al. (2006), this may be as a result of the complex formation between iron ions and dye-products. However, when UV irradiation (maximum energy output at 254 nm) was applied to Fenton, the process achieved complete colour removal. This was as a result of the process ability to degrade the formed iron-ions-dye-byproducts complexes (Kusic et al., 2006). There is no study that has reported treatment of pesticides by the FeGAC/H_2O_2 process or the shortfall in the performance of this process for the treatment of pesticide wastewater.

Summary of Literature Review

Various AOP techniques have been studied from which choices can be made about the most effective techniques for specific wastewater treatment. The review so far presents the state of the art covering pesticides in the environment, the nature of pesticide wastewater, WHO pesticide classification, problems due to presence of pesticides in the environment, its fate and resistance. The fundamental chemistry of the five AOPs have been exhaustively discussed along with its applications. It is important to mention that they are powerful in terms of complete destruction of pollutants in a variety of wastewater. However, some drawbacks are still needed to be overcome. While the Fenton process maybe one of the applicable AOPs, the iron sludge produced maybe a disadvantage in addition to operation in the low range pH 2-3. The UV and solar photo-Fenton maybe a better process as there is less ferrous salt used and hence lower sludge production due to the enhancement of the process by light. While the recycling of iron sludge is possible, it may not be economical until a sustainable reuse of the iron sludge is identified and proposed. On another hand, modified Fenton or Fenton-like processes such as the FeGAC/H_2O_2 process is proposed as an effort to reduce the sludge production, and to possibly carry out treatments at neutral pH which may be more convenient in the real world. The gap of knowledge which exist for these techniques are in areas such as reduction in the secondary waste produced in the various AOPS, optimization of operating conditions for possible scale-up and applicability in terms of efficiency and operating cost for the treatment of an industrial pesticide wastewater together with the formulation agents residual in wastewater. In addition, no study reported treatment of pesticide wastewater having more than 500-600 mg/L total organic carbon (TOC) along with the formulation agents such solvents, adjuvants and stabilizers usually found in the pesticide wastewater. With respect to Malaysia, there is no reported treatment of chlorpyrifos, cypermethrin and chlorpyrifos pesticide wastewater from an existing formulation and production company in the literature, whereas, large numbers of reports are available for the detection of pesticide active ingredient in Malaysian surface water. This maybe owing to about 50% of daily discharge from pollution sources including wastewater treatment plants, and this inadvertently puts surface water under threat. More importantly, pesticides are difficult to degrade under typical environmental conditions and conventional treatment plants are unable to remove them. Therefore, it is pertinent to develop an optimized treatment system which may act as a pre-treatment for pesticide wastewater as presented in this study.

The aim of this study is to meet the Malaysian effluent discharge standard for the selected pollutant category. To achieve this, provision of an efficient wastewater treatment process together with its cost implication is desirable for possible adoption by the pesticide production industry in Malaysia.

Design of Experiment and Set-Up

The traditional approach to experimental work was used in the entire study. In this method, the experiment is performed in such a way that one factor is varied at a time, holding all other factors fixed. This was used to determine the optimum operating conditions for maximum degradation and biodegradability improvement of the pesticide wastewater.

To estimate quantities, the hydrogen peroxide dosage was based on the stoichiometric ratio with respect to COD of the pesticide wastewater. This was estimated with the assumption that the complete oxidation of 1 g COD required 1 g of oxygen (O_2). Using the COD value (wt.) of the pesticide wastewater to divide the molar mass (wt.) of O_2, the outcome was multiplied by the hydrogen peroxide and/or ferrous salt molar mass to obtain actual mass (wt) required. To determine the optimum H_2O_2/COD molar ratio, experiments were carried out by varying the H_2O_2 dosage at constant concentrations of the selected pesticide COD. To determine the optimum H_2O_2/Fe^{2+} molar ratio, experiments were carried out by varying the Fe^{2+} dosage at a fixed concentration of H_2O_2 (Badawy et al., 2006, Elmolla and Chaudhuri, 2010). In a similar way TiO_2 was varied while H_2O_2 was fixed and vice versa. Also, FeGAC was varied while H_2O_2 was fixed and vice versa. Table 8 shows the design of experiments with parameters and ranges.

Pesticide Wastewater

Commercial grade of chlorpyrifos (CPF), cypermethrin (CPT) and chlorothalonil (CTN) used to prepare the pesticide wastewater and was obtained from a commercial source. The pesticide wastewater was prepared by mixing known amounts of CPF, CPT and CTN in distilled water. The wastewater was 400 mg/L of pesticides (100 mg/L of CPF, 50 mg/L of CPT and 250 mg/L of CTN). Table 9 shows the characteristics of the pesticide wastewater.

Fenton, UV Photo-Fenton, Solar Photo-Fenton Process and Ultra Violet Light/Titanium Dioxide/Hydrogen Peroxide

Batch Fenton, UV photo-Fenton, solar photo-Fenton processes were carried out in 600 ml Pyrex reactors with 500 ml of the pesticide wastewater at selected pH. The pH was adjusted to the required value by adding drops of either sulfuric acid (H_2SO_4) or (NaOH). The needed quantity of iron salt was added to the wastewater and mixed by a vortex stirrer to ensure complete mixing. Thereafter, the required

Table 8. Design of experiments for AOP treatment of pesticide wastewater

Process	H_2O_2/COD Molar ratio	H_2O_2/Fe^{2+} Molar ratio	TiO_2 (g/L)	FeGAC (g/L)	H_2O_2 (mg/L)	pH	Time (min)
Fenton	1-4.0	2-150	-	-	-	2-6	0-60
UV photo-Fenton	1-3.5	2-150	-	-	-	2-6	0-60
Solar photo-Fenton	1-3.5	2-150	-	-	-	2-6	0-60
UV/TiO_2/H_2O_2	-	-	0.5-2.5		50-300	6	0-300
FeGAC/ H_2O_2	-	-	-	1-5.0	10-300	2-6	0-60

Table 9. Pesticide wastewater characteristics

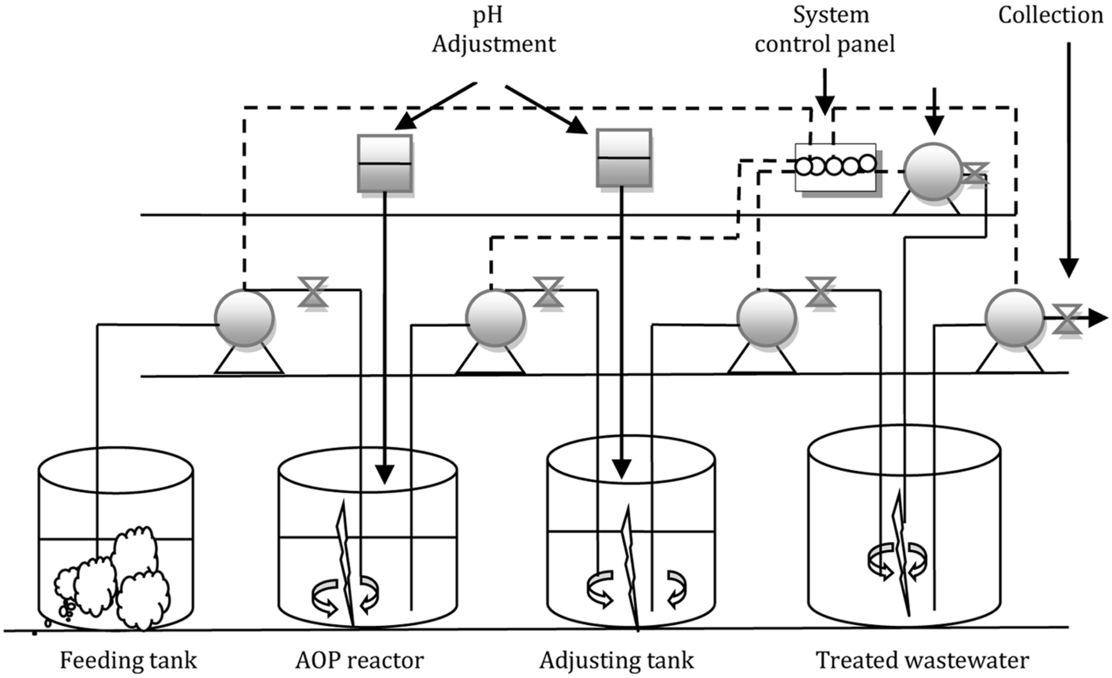
Parameter	Unit	Pesticide wastewater
Chlorpyrifos	mg/L	100 ± 5.0
Cypermethrin	mg/L	50 ± 5.0
Chlorothalonil	mg/L	250 ± 5.0
Chemical oxygen demand (COD)	mg/L	1130 ± 10.0
Total organic carbon (TOC)	mg/L	274.39 ± 10.0
Biochemical oxygen demand (BOD_5)	mg/L	0.0
BOD_5/COD ratio		0.0
Ammonia-nitrogen (NH_3-N)	mg/L	22.0 ± 2.0
Nitrate (NO_3^--N)	mg/L	0.7 ± 0.02
Total phosphate (TP)	mg/L	12.5 ± 0.5
Chloride (Cl^-)	mg/L	160 ± 5.0
Fluoride (F^-)	mg/L	0.05 ± 0.001
Sulfate ($SO^2{}_4^-$)	mg/L	23 ± 5.0
Conductivity	(μS/cm)	60 ± 5.0
Total suspended solids (TSS)	mg/L	5.0 ± 1.0
Total nitrogen	mg/L	26 ± 2.0
pH		6.25 ± 0.5

amount of H_2O_2 was added to the wastewater and the reaction started. In the UV photo-Fenton process, the mixture was subjected to UVA (λ~365 nm) irradiation by placing a UV lamp 5 cm above the reactor. In the solar photo-Fenton process, the mixture was placed inside a solar reactor (Luzchem Solsim v1.2, intensity approximately AM1.5 solar spectrum with a 300 W ceramic xenon lamp, wavelength 280-800 nm and maximum power 1.5 kW/m^2) preset to a light intensity of 0.85 kW/m^2. Batch UV/TiO_2/H_2O_2 process was performed in a 600 ml Pyrex reactor with 500 ml of the pesticide wastewater at chosen pH 6. The required amount of TiO_2 and H_2O_2 were added to the aqueous solution and mixed by a vortex stirrer and subjected to UVA (λ~365 nm) irradiation by placing a UV lamp 5 cm above the reactor. All processes were carried out at room temperature (23±2°C) and samples were taken at pre-selected time intervals, filtered through a 0.45 μm membrane filter for COD, TOC and BOD_5 measurement, and filtered through a 0.20 μm membrane syringe filter for determination of pesticide concentration by HPLC measurement and FTIR spectra.

FE-Granular Activated Carbon/Hydrogen Peroxide Process

Batch process (FeGAC/H_2O_2) was performed in 250 ml conical flasks with 200 ml of the pesticide wastewater at selected pH. FeGAC and H_2O_2 were added as required and the flasks were placed on an orbital shaker at 150 rpm. The process was done at room temperature (23±2ºC) and samples were taken at pre-selected time intervals, filtered through a 0.45 μm membrane filter for COD, BOD_5 and TOC measurement, and filtered through a 0.20 μm membrane syringe filter for determination of pesticide concentration by HPLC measurement and FTIR spectra. The schematic of the AOP is shown in Figure 11.

Figure 11. General schematic of the advanced oxidation process



Fenton, UV Photo - Fenton and Solar-Photo - Fenton Processes

The effect of the operating conditions of the Fenton, UV photo-Fenton and solar photo-Fenton processes such as H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio, pH and reaction time on pesticide degradation, mineralization and biodegradability improvement, and kinetics of degradation were studied and the results are discussed in the following subsections.

Effect of UV and Solar Light Irradiation on Fenton Process

The photolysis of the pesticide due to UV irradiation (λ ~365 nm) and solar light (λ ~790 nm) was studied. Pesticide degradation (COD removal) by UV or solar irradiation per se was quite insignificant. According to UV absorbance spectrum, chlorpyrifos, cypermethrin and chlorothalonil do not absorb UV irradiation at 320 nm (Niazi et al., 2008; Ghauch & Tuqan, 2008; Slotkin et al., 2009) and, therefore, no significant degradation was expected due to UVA irradiation *per se*. In addition, it is known that H_2O_2 has a maximum absorbance at λ 210–230 nm and H_2O_2 proteolysis takes place to a small extent at λ 365 nm (Pignatello et al., 1999) and iron photo-redox also takes place under λ 365 nm (Al Momani, 2006). In the same vein, solar irradiation alone was attempted and it had a low efficiency. It is reported that the possibility of using solar radiation enhances the re-generation of Fe^{2+} ions in order to increase OH● Production in Fenton process. Consequently, degradation of the pesticides when subjected to UV or solar lights alone, will not be sufficient or may require long duration.

Effect of H_2O_2/COD Molar Ratio

In order to understand the effect of H_2O_2 addition to the degradation process, the H_2O_2/COD molar ratio was varied in each process. In all three (Fenton, UV photo-Fenton and solar photo-Fenton) processes, H_2O_2 was varied between 35.3–141.3 mM at initial COD 1130 mg/L (35.3 mM). The corresponding H_2O_2/COD molar ratios were 1, 1.5, 2, 2.5, 3, 3.5 and 4. The other operating conditions were pH 3 and H_2O_2/Fe^{2+} molar ratio 50.

Obtained data from the experiments showed that there was a general reduction in the concentration of COD and TOC, and also an improvement in the biodegradability (COD/BOD_5 ratio) when H_2O_2 was increased beyond a certain point. In the case of Fenton (Figure 12), UV photo-Fenton (Figure 13) and solar-photo Fenton (Figure 14) the maximum efficiency was obtained at H_2O_2/COD molar ratio 3, 2 and 2, respectively. Above these ratios, auto-decomposition of hydrogen peroxide to oxygen and water and the recombination of $OH^\bullet$ radicals are said to occur and hence reduce the efficiency of the entire process (Badawy et al., 2016). This may be due to scavenging of $OH^\bullet$ by H_2O_2 (Kavitha & Palanivelu, 2005a). Similar results were reported by other studies for degradation of herbicides (Badawy et al., 2006) and palm oil mill effluent (Sinnaraprasat & Fongstitkul, 2011).

Effect of H_2O_2/Fe^{2+} Molar Ratio

To study the effect of Fe^{2+} addition to the treatment process, the H_2O_2/Fe^{2+} molar ratio was varied. In all three (Fenton, UV photo-Fenton and solar photo-Fenton) processes, Fe^{2+} was varied from 0.70 to 52.5 mM under operating conditions of pH 3, H_2O_2/COD molar ratio 3 and initial COD 1130 mg/L. The corresponding H_2O_2/Fe^{2+} molar ratios were 2, 5, 10, 25, 50, 100 and 150. The other operating conditions were pH 3 and H_2O_2/Fe^{2+} molar ratio 50. The performance of the three processes showed that COD and TOC removal efficiency and BOD_5/COD ratio improvement had an increase with increase in Fe^{2+} concentration. However, when it reached a certain point, degradation reduced. Presumably, this occurred due to direct reaction of $OH^\bullet$ radical with metal ions at high concentration of Fe^{2+} (Joseph et al., 2000). The H_2O_2/Fe^{2+} molar ratio was 10, 25, 25 for Fenton, UV photo-Fenton and solar photo-Fenton, respectively as seen in Figures 15 -17.

The results are consistent with other studies having different contaminants such as chlorophenol and chlorinated aliphatics (Pera-Titus et al., 2004; Tang and Huang, 1997), creosols destruction (Kavitha & Palanivelu, 2005a), degradation of aromatic amines (Casero et al., 1997) and trihalomethanes (Tang & Tassos, 1997) and landfill leachate (Tengrui et al., 2007).

UV Light/Titanium Dioxide/Hydrogen Peroxide Process

The effect of the operating conditions of the UV/TiO_2/H_2O_2 process such as TiO_2 concentration, H_2O_2 addition and irradiation time on pesticide wastewater degradation, mineralization and biodegradability improvement, and kinetics of degradation were studied.

Effect of Titanium Dioxide Concentration

To observe the effect of titanium dioxide addition to the degradation of the pesticide wastewater was done by varying TiO_2 added between 0.5 and 2.5 g/L with other operating conditions fixed (COD 1130

Figure 12. Effect of H_2O_2/COD molar ratio on Fenton process with respect to COD and TOC removal and BOD_5/COD ratio

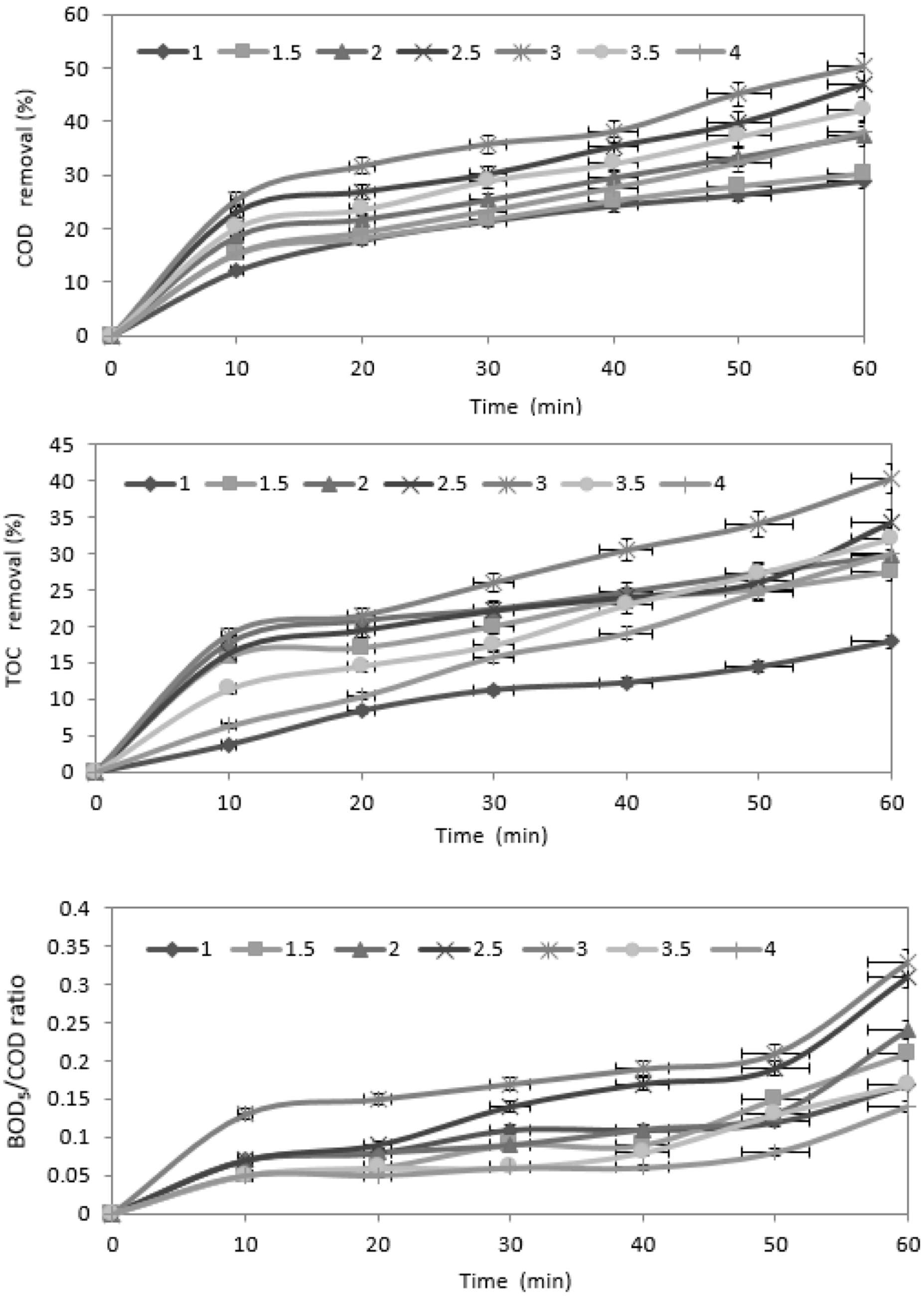


Figure 13. Effect of H_2O_2/COD molar ratio on UV Photo-Fenton process with respect to COD and TOC removal and BOD_5/COD ratio

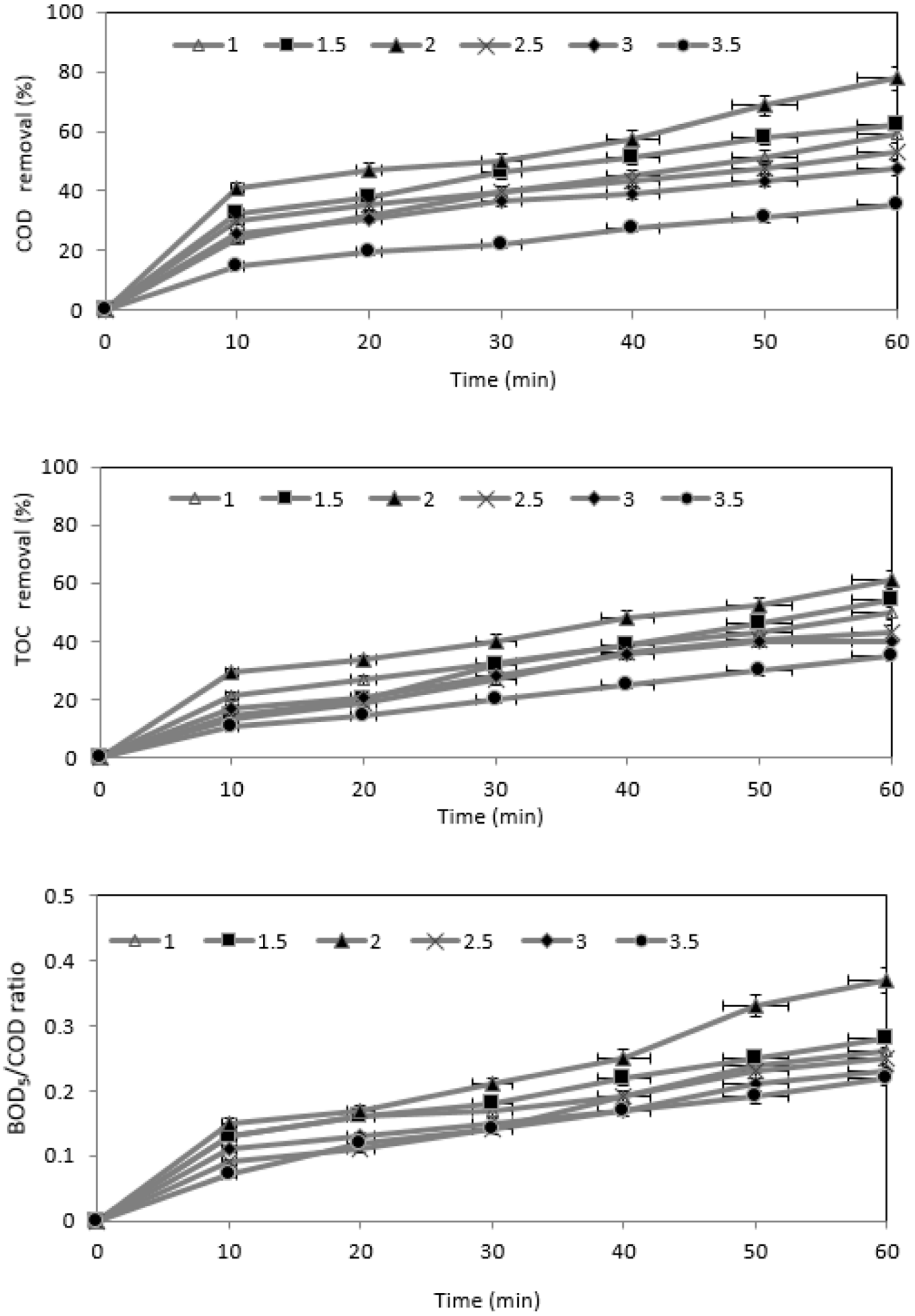


Figure 14. Effect of H_2O_2*/COD molar ratio on solar photo-Fenton process with respect to COD and TOC removal and* BOD_5*/COD ratio*

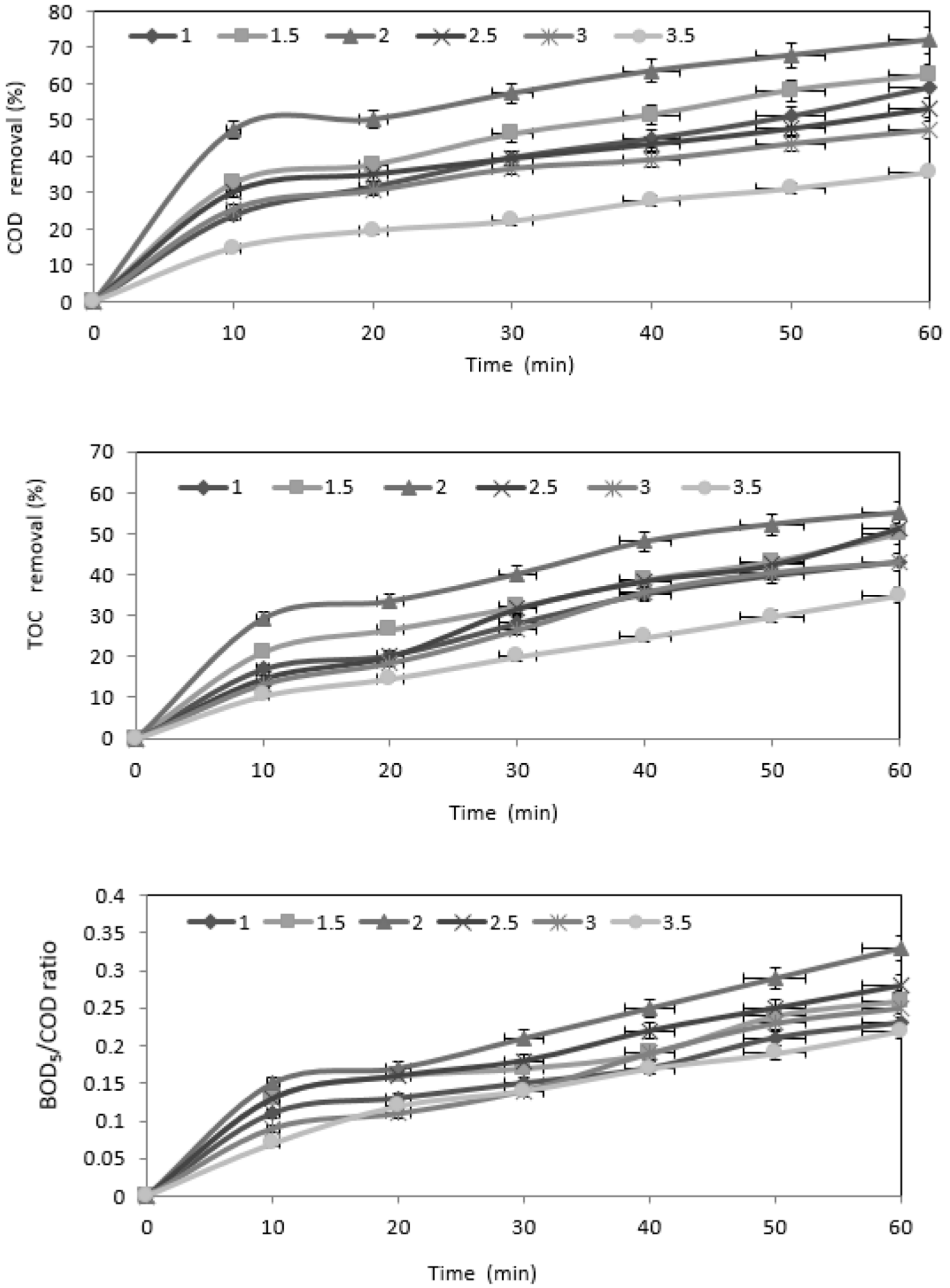


Figure 15. Effect of H_2O_2/Fe^{2+} molar ratio on Fenton process with respect to COD and TOC removal and BOD_5/COD ratio

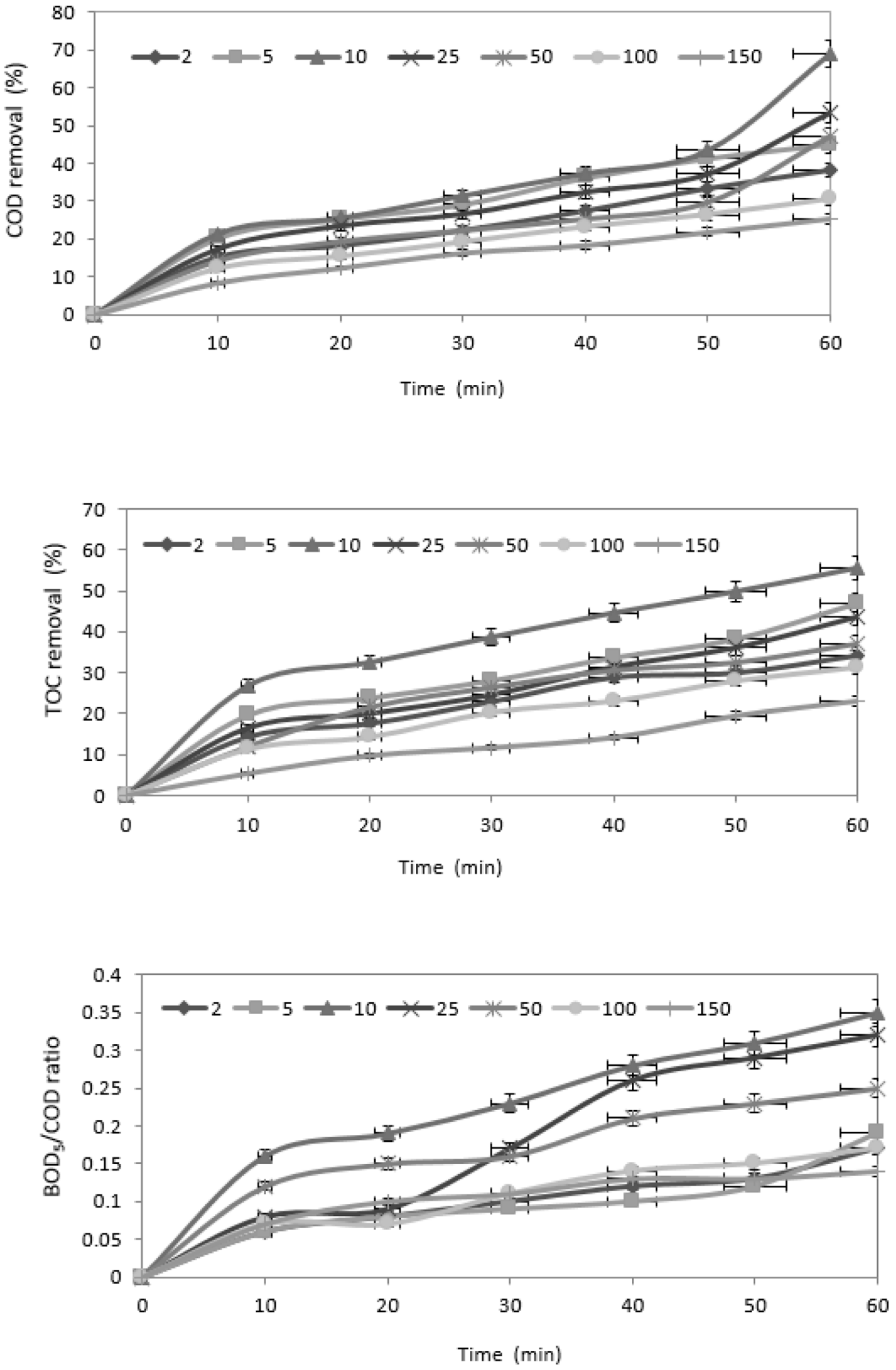


Figure 16. Effect of H_2O_2/Fe^{2+} molar ratio on UV photo-Fenton process with respect to COD and TOC removal and BOD_5/COD ratio

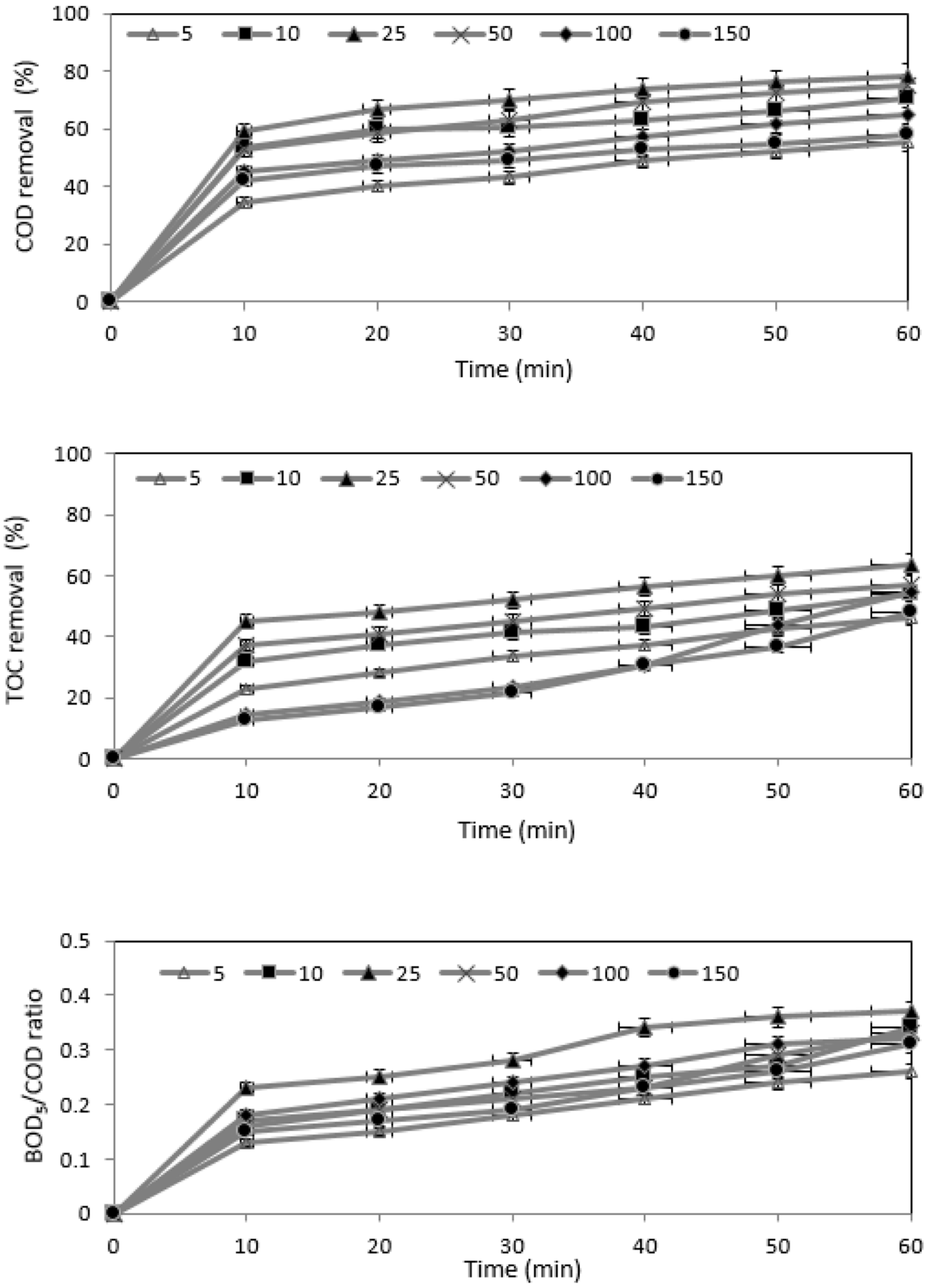
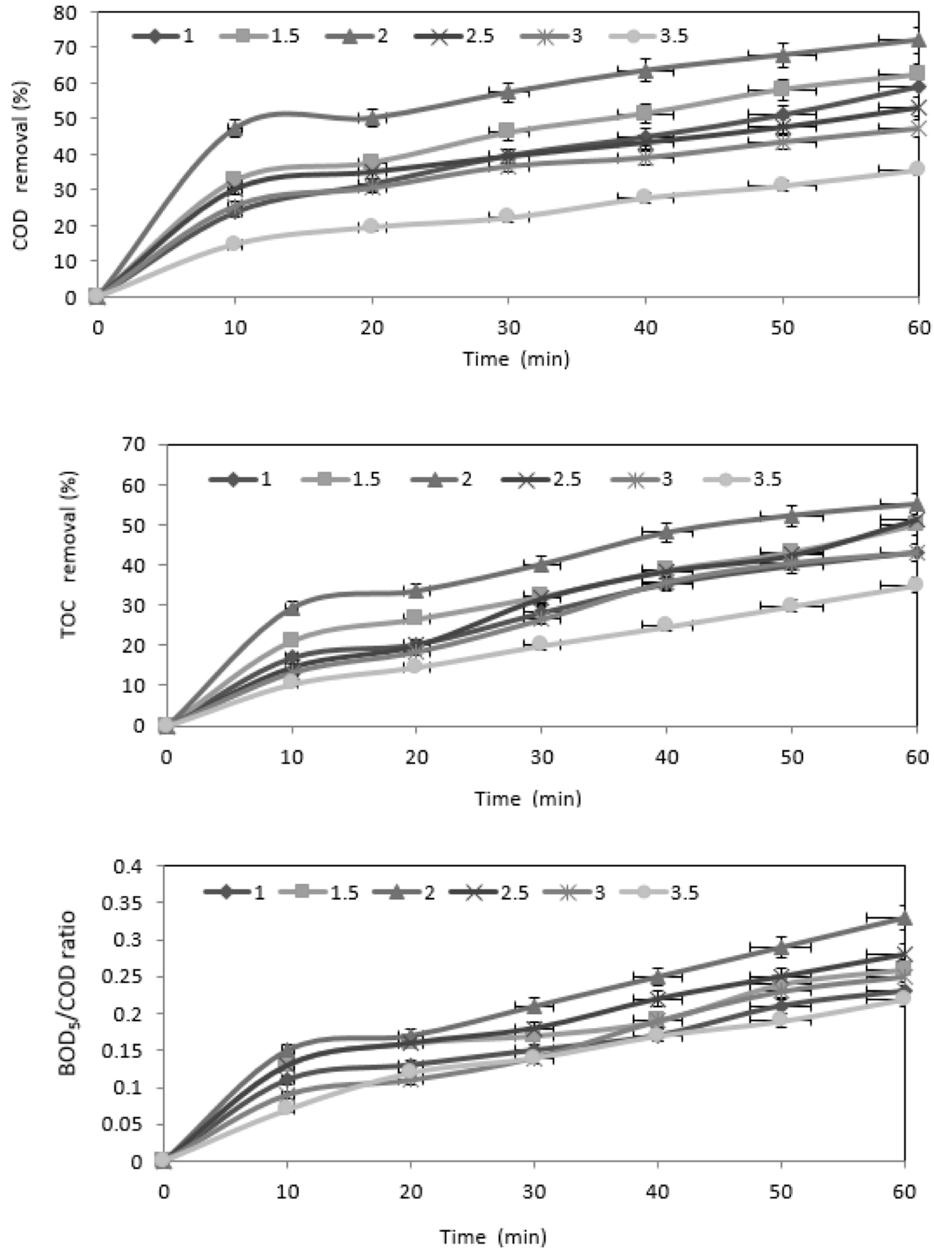


Figure 17. Effect of H_2O_2/Fe^{2+} molar ratio on solar photo-Fenton process with respect to COD and TOC removal and BOD_5/COD ratio

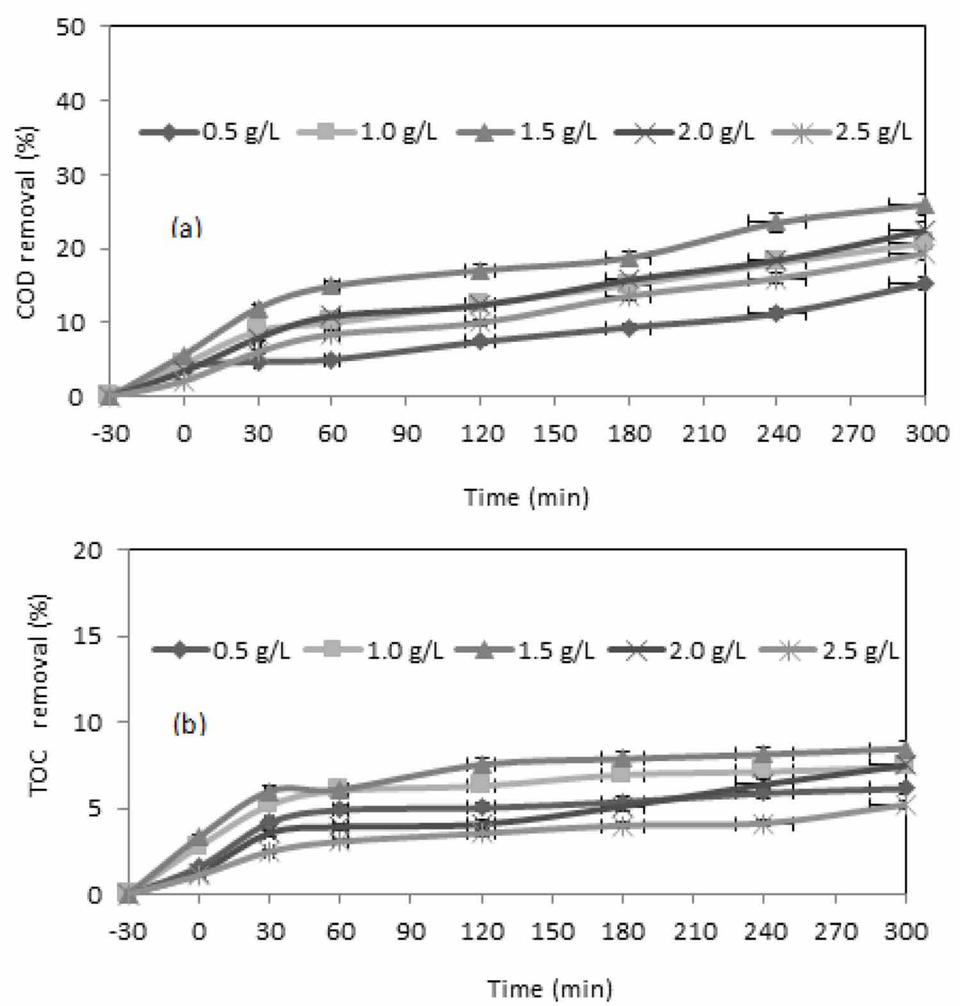


mg/L and pH 6). After a reaction time of 300 min, the highest COD and TOC removal was 25.9 and 8.5%, respectively. It was observed that an increase in TiO_2 concentration above 1.5 g/L led to lower process efficiency (Figure 18). This occurred as a result of possibly accumulated TiO_2 concentration which may reduce light penetration and thereby limiting the reaction mixture and photocatalytic effect to enable degradation proceed (Ahmed et al., 2011; San et al., 2002). The findings are consistent with other studies on bisphenol (Kaneco et al., 2004), hymatoxylin (Sioi et al., 2006), chloramphenicil (Chatzitakis et al., 2008) and paracetomol (Yang et al., 2008).

Effect of Hydrogen Peroxide Addition

Similarly, to investigate the effect of hydrogen peroxide addition, variation of the reagent was done between 50 and 300 mg/L and other fixed operating conditions were TiO_2 1.5 g/L, COD 1130 mg/L and pH 6. Fig. 10 shows the effect of hydrogen peroxide addition to the treatment process. The maximum removal efficiency for COD and TOC was 53.6 and 21.5%, respectively and biodegradability (BOD_5/COD ratio) was 0.26 after 300 min reaction time and this was obtained at a concentration of 100 mg/L H_2O_2. (Figure 19). At a lower concentration, degradation may have proceeded due to photolysis or the photo oxidation of OH^- by holes and this forms a much weaker oxidant $HO_2^\bullet$ (Pekakis et al., 2006),

Figure 18. Effect of TiO_2 concentration on pesticide wastewater degradation in terms of COD and TOC removal



which is capable of scavenging $OH^\bullet$ radicals (Gerischer & Heller, 1991). About the same report was given in other studies for removal of organic pollutants (Chu and Wong, 2004; Chatzitakis et al., 2008). Degradation at lower H_2O_2 concentration was presumably due to direct photolysis of H_2O_2 by UV light which can generate $OH^\bullet$ radical. Also, hydrogen peroxide is reported to be a better electron acceptor than oxygen. Under normal circumstances, this will reduce the chances of an electron–hole pair recombination (Pekakis et al., 2006). In the case of higher concentration of hydrogen peroxide above 100 mg/L, it may absorb and reduce the light penetration required for photocatalytic process (Chu & Wong, 2004; Muruganandham & Swaminathan, 2006).

Iron-Granular Activated Carbon/Hydrogen Peroxide Process

The effect of the operating conditions of the FeGAC/H_2O_2 process was considered in terms of iron-granular activated carbon concentration, hydrogen peroxide addition and reaction time for degradation of the pesticide wastewater. In addition, the wastewater mineralization, biodegradability improvement and kinetics of degradation were studied.

Effect of Iron/Granular Activated Carbon

In order to study the effect of iron/granular activated carbon concentration addition, the adsorbent/catalyst (FeGAC) was varied between 1 and 5 g/L. Other fixed conditions were COD 1130 mg/L and pH 3. The highest COD and TOC removal were 38.2 and 56.9%, respectively at 5 g/L after 60 min reaction time as seen in Figure 20. The obtained results shows that an increase in FeGAC led to an increase in the removal of pollutants in the pesticide wastewater. This may be as a result to high granular structure and increased surface area of FeGAC. Thus providing a large number of sites in the adsorbent for adsorption (Bach and Semiat, 2011).

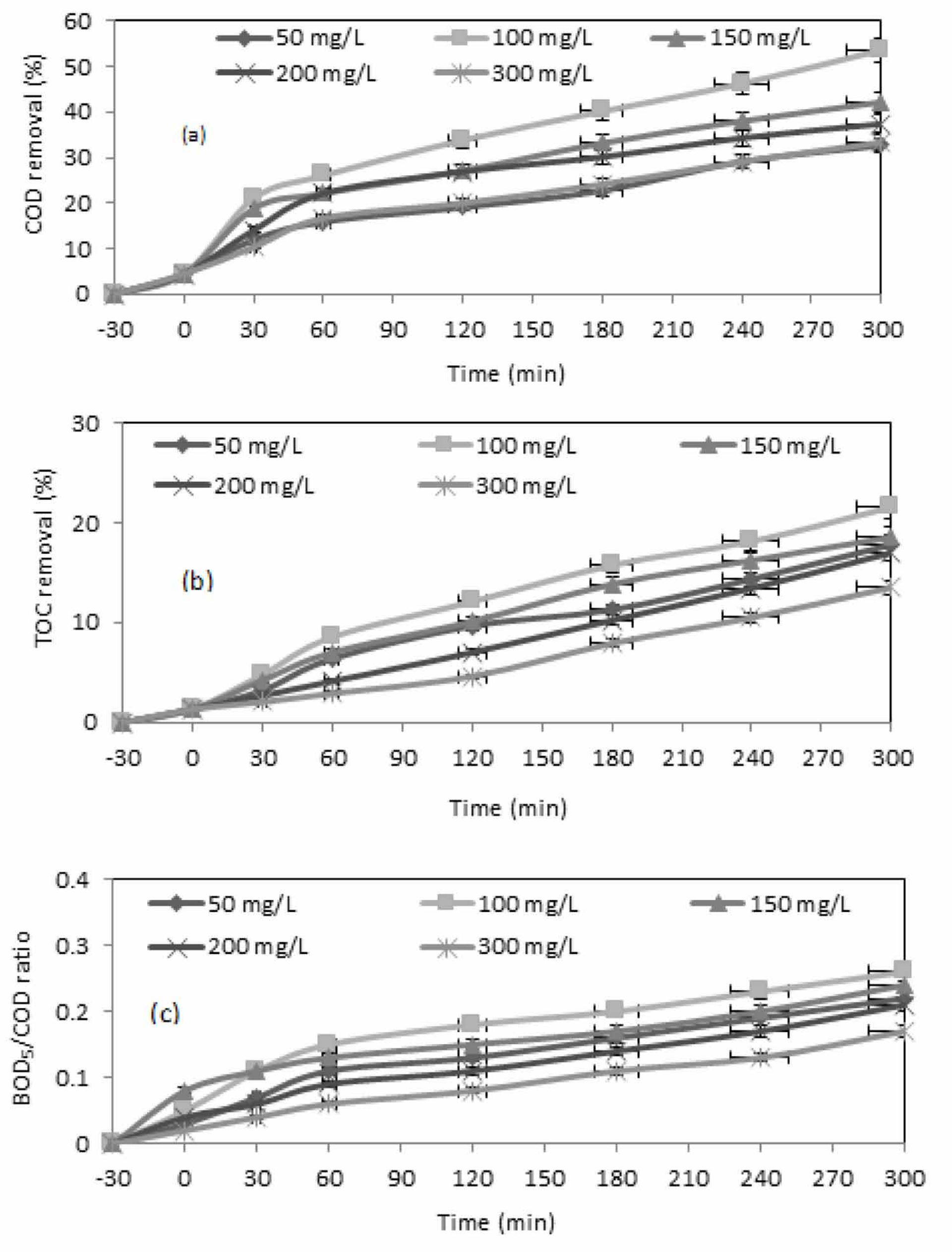
Effect of Hydrogen Peroxide Addition

To study the effect of hydrogen peroxide addition to iron/granular activated carbon adsorbent/catalyst, the hydrogen peroxide concentration was varied between 10 and 300 mg/L. Other fixed conditions were FeGAC dose 5 g/L, initial COD 1130 mg/L and pH 3. The maximum removal of COD and TOC removal and BOD/COD ratio were 96.2, 79.2% and 0.4, respectively at 100 mg/L after 60 min reaction time as seen in Figure 21. The BOD_5/COD ratio of about 0.4 indicates that a further treatment using biological process is possible (Al-Momani et al., 2002). The results show an increase in efficiency with the addition of hydrogen peroxide which increased the catalytic reaction between the activated carbon coated with iron and the oxidative H_2O_2. Decreased efficiency below 100 mg/L was probably due to competitive reaction for available hydroxyl radical (Chen et al., 20011). Over 100 mg/L concentration, the regenerated ferrous ion is likely to have reacted with produced hydroxyl radical to cause scavenging as a result of excess hydrogen peroxide (Fan et al., 2007).

Fourier Transform Infra Red Spectra

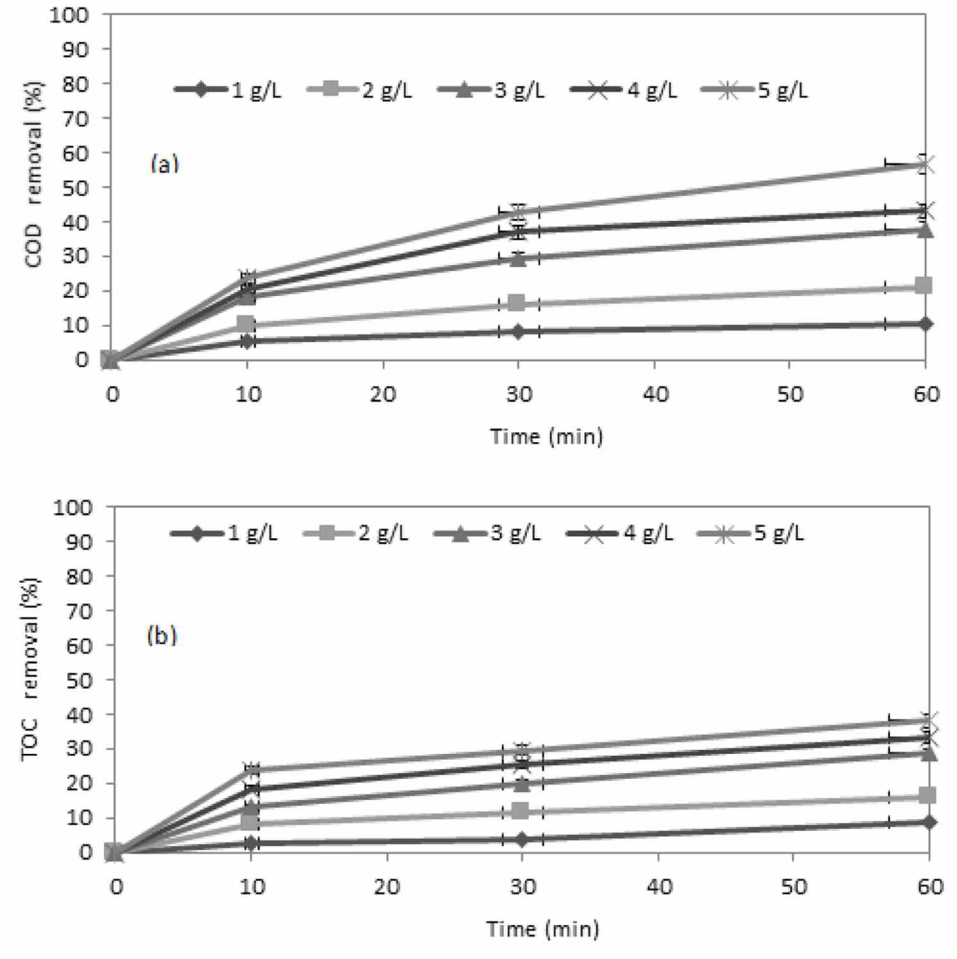
Untreated and treated pesticide wastewater were analyzed by Fourier transform infrared (FTIR) spectroscopy to investigate organic bonds present in the respective sample wastewater. In another study,

Figure 19. Effect of H_2O_2 addition on pesticide wastewater degradation in terms of (a) COD removal (b) TOC removal and, (c) BOD_5/COD ratio improvement



specific organic bonds were observed to know the point they occurred on the band spectrum. Identified tangential C–C stretching in benzene and hexa-substituted benzene derivatives of chlorothalonil were identified in the range of 1548 and 1265 cm^{-1} (Dhas et al., 2010). The cypermethrin spectrum showed strong absorption bands from 1742 to 1076 cm^{-1} due to carbonyl stretching, C=C stretching in chloro-alkenes, ring vibration of benzene, CH_2 deformation in R–CH_2–CN structure and (C=O)–O– stretching,

Figure 20. Effect of FeGAC concentration on pesticide wastewater in terms of (a) COD and (b) TOC removal



whereas the absorption bands of chlorpyrifos were observed between 1549 to 968 cm^{-1} due to C=N stretching, pyridine stretching, ring vibration, ring breathing, Cl–C stretching, trigonal ring breathing and P=S stretching (Armenta et al., 2005).

The untreated pesticide wastewater is seen in Figure 22a. In the Fenton process (Figure 22b), FTIR spectra of the untreated and treated pesticide wastewater found the absorption bands at 1650.95 cm^{-1} in the untreated pesticide wastewater was modified to 1623.95 cm^{-1} in the treated sample. While in the UV photo-Fenton (Figure 22c) and solar photo-Fenton (Figure 22d) processes, it shifted to 1622.02 and 1623.95 cm^{-1}, respectively, in the treated pesticide wastewater, indicating degradation of the pesticide organic bonds (Figure 22). In the UV/TiO_2/H_2O_2 and FeGAC/H_2O_2 processes, the modification of the organic bonds were also observed. The organic bond measured at 1650.95 cm^{-1} in the untreated wastewater was modified to 1634.16 cm^{-1} and 1618.17 cm^{-1}, after 60 and 300 min reaction time, respectively (Figure 23), indicating degradation of the organic bonds present in the pesticide wastewater.

Figure 21. Effect of FeGAC and H_2O_2 addition on the degradation of pesticide wastewater in terms of (a) COD (b) TOC removal and (c) BOD_5/COD ratio

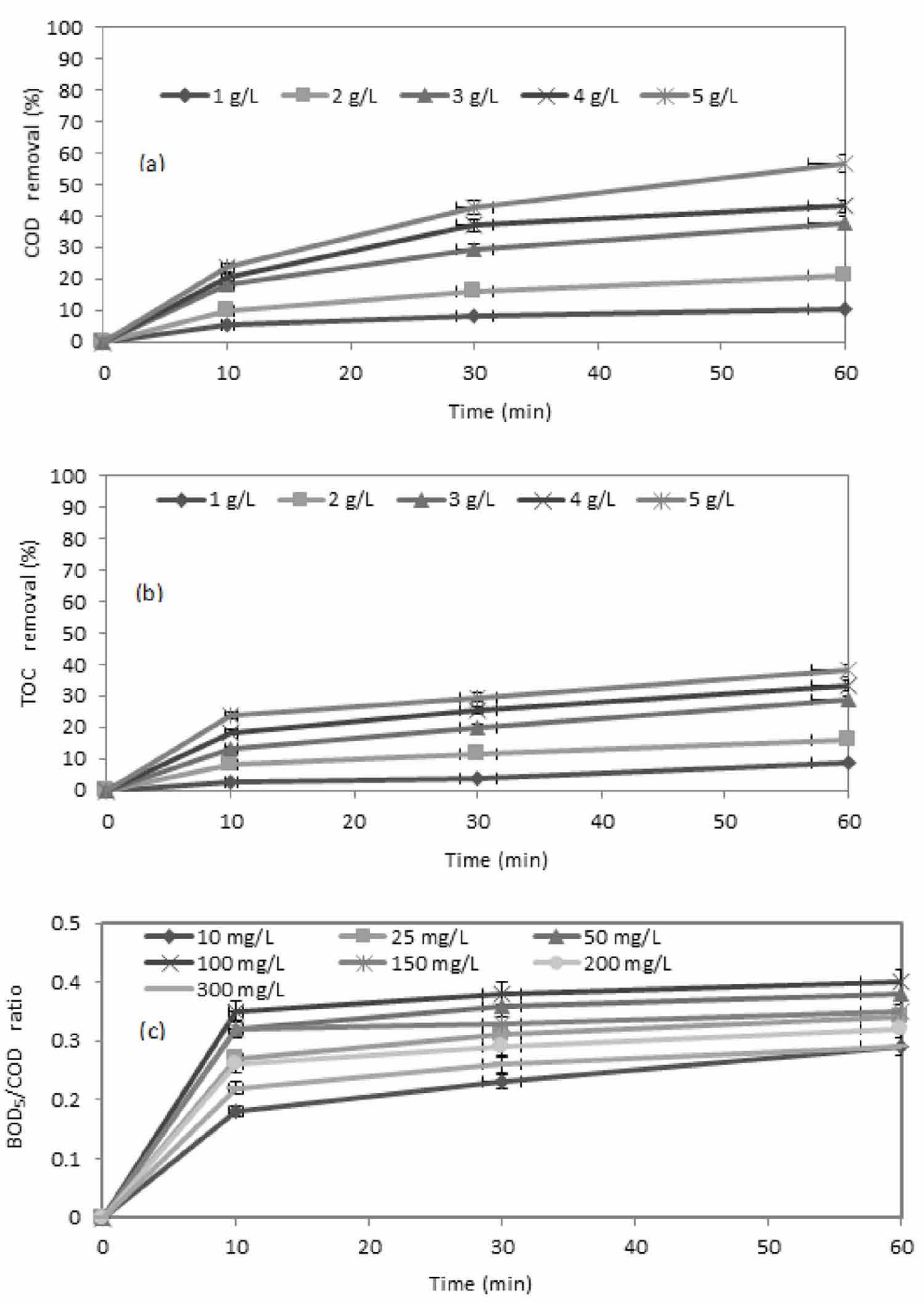


Figure 22. Fourier Transform Infrared Spectra of (a) untreated pesticide wastewater (b) Fenton (c) UV photo-Fenton and, (d) solar photo-Fenton treated pesticide wastewater

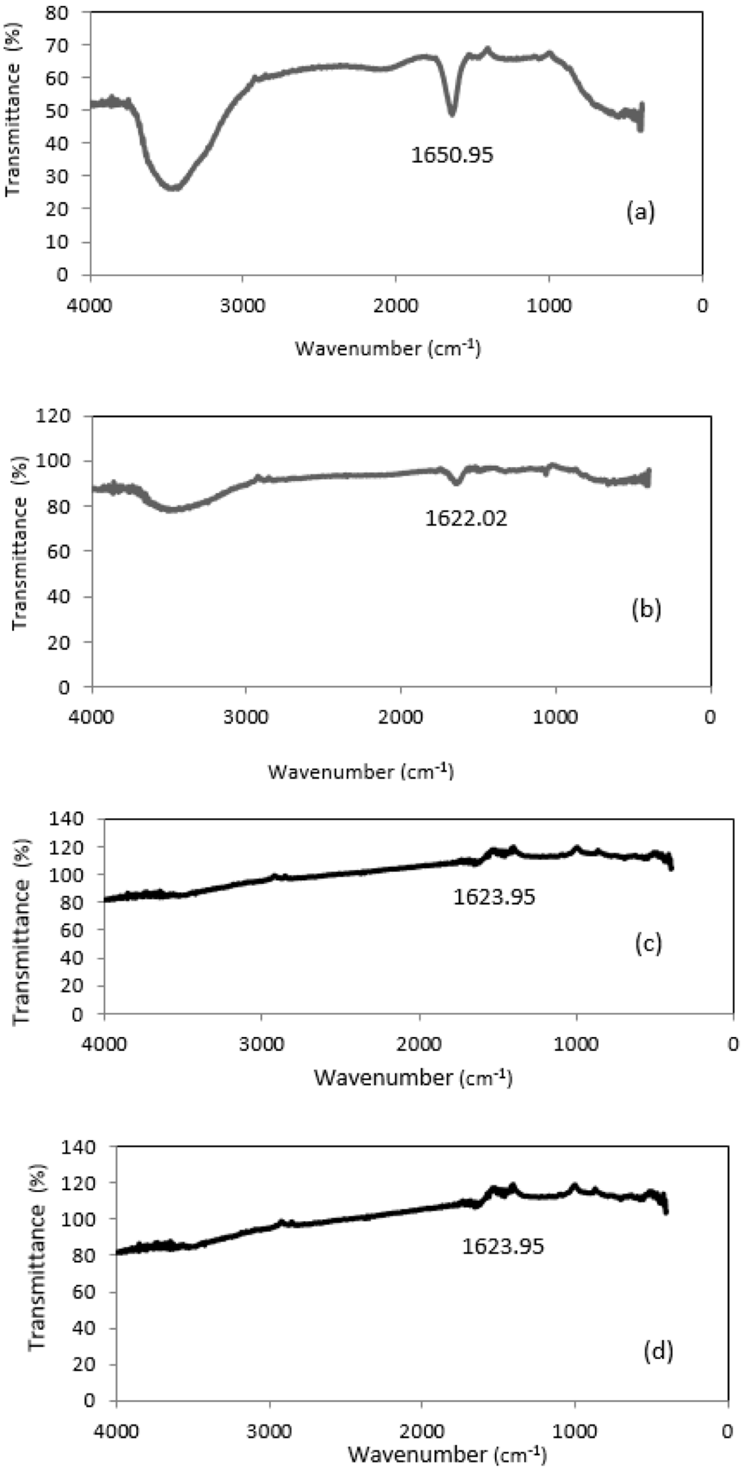
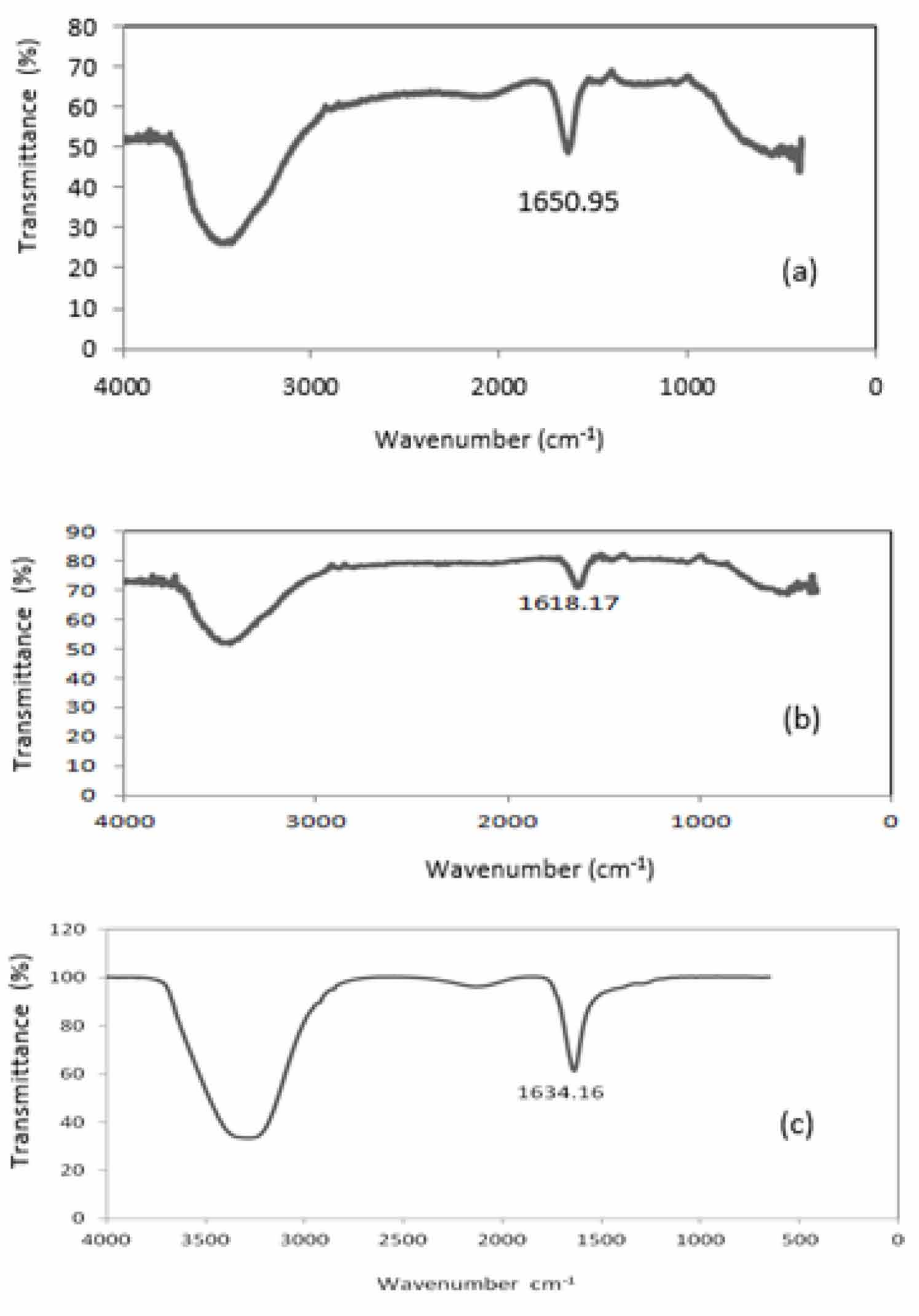


Figure 23. Fourier Transform Infrared Spectra of (a) untreated pesticide wastewater (b) Fenton UV/TiO_2/H_2O_2 and, (c) FeGAC/H_2O_2 treated pesticide wastewater



Degradation of Pesticide, Biodegradability Improvement and Mineralization Under Obtained Operating Conditions

Degradation of CPF, CPT and CTN pesticide active ingredients in the wastewater under the obtained operating conditions (in the Fenton, UV photo Fenton and solar photo-Fenton) was studied. Complete degradation of all three pesticides was achieved in 1 min in all three cases. Figure 24 and 25 shows pesticide degradation in terms of COD and TOC removal and biodegradability (BOD_5/COD ratio) improvement. For Fenton, UV photo-Fenton, solar photo-Fenton UV/TiO_2/H2O_2 and FeGAC/H_2O_2 processes, COD and TOC removal at their given biodegradability index (BOD_5/COD ratio) was 69.0 and 55.6% at 0.35,78.6 and 63.8% at 0.38, and 74.2 and 58.3% at a BOD_5/COD ratio 0.36, 53.6 and 21.5%, at 0.26, and 96.2 and 79.2% at 0.4, respectively. The obtained BOD_5/COD ratios are considered adequate for biological treatment (Al-Momani et al., 2002). In terms of mineralization, the concentration of ammonia-nitrogen (NH_3-N) decreased from 22 to 6.1 mg/L and nitrate-nitrogen (NO_3^--N) increased from 0.7 to 15.2 mg/L(Fenton) NH_3−N from 22 to 3.9 mg/L and increased NO_3^-−N from 0.7 to 19.3 22 to 4.3 mg/L (UV photo-Fenton), and nitrate-nitrogen (NO_3^--N) increased from 0.7 to 18.1 mg/L (solar Photo-Fenton) in a reaction time of 60 min. In the UV/TiO_2/H2O_2, ammonia-nitrogen (NH_3-N) decreased from 22 to 7.8 mg/L and concentration of nitrate-nitrogen (NO_3^--N) increased from 0.7 to 13.8 mg/L in 300 min whereas in the FeGAC/H_2O_2 process, concentration of ammonia-nitrogen (NH_3-N) decreased from 22 to 2.1 mg/L and NO_3^-−N increased from 0.7 increased to 21.1 mg/L in 60 min.

Kinetics of Degradation

The kinetics of degradation of the pesticide wastewater by the Fenton, UV photo-Fenton and solar photo-Fenton processes were studied. The kinetics of degradation is vital for estimating and the design of wastewater treatment plant for optimization and low-cost efficiencies (Scott and Ollis, 1995). The approach to the study was in accordance with similar studies by Zhang et al. (2010a) and can be represented by the expression as in Eq. (29).

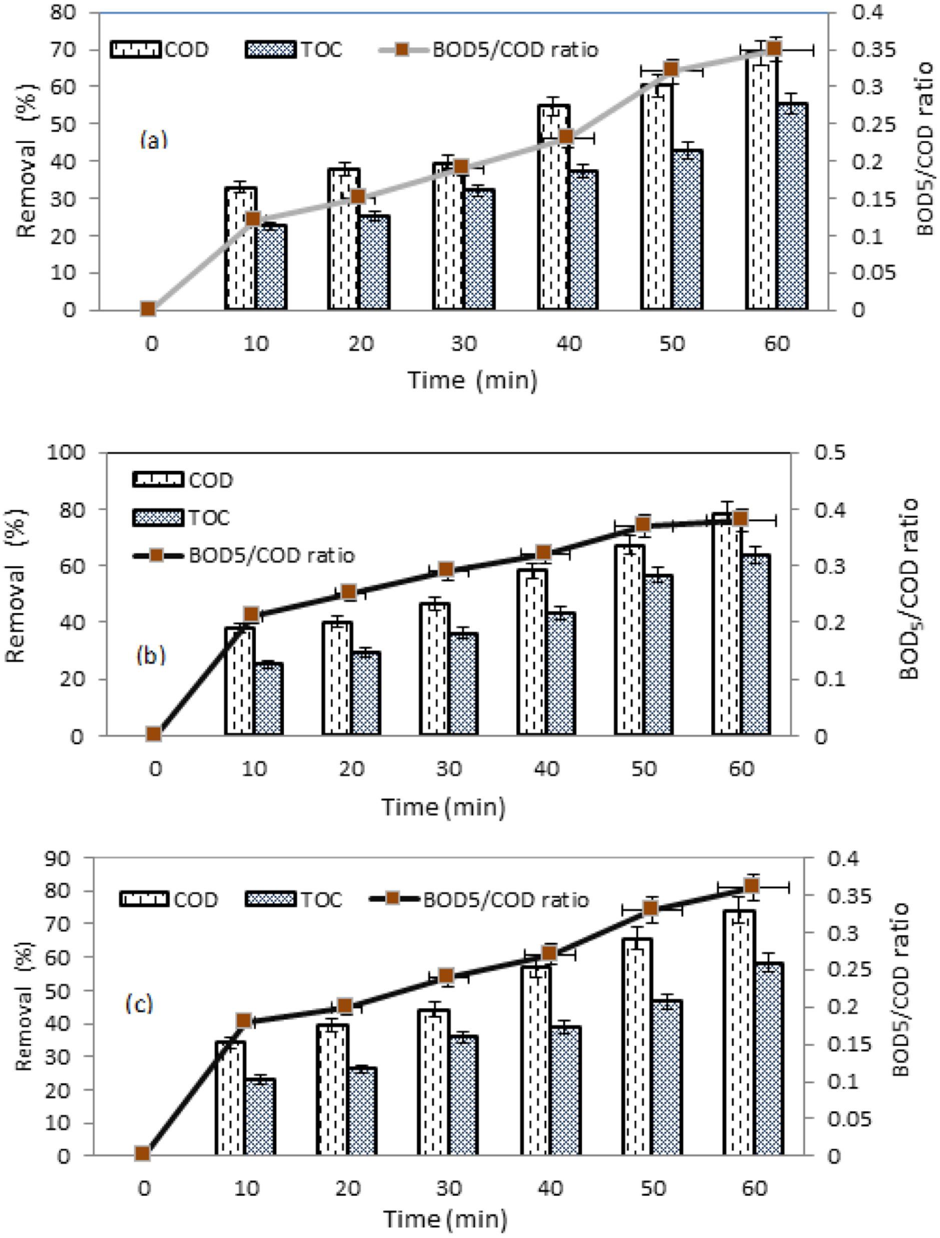
$$\ln\left(\frac{C_t}{C_o}\right) = -k * t \tag{29}$$

where, k is a pseudo-first-order rate constant, t is the irradiation time in min; C_o the initial concentration of TOC in the wastewater and C_t is the residual concentration of TOC at time t. The half-life ($t_{1/2}$) is the time required to decrease the concentration of the reactant (TOC) to half the initial value. It was calculated according to Eq. (30).

$$\frac{0.693}{k} \tag{30}$$

By plotting Eq. (5.29), the rate constant (k) is determined from the slope of the straight line. The degradation of the pesticide wastewater as a function of reaction time is shown in Figure 11. The degradation followed pseudo-first order kinetics in all cases. The rate constant, R^2 and half life time and were

Figure 24. Degradation by (a) Fenton (b) UV photo-Fenton and (c) solar photo-Fenton processes under obtained operating conditions in terms of COD and TOC removal, and BOD_5/COD ratio



k 0.0115 min^{-1}, 0.9433 and 60.3 min, respectively. The summary of rate constants (k), R^2 and half life time is shown in Table 10. The reactions followed pseudo-first order kinetics with rate constants and R^2 values as follows - k_1 0.0115 min^{-1} and R_1^2 0.94; k_2 0.0156 min^{-1} and R_2^2 0.97; k_3 0.0119 min^{-1} and R_3^2 0.96; k_4 0.0008 min^{-1} and R_4^2 0.97; (k_5) 0.0246 min^{-1} and R_5^2 0.86 for Fenton, UV-photo-Fenton, solar-photo Fenton, $UV/TiO_2/H_2O_2$ and $FeGAC/H_2O_2$, respectively.

Figure 25. Degradation by (a) UV/TiO$_2$/H2O$_2$ and (b) FeGAC/H$_2$O$_2$ processes under obtained operating conditions in terms of COD and TOC removal, and BOD$_5$/COD ratio

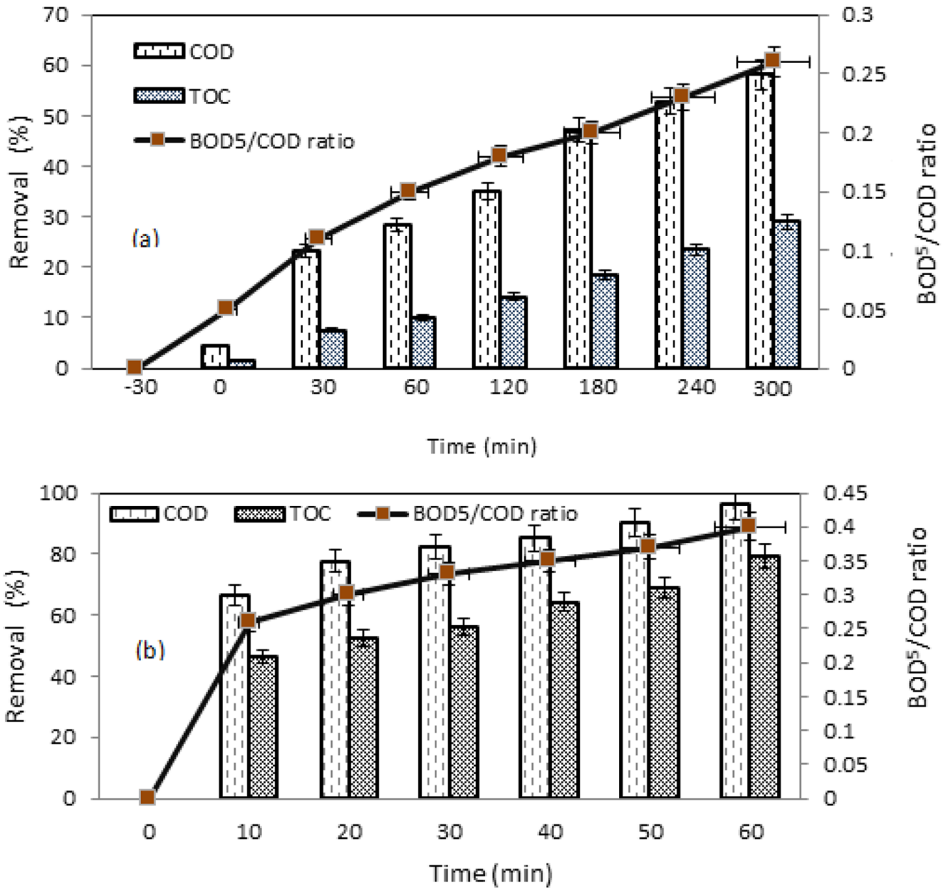


Table 10. Pseudo-first order rate constant and half-life

AOP Process k (min $^{-1}$) $t_{1/2}$ (min) t, exp. (min) R^2		
Fenton UV-Fenton	0.0115 60.3 60 0.9433	
	0.0156 44.4	60 0.9653 60 0.9627 300 0.9686 60 0.8564
Solar-Fenton 0.0119 58.2 UV/TiO$_2$/H$_2$O$_2$ 0.0008 866.3 FeGAC/H$_2$O$_2$ 0.0246 28.2		

Catalyst, Energy, and Cost Requirements

The cost requirement for the five processes is one of the most important factors to consider in choosing an appropriate AOP treatment process and this is the primary concern of this study. The overall costs are usually the sum of capital cost, operating and/or energy cost and maintenance cost. For a full-scale system these costs strongly depend on the nature and the concentration of the pollutants, the flow rate of the effluent and the configuration of the reactor (Cañizares et al., 2009). Efforts to develop standard procedures to estimate UV lamp electrical consumption has been reported (Andreozzi et al., 1999; Saritha et al., 2007). Cost evaluation for UV incorporated treatment was based on electrical energy per order (EE/O) and calculated using Eq. (31)

$$EE\,/\,O(kWh\,/\,m^3) = \frac{pt \times 1000}{V \times 60 \log(C_{ini}\,/\,C_{fin})} \quad (31)$$

where, EE/O is the energy requirement (kWh/m^3), p is the rated power of the lamp (kW), V is the pesticide aqueous solution volume (L), t is the half-life time in min for achieving 50% reduction of TOC, C_{ini} and C_{fin} are the initial and final concentration of the compound treated in terms of TOC, and the factor of 1000 was for conversion to cubic metre (m^3) (Cañizares et al., 2009). Cost of electricity depends on applicable country, the rate used was \$0.10 kWh according to similar studies (Cañizares et al., 2009). The average prices of reagents were obtained from related study (Table 11) (Integra Chemical, 2013; Calgon, 2013). Table 12 shows an estimation of the cost of operation per kg of TOC (per litre wastewater) and this was calculated for the mineralization of 50% (half-life) of the initial TOC. As regards the operating costs, UV/TiO_2/H_2O_2 photocatalytic process was considerably the most expensive than the others owing to the nominal power of the UV lamp and the time required for pesticide degradation. However, costs could be considerably reduced when solar light is used (Zhang et al., 2010a). The FeGAC/H_2O_2 process was found to be the most attractive option for the pesticide wastewater degradation.

CONCLUSION

The five AOPs (Fenton, UV photo-Fenton, solar photo-Fenton, UV/TiO_2/H_2O_2 and FeGAC/H_2O_2) were all effective for degradation and improvement of the biodegradability of the pesticides aqueous solution. The technical efficiency and cost requirements of each process under the best operating conditions indicate that UV/TiO_2/H_2O_2 was the least attractive option, whereas FeGAC/H_2O_2 was the preferred alternative. In addition, the highest rate constant obtained in FeGAC/H_2O_2 process could be due to the available adsorption sites on the FeGAC surface and catalytic property of the FeGAC and hence an increased OH. production. The study found FeGAC/H_2O_2 process to be cost effective in comparison to the other AOPs. The finding in this study is suitable for wastewater treatment at pesticide production industrial companies and not for wetlands or open plantation system. This work contributes an understanding in the treatment of high-strength industrial pesticide wastewater normally inhibitory to microbial growth in conventional wastewater treatment plants and meets the Malaysian industrial effluent discharge standard.

Table 11. Price of reagent

Reagent	Unit	Price (\$)
H_2O_2 (Integral Chemical, 2013)	kg	0.95
$FeSO_4{\cdot}7H_2O$ (Integral Chemical, 2013)	kg	1.2
TiO_2 (Integral Chemical, 2013)	kg	3.5
GAC (Calgon, 2013)	kg	0.09
$Fe(NO_3)_3{\cdot}9H_2O$ (Integral Chemical, 2013)	kg	3.0

Table 12. Comparison of the AOPs in terms of operating cost

	Reagent	**Fenton**	**UV Photo-Fenton**	**Solar Photo-Fenton**	**$UV/TiO_2/H_2O_2$**	**FeGAC/ H_2O_2**
Chemical Requirement (mg/L)	H_2O_2 $FeSO_4{\cdot}7H_2O$ TiO_2 $Fe(NO_3)_3{\cdot}9H_2O$ GAC	3602 2945	2401 785	2401 785	100 1500	100 200 5000
Cost Estimation ($/kgTOC)	H_2O_2 $FeSO_4{\cdot}7H_2O$ TiO_2 $Fe(NO_3)_3{\cdot}9H_2O$ GAC	18.4 21.5	24.4 5.7	24.4 5.7	2.2 3.8	0.26 0.44 0.036
Cost of Electricity ($/kgTOC)	UV		*4.0		*233	
Total cost ($/kgTOC)		39.9	34.1	30.1	239	0.74

*Cost of electricity (UV lamp energy)
NB: Cost obtained is for treatment of 1 litre pesticide wastewater

In addition, adsorbents can be used as support for catalysts or salts and be can incorporated into AOPs for sustainable and improved overall performance in pretreatment of pesticide wastewater before biological treatment. Iron-granular activated carbon (FeGAC) prepared from granular activated carbon (GAC) can be regenerated and reused and it could be economical as well. Finally, due to limited research, it is suggested that DOE includes pesticide monitoring in their annual quality exercise and more research in detection of pesticides in the Malaysian surface water be conducted. Based on the aim outlined at the beginning of this study current knowledge on the degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticide wastewater has been extended. In addition, selection of advanced oxidation process for application in future would be certainly guided by the cost of operation and thus this study has provided an insight to assist researchers in their work.

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Chapter 12

Ozonation With Catalyst in Landfill Leachate Treatment

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ABSTRACT

Landfill leachate is a hazardous pollutant generated from a landfill site. Discharge of landfill leachate has caused a major contamination to the environment and detrimental to human health. This chapter introduces an alternative method to treat recalcitrant pollutant in leachate by using ozonation with catalyst. The production of hydroxyl radical in ozonation was not enough to oxidize complex molecular structure in the leachate. Theoretically, the addition of catalyst enhances the capacity of radical and accelerates the chemical reaction. The effectiveness of ozonation with Fenton (O3/Fenton), hydrogen peroxide (O3/H2O2), and zirconium tetrachloride (O3/ZrCl4) in removing pollutant such as chemical oxygen demand (COD), color, and improvement of biodegradability by using this process were also discussed in this chapter. Comparison in term of treatment cost and benefits of the application of chemical as catalyst are briefly elaborated at the end of this chapter.

INTRODUCTION

The sanitary landfill has been practice worldwide as municipal solid waste (MSW) disposal. This method has become a favourite in most of the country due to the low cost and easy handled. In Malaysia, there are 296 landfills reported and about 166 are still operating. It was also noted that, out of the 166 operating landfills, only 11 of them are sanitary landfills and capable of preventing the landfill gas and leachate from escaping to the environment (Johari et al., 2014). The general composition of solid waste in landfill are food waste, plastic, paper, wood, textile, glass, rubber and metal as depicted in the Figure 1 (Aziz, 2016).

Variety sources of MSW in the landfill make the wastewater is more complex and difficult to be remediated. The by-product produce from landfill is called as landfill leachate. Meanwhile, the summary of landfill leachate characteristic at Alor Pongsu landfill site, Pulau Burung landfill site and Kulim landfill site, Malaysia is summarizes in the Table 1.

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Figure 1. General solid waste composition in Pulau Burung Landfill Site, Malaysia

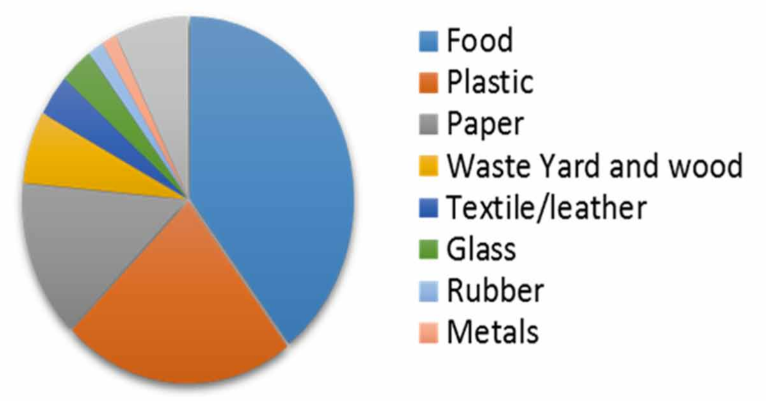


Table 1. Summary of leachate landfill characteristics at nearby landfill site

Parameter	Unit	Value	Location	MEQA*
Temperature	°C	29-33.5	Matang landfill site	40
		30.5-34.7	Pulau Burung landfill site	
pH		8.1-8.5	Pulau Burung landfill site	6.00-9.00
		8.05 - 8.66	Matang landfill site	
		7.59 - 8.25	Kulim landfill site	
Color	PtCo	2933-3615	Pulau Burung landfill site	-
		2220-6398	Matang landfill site	
		279-3029	Kulim landfill site	
COD	mg/L	1123-3180	Pulau Burung landfill site	400
		770 - 1456	Matang landfill site	
		110-1295	Kulim landfill site	
BOD_5	mg/L	60-243	Pulau Burung landfill site	20
		100 - 257	Matang landfill site	
		29-285	Kulim landfill site	
NH_3-N	mg/L	620 - 2050	Pulau Burung landfill site	5
		500 -857	Matang landfill site	
		210 - 720	Kulim landfill site	
BOD_5/COD		0.05-0.10	Pulau Burung landfill site	-
		0.14 - 0.39	Matang landfill site	
		0.20-0.24	Kulim landfill site	
DO	mg/L	0.14	Pulau Burung landfill site	-
TDS	mg/L	5306	Pulau Burung landfill site	-

(Pulau Burung, Matang and Kulim landfill site) from 2010 until 2015 (Zin et al., 2012; Aziz and Bashir, 2015; Zakaria et al., 2015; Amr et al., 2013; Othman et al., 2010; Zainol et al., 2012; Zainol et al., 2011; Aziz et al., 2010)

*Environmental Quality (control of pollution from solid waste transfer station and landfill) Regulation 2009 under the Laws of Malaysia Environmental Quality Act (MEQA) 1974 (MDC, 1997).

Leachate is well known as the hazardous wastewater that threatens the environment and human health. Although it gives minimal impact on groundwater quality, the contamination is still occurs (Aderemi et al., 2011). Leachate has a dark color, unpleasant odor, and excessive concentrations of biodegradable and non-biodegradable matter (Kamaruddin et al., 2015; Raghab et al., 2013). Based on Table 1, most of the parameters has exceed the discharge limit set by MEQA such as COD, NH_3-N and BOD_5. Therefore, discharge of effluent to the environment without intensive treatment tendency to the groundwater and water body pollution. The lower biodegradability value in the leachate also restricting the biological process to eliminated unwanted element. Thus, a strong method such as advanced oxidation process is needed in order to break down the complex substances and prevent serious pollution to the environmental.

Ozonation is a part of advanced oxidation process (AOPs). The decomposition of ozone during interaction with OH^- ions in water has generates strong hydroxyl radical (OH●). This powerful hydroxyl radical with the potential of $E = 2.80$ V able to oxidize complex molecular structure into simpler element or mineralization (water, corbon dioxide and inorganic salt) (Wang and Xu, 2012). Moreover, in wastewater treatment industries, ozonation is familiar used as disinfection and removed organic matter, such as humic substances, ammonia, and color (Multani & Shah, 2014). The efficiency of ozonation in remediate low to mile pollutant strength is well documented (Zhu et al., 2011) but most of the studies failure to record the effectiveness of ozone alone in treating recalcitrant pollutant i.e. leachate. The scarcity of hydroxyl radical in ozonation became the main barrier for ozone to completely remediate leachate (Gracia et al., 2000). Thus, new method to improvise the performance of advanced oxidation process such as combining ozone with catalyst is explored.

This technique (ozone/catalyst) can enhance the production of hydroxyl radical as well as increased the oxidation activities. In this chapter, the performance of ozonation with catalyst AOPs toward landfill leachate treatment is highlighted as follows:

1. Types of catalysis and it function in advance oxidation process.
2. The general idea how advance oxidation process works.
3. The studied of ozonation with catalyst in landfill leachate treatment such as ozone/Fenton, ozone/hydrogen peroxide and ozone/zirconium tetrachloride
4. Biodegradability improvement by using ozonation with catalysts.
5. Comparison based on removal efficiencies and treatment cost.

CATALYSIS

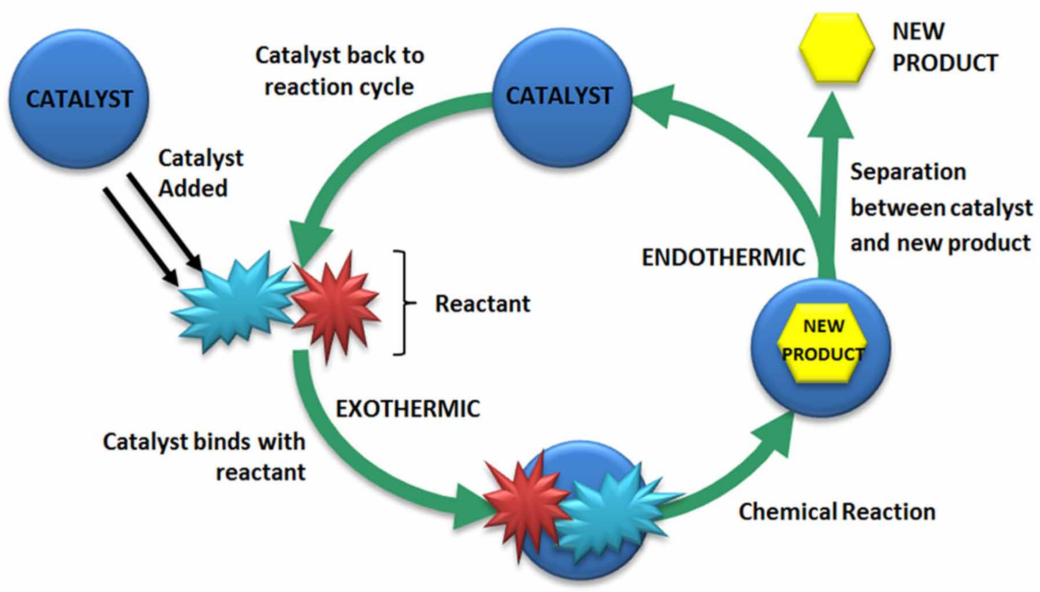
Catalyst is function as an accelerator in chemical proses. Catalyst present in various forms such as atom, molecular or aggregate. There are two general types of catalysis which are homogeneous catalysis and heterogeneous catalysis. Additional, the green catalyst has become researcher favourite currently. Application of catalysis is widely used especially in metal industrial and organic synthesis (Firouzabadi & Jafarpour, 2008). Catalyst works as a binder to tie the different molecular and provides a platform for them to react as well as produces new products. This catalysis process is generated by exothermic step which reduces the potential energy of substance. The process is illustrated in Figure 2. Catalysis also labelled as cycle reaction. After a new product is produce, catalyst will separates from the new product under endothermic process and ready for repeating the same reaction as previous. This complex process is rotatable until certain condition. It is important to note that not all catalyst function well with reactant and the bonding strength for both elements influences the compatibility.

Catalysis plays a part of important roles in AOPs especially to increase the reaction rate in oxidation process. Several properties of a good catalyst in advanced oxidation process are listed such as homogeneity, pore structure, activity and selectivity, hydrolysis, non-toxic and economic (Atalay & Ersoz, 2016). The structure of catalyst gives high influences in terms of workability because more surface area will provided larger platform for catalysis to perform. The effectiveness of catalyst in AOPs can be determines by measured three method of analysis. First, comparing the removal of parameter between catalyst and non-catalyst method after experimental. Second, measures the amount of hydroxyl radical produces using electron spin resonance (ESR) spectroscopy machine, to prove the catalytic activities (Zhai et al., 2009). Third is by using kinetic study. The analysis can be done by plotting the linear graph, concentration performance versus time (Asaithambi et al., 2015). Reaction kinetics is defined as the rate to measure the degree of performance or to design a solution by considering time as a factor. Most researchers reported that the ozonation process agrees with the pseudo first-order kinetics (Badawy et al., 2013; Asaithambi et al., 2015). An example of a good catalyst with ozonation is Fenton. This combination has increased the decomposition of ozone as well as hydroxyl radical production and removal pollutant. The details about this treatment will be explains in the next section.

Homogenous Catalysis

Homogenous catalysis is a process which involves the same physical phase of reactants and catalyst. Homogeneous has an advantage because it has larger surface area and promotes more catalytic activities. However, mixing both in the similar phase makes catalyst and reactants difficult to be separated after reaction (Atalay and Ersoz, 2016).

Figure 2. General catalysis process



The most popular homogeneous catalyst is in the group of transition metal such as Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ag^{+}, Cr^{3+} and Zn^{2+} (Shahidi et al., 2015). This homogenous catalyst has catches the researcher attention to be explored specifically in AOPs industry. The possible mechanism involved for homogeneous catalyst in AOPs is the decomposition of ozone and indirect pathway reaction. For example, the combination of hydrogen peroxides catalyst with ozone. The reaction is explained in equation 1 and 2 (Aziz & Amr, 2015).

$$H_2O_2 + 2O_3 \rightarrow 2OH^{\bullet} + 3O_2 \tag{1}$$

$$HO_2^- + O_3 \rightarrow OH_2^{\bullet} + O_3 \tag{2}$$

Equation 1 shows the decomposition of ozone after interacts with hydrogen peroxide and as a result, strong hydroxyl radical ($OH^{\bullet}$) is generated. Hydroxyl radical are able to breakdown the complex structure and mineralise organic matter. Moreover, hydrogen peroxide is easily dissolved in water and hydrolysed as hydroperoxide ion (HO_2^-). A second stage of decomposition process is occurs as depicts in equation 2. Again, strong hydroxyl radical is generated and this process is continuously repeating. Recirculation of this reaction has produce more radical which leads to more oxidation of pollutant in the sample.

Heterogeneous Catalysis

Heterogeneous catalysis is a reaction that involves catalyst and reactant in different physical phase such as catalyst in solid phase while reactant in liquid form. Contrast with homogeneous catalyst, this catalyst is more favourable because it is easy to recycle and handle, regenerable, long life time, higher stability and inexpensive for recovery (Atalay & Ersoz, 2016; Guo et al., 2012).

Heterogeneous catalyst in advance oxidation process may involve three possible mechanisms which are (Fajardo, 2011):

- Hydroxyl radical mechanism
- Adsorption of organic pollutant
- Adsorption of both reactants in catalyst surface with further reaction.

Hydroxyl radical generated from decomposition of ozone in heterogeneous catalyst surface is similar with the mechanism explained in homogeneous. Production of hydroxyl radical makes organic matter in the sample oxidise completely. Second mechanism is adsorption of organic by catalyst. This is related to the potential of catalyst functional as absorption material and attracts organic pollutant by its surface charge. Lastly is interfacial reaction mechanism which involved both absorption and decomposition of ozone in the surface of catalyst structure.

Application of heterogeneous catalyst in AOPs such titanium oxide (TiO), cobalt (II) oxide (CoO), nickel (II) oxide (NiO), copper (II) oxide (CuO) and zinc oxide (ZnO) has been successfully reported (Pines & Reckhow, 2003). The performance of each metal oxide is different and it is depends on two factors which are physical and chemical properties. The physical properties is more related to the surface area of metal oxide (for reactant to attach), pore size and surface charge for adsorption while the chemical part is referred to the chemical stability and pH which related to the active surface area. Combination of TiO with UV (phytochemical process) in leachate treatment has been studied by (Chemlal et al. 2014). The optimum removal for COD using this process is between 50% until 84% while biodegradability ratio (BOD_5/COD) increased to 0.2-0.6. Improvement of BOD_5/COD allowed biological process to takes place in post treatment.

ADVANCED OXIDATION PROCESS (AOPS) IN LANDFILL LEACHATE TREATMENT

Landfill leachate treatment can be classified into four types, namely, biological processes, physicochemical processes, chemical processes and physical processes as shows in Figure 3 (Jelonek & Neczaj, 2012; Renou et al., 2008).

The treatment normally selected based on the pollutant strength and types of leachate itself. Biodegradability ratio (BOD_5/COD) of the sample has been used as indicator parameter to determine the suitable treatment. The classification of leachate treatment by BOD_5/COD parameter can be seen in Table 2. Lower biodegradability ratio indicated that the leachate is stabilized and difficult to degrade the organic matter by aeration (biological process). Advance oxidation process is a part of chemical processes. It is a matched method for leachate treatment since average of the biodegradability ratio of leachate is lower than 0.1 and the composition of pollutant inside leachate is too strong for biological process.

Advance oxidation process is an advance technology in removing pollutant from liquid waste by using hydroxyl radical. This method has offered the demolishment of complex organic matter and mineralization. The main mechanism involved in this technique is oxidation. The advantageous and disadvantageous of AOPs in wastewater treatment is summarize in Table 3 (Atalay & Ersoz, 2016; Sharma et al., 2011).

Generally, advance oxidation process can be divided into two types which are photochemical and non-photochemical. Photochemical is a method using energy from the light to generate radical while non-photochemical is contradicting. There are several studied has been done on photochemical method i.e. combination of H_2O_2/UV, UV/O_3, photo-fenton, 0_3/UV/H_2O_2 (Arslan et al., 2017), combination of TiO_2/UV (photocatalyst) with biological treatment in wastewater (Oller et al., 2011) and photocatalytic oxidation (UV/TiO) (Sharma et al., 2011; Chemlal et al. 2014). Even though this method was recorded as high percentage removal for selective parameter, however these techniques are only effective for low or intermediate pollutant concentration such as ground water, dye and river.

This chapter is focusing on landfill leachate treatment, thus non-photochemical is more suitable to be studies and discussed here. Moreover, non-photochemical has promising a powerful oxidation process and it is capable to treat strong pollutant like landfill leachate. To give an easy understanding on how oxidation in non-photochemical process works, a general illustration of mechanism involved with or without catalyst is sketched and depicts in Figure 4.

There are two stages of oxidation involves in these techniques which are (Estrada et al., 2012):

1. Production of oxidant agent (direct or indirect process).
2. The oxidation of organic compound by oxidative agent.

Figure 3. Types of landfill leachate method

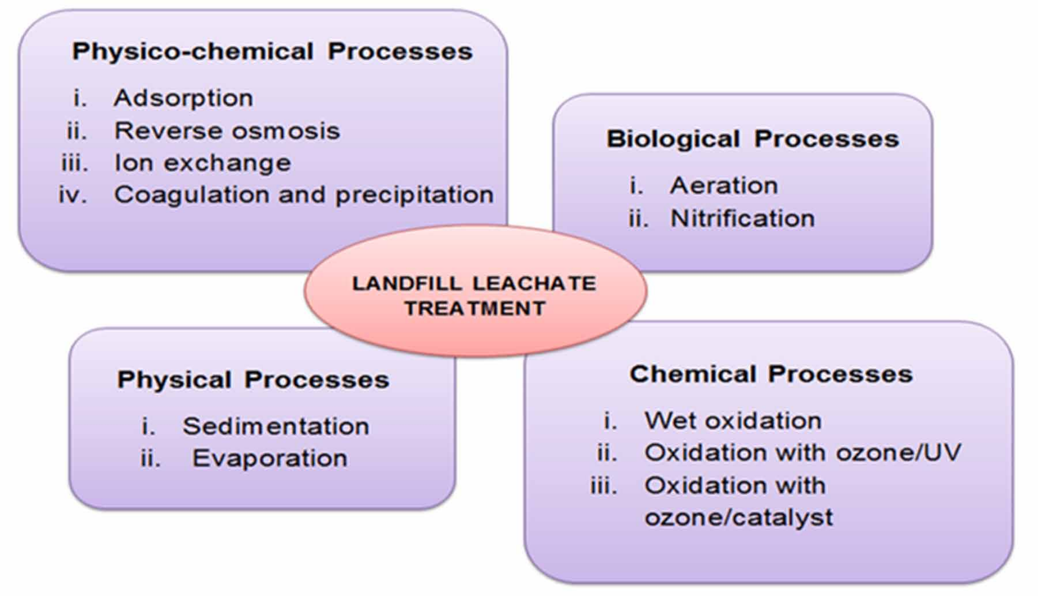


Table 2. Leachate classification at different landfill ages and types

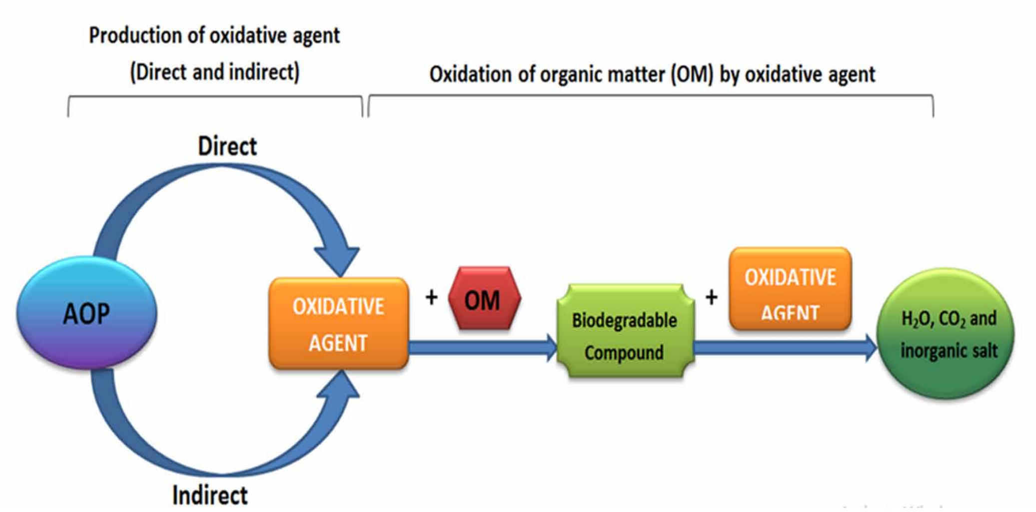
Constituent	**Landfill age and leachate type**		
	Young (<5 years)	**Intermediate (5-10 years)**	**Stabilized (>10 years)**
BOD_5/COD	>0.5	0.1-0.5	<0.1
Treatment	Biological, physical	Biological, physical, physiochemical and chemical	Physiochemical, chemical and physical

(Lim et al., 2016)

Table 3. Summary of advantageous and disadvantageous of advanced oxidation process in wastewater treatment

Advantageous	**Disadvantageous**
1. Provide complete oxidation of organic matter and mineralization	1. Not all processes can be scaled-up to industrial needs
2. Improve biodegradability of sample and allow biological proses as a post treatment.	
3. Able to apply on recalcitrant pollutant sample which biological proses also resistance to treat it.	2. Higher capital and operating costs compared with conventional treatment
4. Minimum by-production generated	
5. Rapid reaction rates	3. In some cases, required pH adjustment and controller of oxidant concentration
6. Able to combine with other processes	
7. By-product produce does not required further treatment	
8. In many cases, consume less energy	4. For some application, quenching of excess peroxide is required.
9. Does not concentrate waste for further treatment with costly methods.	

Figure 4. General mechanism of AOPs in remediates wastewater



First stage is related to the formation of oxidative species i.e., hydroxyl radical. Free radical is not naturally present in water and most of them were generated from the chemical reaction. In ozonation, the decomposition of ozone in water has produces free radical such as superoxide ion radical and hydroperoxide ion radical. Continuing the reaction has led to the production of strong hydroxyl radical as shown in equation 3 to 5.

$$O_3 + OH^- \rightarrow \bullet O_2^- + HO_2\bullet \tag{3}$$

$$O_3 + \bullet O_2^- \rightarrow \bullet O_3^- + O_2 \tag{4}$$

$$\bullet O_3^- + H^+ \rightarrow \bullet HO_3 \rightarrow \bullet OH + O_2 \tag{5}$$

Strong oxidant agent is important in oxidation-reduction reaction. The strength of oxidative species is described based on their standard potential redox as listed in Table 4 (Beltrán, 2003).

The second part is about the interaction between oxidative agents (radical) with organic matter. The present of powerful hydroxyl radical has oxidized of complex organic matter into smaller structure or biodegradability substance. Subsequently, continues introduce biodegradable product to hydroxyl radical has mineralizing it into the water, carbon dioxide or inorganic salt form. This reaction is illustrated in equation 6 (Ghazi et al., 2014).

$$\text{Dissolved Organic Matter (DOM)} + OH^\bullet \rightarrow \text{Biodegradable product} \tag{6}$$

Table 4. Standard redox potential of oxidant species

Oxidant Species	E●, Volts
Fluorine	3.06
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Hydroperoxide radical	1.70
Permanganate	1.67
Chlorine dioxide	1.50
Hyprochlorous acid`	1.49
Chlorine	1.36
Bromide	1.09
Iodine	0.54
Oxygen	0.40

Ozonation in landfill leachate treatment has been studied by many researchers. Ozone is generated by four methods which are (Smith, 2011):

1. Electrical discharge/ corona discharge. Used high voltage of electricity across a gap which presents flowing pure oxygen (O_2).
2. Electrolytical, Electrolysis of an acid.
3. Photochemical. For example ultraviolet radiation (UV light).
4. Radiochemical. Used high energy irradiation on oxygen to produce ozone. However this method less used because of the fear of radiation toward environment and human life.

Electrical method has become favourite researcher because of easy to handling, most effective, economical, easy to control ozone production and safest compared to others. The production of ozone using this method is explained in equation below (Parsons, 2004):

$$O_2 \rightarrow O^{\bullet} + O^{\bullet} \tag{7}$$

$$O^{\bullet} + O_2 \rightarrow O_3 \tag{8}$$

Ozonation is also proven as a good method to increase the biodegradability ratio of the sample. However, majority of them have agreed that ozonation alone as a single method cannot completely remediate the recalcitrant pollutant in leachate due to the complicity organic compound in it. Amr et al., (2016) have makes a comparison performance between ozone alone and ozonation with catalyst (ozone/fenton and ozone/persulfate). The result shown that the ozonation alone is poor compared to the others in term of percentage removal of pollutant (COD, Color and NH_3-N). Zakaria et al. (2015) also congruent with other scholar and face the same situation; ozonation can only remove 4% of COD, whereas combining ozone with a catalyst has increases the performance to 48%. Judging from the data recorded, it is explained that the production of $OH^\bullet$ by a single O_3 is insufficient to oxidising high pollutant. Thus, improvising advance oxidation process by combining catalyst with ozone is one of a novelty technique in leachate treatment.

Application of advanced oxidation process in leachate treatment does not rigid for single treatment. A several studies have used ozonation as preliminary treatment and post treatment. In simple words, ozonation process is combined with other methods (before or after) to elevate the performance. Cortez et al. (2011) has investigated the removal of nitrate from mature landfill by using pre ozonation and rotating biological contactor (RBC). Pre-ozonation was applied before RBC in order to increase biodegradability and to reduce the organic content in the RBC. The total organic carbon (TOC) value showed 28% decreased during pre-ozonation. Improvement of biodegradability value by AOPs also has been proven by others studies (Cortez et al., 2010).

Ozonation with catalyst can increased the production of hydroxyl radical as well as the oxidation of organic matter. This fact has been supported by Zhai et al. (2009). The experimental of ozonation only and ozone with catalyst (H_2O_2 and MnO) has been run. The effluent sample was tested using electron spin resonance (ESR). The result shows that, sample which undergoes ozonation with catalyst has high peak of intensity compared to ozone only. High intensity is representing the high amount of hydroxyl radical in solution (Zhai et al., 2009). Therefore, the ability of catalyst in enhancing the performance of ozonation cannot be denied. The behaviour of catalyst dosage which increased with percentage removal may classify this mechanism in pseudo first order kinetic.

An additional catalyst in the ozonation method has been studied by numerous researchers. Amr et al. (2013) used Fenton and persulfate to improve ozonation for stabilized leachate treatment. Tizaoui et al. (2007) has employed H_2O_2 for enhanced ozonation of landfill leachate while Cong et al. (2015) added peroxymonosulfate as catalyst to enhance ozonation of para-chlorobenzoic acid in an aqueous solution. Next subtopic will be discussed about ozonation with catalyst which has been experimental and studies by previous researcher.

LANDFILL LEACHATE TREATMENT USING OZONATION WITH CATALYST

Catalytic ozonation is a novel method of advanced oxidation, which combines ozonation with the adsorptive and oxidative properties of solid-phase metal oxide catalysts or homogeneous catalyst to achieve mineralization of organic pollutants (Parvin et al., 2014). The main purpose of combining ozone with catalyst is to increase the production of radical especially hydroxyl radical in concentrated wastewater treatment such as leachate. The catalysis played an important role and occurs at the first stage of oxidation in AOPs. As mention in previous section, the catalyst is grouping into two types which are heterogeneous and homogeneous catalyst as well as in AOPs. Those type of catalyst is react differently with discrepant mechanism occur. Therefore, to get a clear understanding about ozonation with catalyst, Legube and Leitner (1999) has sketch a main possibilities reaction and process occurs in boths methods as demonstrated in Figure 5 and Figure 6 below.

Figure 5. Mechanism in ozonation with heterogeneous catalyst

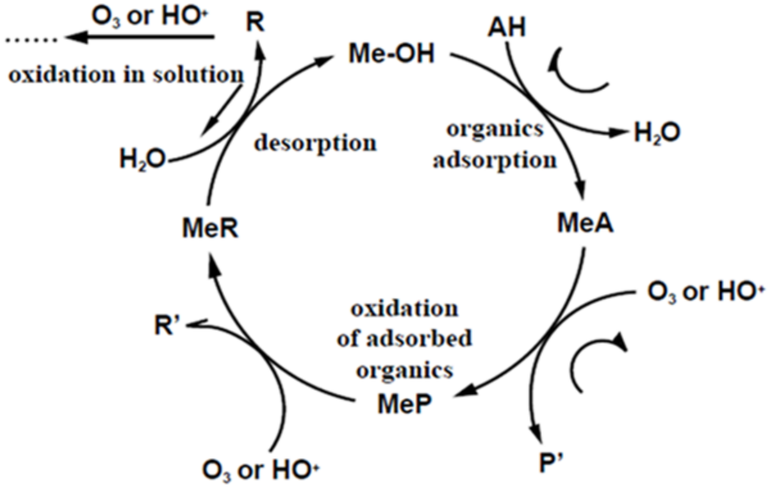
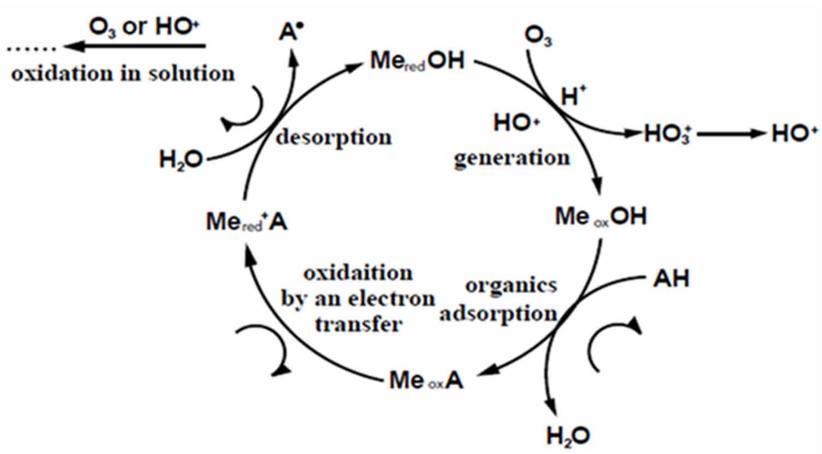


Figure 6. Mechanism in ozonation with homogeneous catalyst



Heterogeneous and homogeneous catalytic in ozonation have different mechanism involved on it. In ozonation with heterogeneous catalytic, Legube and Leitner (1999) has labelled catalyst as an adsorptive material only (Me-OH). Me-OH has provided active adsorption site to adsorb the target compound (organic acid) and formed as MeA (Figure 5). On the other side, the interaction of ozone with OH ion is occurs and has produces radical such as hydroxyl radical to act as oxidative agent. Subsequently, the reaction is continued by the oxidation process of organic matter in the surface of adsorbent or aqueous by oxidative species. The P' and R symbol are representing first and last oxidation by-product in this reaction. Recently, a metal ion has become researcher favourite catalyst in AOPs. It is relevant because metal ions have high homogeneity and allowed easy chemical process to occur. There are almost 50 compounds has been reacted well with ozone and some of it reaction reactively with ozone in any pH condition (either in acidity or alkaline solution) (Loures et al., 2013).

Figure 6 explained the mechanism present in ozonation with homogeneous catalyst. In this method, oxidation process conquers the reaction but catalyst ($Me_{red}OH$) still can be functional as adsorptive agent. It is starts with the production of oxidative agent ($OH^{\bullet}$) by interaction of ozone with OH ion or catalyst. The present of organic acid (AH) in aqueous is absorbed by oxidized catalyst ($Me_{ox}OH$) and produce $Me_{ox}A$. Again, $Me_{ox}A$ is oxidise by an electron transfer reaction and formed in $Me_{red}A^{\bullet}$. The A● is representing the organic radical which is easily desorbed and oxidise by OH radical or ozone after separated with catalyst (Me). After the separation, catalyst is continued recycling the process (Legube and Leitner, 1999).

Generally, the performance of ozonation with catalyst on leachate is influences by ozone dosage, catalyst molarity, pH aqueous and reaction time. Additional, Aziz and Amr, (2015) has recorded that the pollutant strength also affect the efficiency of AOPs. The range of chemical oxygen demand was varied from 250 mg/L to 2360 mg/L and used as indicator in this study. Afterwards, the experiment was run at condition; ozone dosage 80 g/m^3, H_2O_2 1700 mg/L, Fe^{2+} 2800 mg/L, pH 8.3 and reaction time 60 minutes. The result shows that low COD (250 mg/L) in leachate sample produces higher removal (87%) compared to high value. Whilst, at high concentration (COD>500 mg/L), percentage removal of COD start decreased from 80% to 60% (COD = 2360 mg/L) (Aziz and Amr, 2015). This experimental explained that the oxidation by radical function well on organic matter however more amount of hydroxyl radical is needed to oxidise large number of organic compound in high concentration of pollutant sample. Most of the ozonation with catalyst in AOPs is still in earlier stage and the data is obtained from laboratory not well documented. A good catalyst do not only depends on reaction rate but the selectivity and consumption of ozone also in count.

The law of rate in AOPs is normally depend on types of reactor and the classification is based on the way of O_3 feeds the reactant. Generally, there are four general types of reactor used in ozonation test which are (Langlais et al., 1991):

1. Batch reactor (O_3 already mixed well in water and placed in covered reactor).
2. Semi batch reactor (ozone gas is continuously introduce in bubble form but the volume sample is fixed).
3. Continuous flow series reactor.
4. Continuous flow reactor.

Those reactor works differently and the ideal of kinetic study for each reactors also different. Beltrán et al. (2003) categorized that the flow of reactor is present in ideal or non-ideal and each flows has its own situation. The common reactor used in ozonation alone or ozonation with catalyst test is semi batch reactor i.e. removing dye from wastewater (Gharbani et al., 2008), wastewater treatment using catalytic ozonation-biological processes (Li et al., 2010) and treatment of diary effluent by ozone/iron ion (Messias et al., 2015). Moreover, this type of reactor is also favourable used by contractor on the site. There are many advantageous using this method such as low operating and maintenance costs and the excellent mass and heat transfer (Cardona et al., 2010).

The experiments of ozone/Fenton, ozone/H_2O_2 and ozone/zirconium tetrachloride also used semi batch reactor in oxidation process. Methodology of this experiment is started with supply 99% of pure oxygen to ozone generator and passing through high voltage rode to generate ozone. Afterwards, ozone generated is flowing to reactor through small nozzle (at the base of reactor) to formed fines bubble before it enters onto the chamber (Summerfelt et al., 2003). Ozone bubbles from the base reactor were diffused through the sample until it completely reacted or until the excess O_3 (off gas) escapes at the top. This reactor is fully covered. The sample and catalyst is initially mixed and places inside the reactor before ozone gas is supplied (Amr et al., 2016). Ozonation process needs to be experimental in low temperature (below 15°C) because it is the optimal condition to maintain the half-life of dissolved O_3 (30 minutes) in water (Block & Brown, 2004). Usually, a water bath and cooling system is provided in AOPs in order to constant the temperature.

In this section, mechanism involved, factors influent and the performance of ozone with several chemical catalysts i.e. Fenton (Fe^{2+} and H_2O_2) , hydrogen peroxide (H_2O_2) and zirconium tetrachloride ($ZrCl_4$) in landfill leachate treatment will be discussed. The data obtained from previous researchers will be used as preferences to elaborate this technique.

Ozonation With Fenton

Ozonation with Fenton is a combination of ozone, hydrogen peroxide and ferrous. Application of ozone with Fenton has been tested on various types of waste water such as textile industrial wastewater and landfill leachate (Duyar & Cirik, 2016; Aziz & Amr, 2015). Amr et al. (2016) has recorded high percentage removal of color and COD which is 95% and 78% respectively. However, disinfection of ammonical-nitrogen by using this method is relatively low. NH_3-N removal is caused by the present of sulphate (alkaline condition) in ferrous sulphate which is used in Fenton test (Aziz & Amr, 2015; Deng & Ezyske, 2011). These studies also has reported that the effluent of sample after undergoes ozone/Fenton treatment has obey the Malaysian standard discharge limitation (MEQA). Other advantageous using AOPs in leachate treatment is it capability to improve the biodegradability of waste especially in the stabilized landfill leachate. Stabilized landfill leachate is well known as lower biodegradability ratio and biological treatment do not functional on it. Thus, applying ozone/Fenton treatment onto it has improved and increases the BOD_5/COD value from 0.034 to 0.14 (Amr et al., 2015). The efficiency of ozone with Fenton in treating landfill leachate is a novelty achievement in wastewater treatment industry.

The mechanism involved in ozone/Fenton treatment is oxidation of organic matter by hydroxyl radical. The production of hydroxyl radical in this process is generates from these two reaction process which are:

1. Decomposition of ozone (indirect)
2. Chemical reaction between hydrogen peroxide and ferrous (direct).

Catalysts added in this process not only works as accelerator in the decomposition of ozone but the interaction between them (Fe^{2+} and H_2O_2) also has contribute to the production of hydroxyl radical (Miranzadeh et al., 2015). Fenton only (using conventional jar-test method) also has been studied by scholars as oxidative agent in landfill leachate (Vilar, et al., 2013; Boumechhour et al., 2013; Deng and Englehardt, 2006). Oxidation of Fenton in leachate treatment has achieved 64.18% to 89% of removal COD and improved biodegradability ratio from 0.02 to 0.33 under acidic condition pH 3 (Vilar, et al., 2013; Boumechhour et al., 2013). The lack of this method is Fenton needs long reaction time to obtained optimum condition which is 2 hours, needs pH adjustment to pH 2.5 - 3.0 to keep the iron in solution form, required larger space for conventional treatment method (coagulation, flocculation and sedimentation process) and additional post treatment for sludge (Van et a., 2011; Vilar, et al., 2013). This factor has increased the operation cost (energy used, chemical reagent and used of area). Therefore, combination Fenton with ozonation is a good study in wastewater treatment industry. This method give advantageous on several prospective such as reduce the size of area used, no pH correction (oxidation ozone/Fenton is efficient in alkaline condition which is similar with pH raw sample), reaction time taken and improved the efficiency of oxidation as well. In this combination, Fenton reagent is initially mixed with the sample in stainless steel column reactor before ozone gas (in bubble formed) will be supplier onto it. All oxidation process will be occurs in single reactor chamber only and effluent will be sampling at the bottom of chamber. The reaction occurs in this method is described in equation 9 -13 (Roudi et al., 2015; Munter, 2001).

$$H_2O_2 + 2O_3 \rightarrow 2OH^\bullet + 3O_2 \tag{9}$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{10}$$

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3 \tag{11}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{12}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{13}$$

The performance of advance oxidation process depends on three crucial parameters which are dosage of ozone and catalyst, pH of aqueous and reaction time. In this treatment, the influence of ozone/Fenton dosage toward oxidation process is proportional. Increase the amount of ozone and Fenton will increase the direct and indirect reaction. According to Amr (2013), the best molarity dosage ratio for Fenton is 0.5:0.5 (H_2O_2:Fe^{2+}). However, adding of too much ferrous ion in solution will create a competition between Fe^{2+} with others organic matter to consume hydroxyl radical. This phenomenon is explained in equation 12. Thus, the amount of Fe^{2+} in this process is needs to be control and avoid redundant of Fe^{2+} which can reduces the removal efficiency of target parameter.

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{14}$$

The second factor which affects the performance of ozone/Fenton is pH. Amr, (2013) reported that ozone/Fenton is effective at pH 7 -9 compared to acidic solution. These results indicated that indirect reaction pathway dominant the oxidation process. Indirect reaction is a process of oxidising organic matter using hydroxyl radical by decomposition of ozone. It is more powerful and resulting high percentage removal of pollutant compared to direct reaction. The production of hydroxyl radical by indirect pathway is efficient in alkaline condition pH > 9 (Li et al., 2015). Contradiction, direct reaction is normally occurs in acidic condition at pH range 3 to 5 (Cortez et al., 2011a). The present of OH ion also helps to decomposed ozone and generates more hydroxyl radical. The equation 3 to 5 give a clear picture of chemical reaction occurs in this technique. Moreover, the decomposition of H_2O_2 by $Fe2^+$ and Fe^{3+} also has produce free radical and hydroxyl radical. Increased the amount of radical has empower the oxidation of organic matter in this treatment. These reactions are explained in equation 12 and 13. It is important to pay an attention on iron residual which is present after used ferrous sulphate solution in treatment. Iron tends to precipitate at alkaline condition (pH 7 – 8). According to Hove et al. (2007), large particle size of iron oxide hydroxides occur at pH 8 due to Van der Waals induced coagulation since the point of zero discharge for this compound is at pH 7 to 8. The residual of iron can be removed by physical-chemical method such as sedimentation, chlorination, electro-Fenton, filtration, adsorption, biological assimilation, chemical transpiration and volatilization as post treatment (Justin et al., 2008; Amr et al., 2015).

The reaction time also plays an importance role in this treatment. Provided enough time for reaction to react will allows complete or maximize oxidation process. Amr, (2013) again recorded that the minimum reaction time required to achieve maximum oxidation process using Ozone/Fenton is 90 minutes. The strength of pollutant in the sample may also influence the reaction time.

Ozone With Hydrogen Peroxide (O_3/H_2O_2)

Another potential combination of ozone/catalyst in leachate treatment is ozonation with hydrogen peroxide. Hydrogen peroxide has standard redox potential 1.77 V (Beltrán, 2003). The improvement of biodegradability and removal of organic compound by using O_3/H_2O_2 has been agreed by many scholars (Munter, 2001; Tizaoui et al., 2007; Matilainen & Sillanpää, 2010). Moreover, the excellent performance of Fenton ($Fe^{2+} + H_2O_2$) has also increased the confidence of researcher that hydrogen peroxide can also performance well as oxidant in AOPs. Hydrogen peroxide has been selected as catalyst by many researchers because of its characteristic i.e. non-toxic, inexpensive, readily available chemical, did not release hazardous gaseous during reaction and nor chemical residues like others catalyst (Kehinder & Aziz, 2014; Munter, 2001). Moreover, its capability as catalyst in ozonation has been tested in various types of water and wastewater such as hydrocortisone pharmaceutical wastewater as pre-treatment (Li et al., 2015), pharmaceutical wastewater (Hye et al., 2014), river (Miguel et al., 2007) and natural ground water and surface water treatment (Acero & Von Gunten, 2001). Therefore, an alternative by combining hydrogen peroxide as catalyst in ozonation was a smart decision.

Application of ozone with hydrogen peroxide in leachate treatment has been studied by Tizaoui et al. (2007) and Amin and Moazzam, (2014). Both studies have recorded an improvement of percentage removal of COD (48% to 94%) as well as color compared to ozonation alone. The biodegradability of leachate was also improved to 0.7 and allowed effluent leachate to undergo biological proses as a post-treatment. The mechanism involved in leachate treatment using ozonation with hydrogen peroxide technique is indirect reaction. Hydrogen peroxide itself does not functional as a removal agent of pollutant, but H_2O_2 help to promote indirect pathway by accelerate the decomposition of ozone to produce reductive radical ($HO_2^{\bullet}, O_3^{\bullet -}$) as well as hydroxyl radical (Hey et al., 2014). In short, H_2O_2 increased the reaction rate of the AOPs. This concept is similar with other indirect method in ozonation alone or ozonation with catalyst AOPs. However, after reached optimum dosage, the percentage removal start to decrease. The reaction is explained in equation 9, 10 and 11.

The workability of ozone/hydrogen peroxide is influences by the ozone dosage, hydrogen peroxide concentration, pH sample as well as reaction time. Increase the concentration of O_3/H_2O_2 will increase the efficiency of removal pollutants. However, needs to be careful on adding too much H_2O_2 concentration. Some of researchers have reported that, the excessive amount of H_2O_2 will reduce the performance of AOPs. Hydrogen peroxide can changes its roles from initiator of hydroxyl radical production to inhibitor of decomposition of ozone as well as OH● scavenger. The reaction is explained in equation 15 to 17 (Li et al., 2015). Tizaoui et al. (2007) also reported that H_2O_2 performed more efficient at concentration 2 g/l compared to 6 g/L of H_2O_2. The data has been plotted in figure 7.

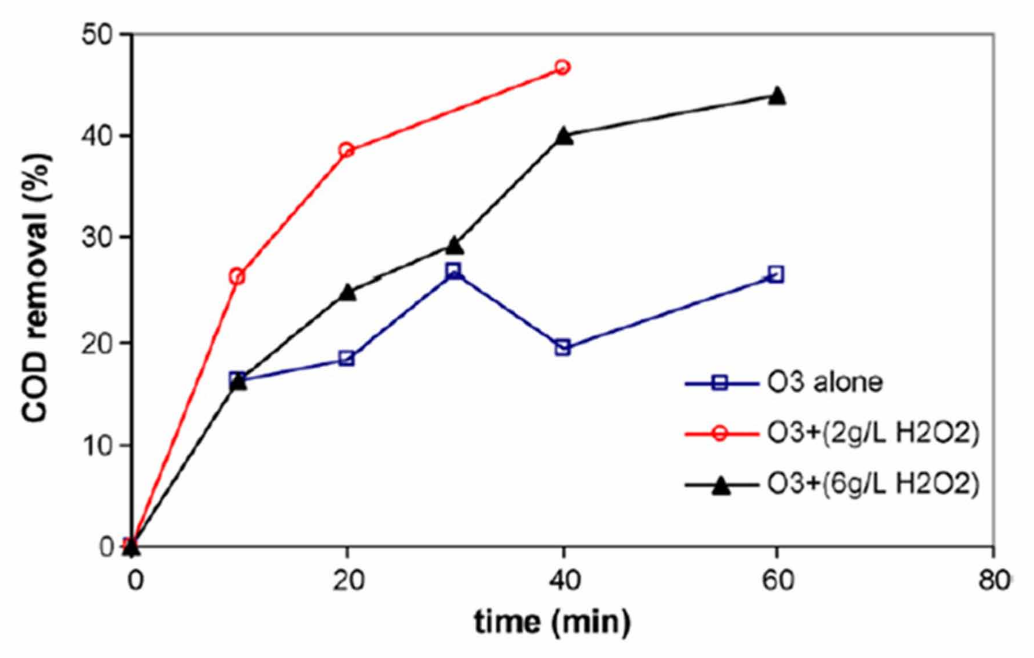
$$H_2O_2 + OH^{\bullet} \rightarrow HO_2 + H_2O \qquad (15)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \qquad (16)$$

$$HO_2^- + OH^{\bullet} \rightarrow H_2O + O_2 \qquad (17)$$

Tizaoui et al. (2007) obtained optimum H_2O_2 concentration at 2 g/L while Amin and Moazzam, (2014) record 2.5 g/L. The difference value obtained by both studies may cause of the different of experimental condition i.e. pollutant strength of the sample and ozone dosage used. Furthermore, high pollutant concentration required high dosage of ozone and catalyst to produce more radical and encourage the oxidation process. Li et al. (2014) records the optimum concentration of H_2O_2 used with ozonation is

Figure 7. Comparison performance of ozonation alone, O_3/H_2O_2 (2g/L) and O_3/H_2O_2 (6g/L) with COD removal (Tizaoui et al., 2007)

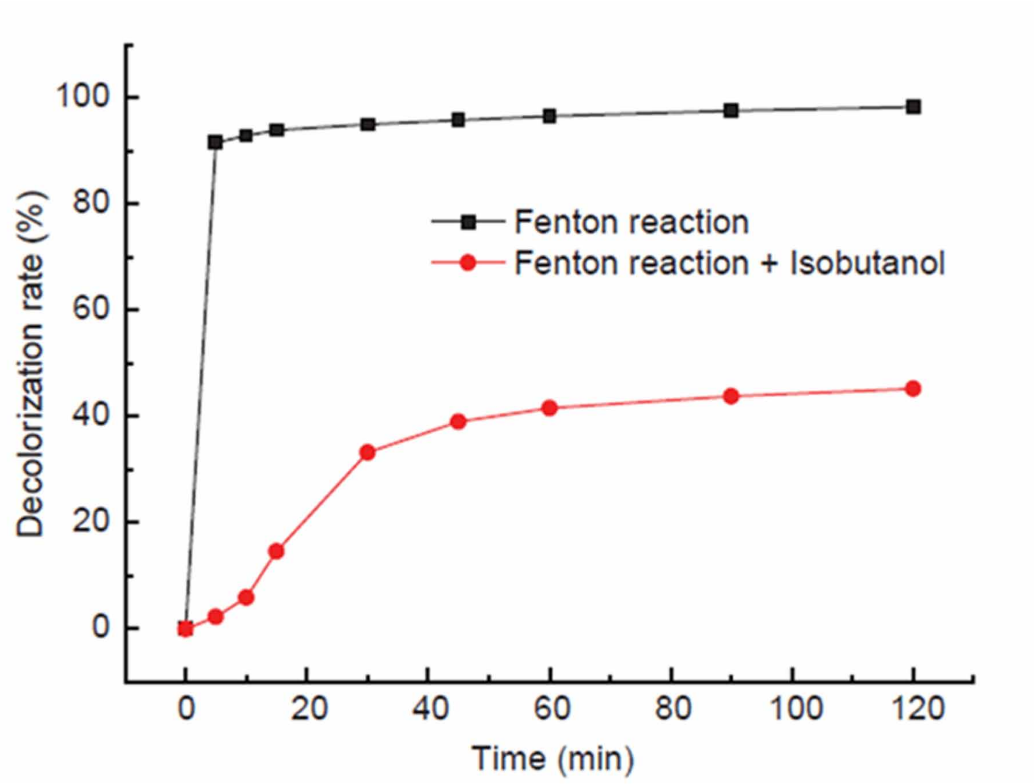


0.72 g/L at COD concentration 5280 mg/L. Thus, calibration of ozone: H_2O_2 molarity ratio in water and wastewater treatment is needs to be studied and understand the details before those treatments can be applied on site.

Another critical factor influences the performance of ozone with hydrogen peroxide is pH. As expected, ozonation with hydrogen peroxide is excellent performed in alkaline condition (pH 7>) which explained indirect pathway controlled the reaction (Amin and Moazzam, 2014). The efficiency of O_3/H_2O_2 in alkaline condition gives an advantageous for leachate treatment because normal pH for raw landfill leachate is characterized at pH 7.5 and above (Amr et al., 2016). Therefore, no pH adjustment is required and the operation cost is reduced. It is importance to notes that the production of hydroxyl radical can be impeding by wastewater that contains isobutyl acetate. This fact has been proven by Li et al. (2015) which have study in hydrocortisone pharmaceutical wastewater treatment using O_3/H_2O_2. In this experiment, the performance of ozone with hydrogen peroxide is efficient in acidic condition (pH 5.76) which is contrasts with Amir and Moazzam (2014). This condition described that, direct reaction pathway is conquers the reaction, not hydroxyl radical effect (indirect) due to the present of isobutyl acetate. The theory was support with the recession of percentage decolorizarion compared to sample without isobutanol as depicts in figure 8 (Li et al., 2015).

The third influence parameter is reaction time. Theoretically, additional hydrogen peroxide in ozonation has reduced the reaction time in advance oxidation process compared to ozonation only. The optimum ozonation time recorded for leachate treatment using ozonation with hydrogen peroxide is between 40

Figure 8. Comparison of Fenton oxidation reaction with and without isobutanol on decolourization



minutes to 270 minutes (Tizaoui et al. 2007; Amin & Moazzam, 2014). However, increasing the reaction time does not mean the effectiveness of treatment will also be increased. Most of scholars have reported that AOPs performed well at first 30 minutes ozonation and the performances start to slow down after achieved an optimum condition. At this stage, organic matter which is easier to oxidize has becomes less available (mineralize to carbon dioxide, water and inorganic salt) while recalcitrant compound remains in the solution. This situation has reduces the reaction rate. However, some of experimental still obtained reduction of pollutant after reaction achieved optimum or equilibrium condition. This may be due to the continuous degradation of intermediates and organic fragments from the organic compounds (Cortez et al., 2011a). As additional information, not all pollutant compounds can be effectively removed by O_3/H_2O_2. Miguel et al. (2007) has reported that performance of O_3/H_2O_2 in degrade pesticides in surface water is lower than ozonation only. Ozonation gives the average percentage removal 72% while AOPs using O_3/H_2O_2 only oxidise 40% to 51% of pesticides at molarity ratio 0.5.

Ozone With Zirconium Tetrachloride ($O_3/ZrCl_4$)

Currently, a new potential catalyst in advanced oxidation process which is zirconium tetrachloride is studied. Zirconium tetrachloride ($ZrCl_4$) has becomes scholar choice because of its attractive characteristic i.e. a good catalyst in synthesis organic matter (Firouzabadi et al., 2008; Patil et al., 2011), has higher charges compared to other coagulant materials (Hussain et al., 2014; Jarvis et al., 2012), affordable, widely used, easily handled, and has low toxicity (Fang, 2014; Firouzabadi et al., 2008). Rani et al. (2016) has used zirconium oxide as oxidative agent in photochemical proses to remove methylene blue and rhodamine-B dye from water. High percentage removal of both dye using this method has been recorded which is 98% and 99% for methylene blue and rhodamine-B dye respectively. Moreover, Zr also reported as a good coagulant in removing organic matter form water resources compared to other conventional coagulants (Hussain et al., 2014). The modification of zirconium oxide used to remove antimony (II, V) from contaminated water was also studied and presented a good result (He at al., 2017). However, the good side of Zr in advanced oxidation process was not well documented. Thus, the study about zirconium tetrachloride with ozonation in leachate treatment is currently working on. This effort can be a good knowledge-based line in AOPs and landfill leachate treatment industry.

Combination of ozonation with zirconium tetrachloride in advanced oxidation process still in earlier studies stage. The main focus of this combination is to treat recalcitrant pollutant and improved the biodegradability of landfill leachate. Therefore, the preliminary study about zirconium tetrachloride as catalyst in ozonation is experimental by Zakaria et al. (2015). In this study, $ZrCl_4$ (Molarity = 233.04 g/mol) is initially mixed with 500 ml of leachate sample in 1L biker before that mixture is places into the stainless steel reactor. Pure dry oxygen (99%) is supply to ozone generator to produce concentrated ozone gas and continuously 27 g/m^3 of ozone is feed into reactor to start the oxidation process. The performance of $O_3/ZrCl_4$ also compared with ozonation only. This experiment was run under constant pH (pH 8) and reaction time 60 minutes. Three parameters which is color, COD and NH_3-N is used as indicator to describe the performance of this technique. The comparison data is presented in Table 5.

Based on the data in Table 5, the performance of ozone with zirconium tetrachloride in term of percentage removal is excellent compared to ozonation alone. Ozonation with zirconium tetrachloride has successfully oxidise 75% color, 48% COD and 69% NH_3-N. Zirconium tetrachloride catalyst has increased the reaction rate of oxidation. According to Brown et al. (2005), zirconium tetrachloride is easily hydro-

Table 5. Summary performance of ozonation alone and $O_3/ZrCl_4$

Parameter	% Removal	
	O_3	$O_3/ZrCl_4$
Color	22	75
COD	4	48
NH_3-N	36	69

lyseintodifferenceformsofzirconiumhydroxidei.e. $\left(Zr\left(OH\right)_2^{2+}\right)$, $\left(Zr\left(OH\right)_3^{+}\right)$, $\left(Zr\left(OH\right)_4^{-}\right)$, $\left(Zr\left(OH\right)_5^{-}\right)$ and $\left(Zr\left(OH\right)_6^{2-}\right)$. This formation is normally occurs in low temperature and that condition is vital in the ozonation process. Zirconium hydroxide has provides an alkaline condition which is suitable for the production of hydroxyl radical in ozonation. The reaction is shown in equation 18 (Brown et al., 2005).

$$ZrCl_4 + 4OH^- \leftrightharpoons Zr\left(OH\right)_4 + 4Cl^{2-} \tag{18}$$

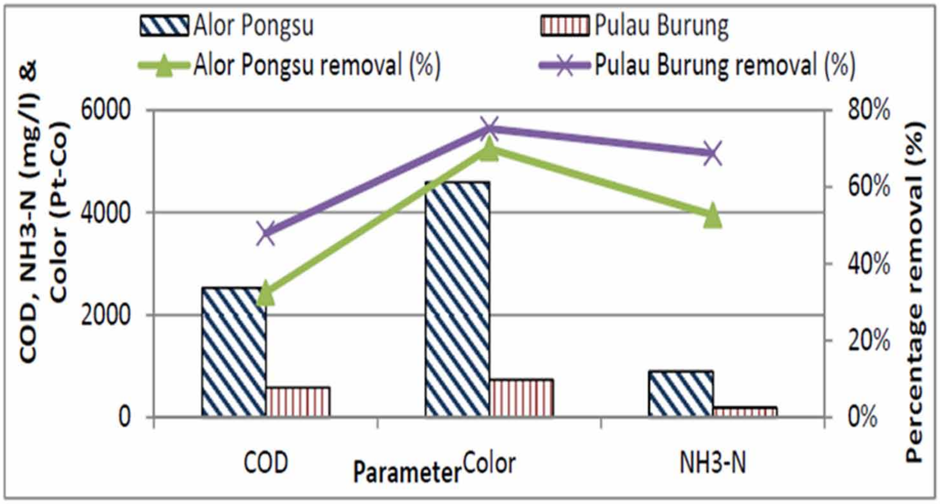
As known, in ozonation process, the pollutants or complex molecular structures are oxidized into simpler forms by a powerful radical called the hydroxyl radical (indirect path). The formations of hydroxyl radicals through decomposition of ozone (indirect process) are efficient in alkaline conditions. Thus, increased of $ZrCl_4$ dosage will increase the formation of zirconium hydroxide as well as hydroxyl radicals and the performance of AOPs also will be increase. Amr et al. (2016) has recorded percentage removal of COD and color which is 88% and 100% respectively, at (COD: ZrCl4) dosage ratio 1:2 g, pH 6 and 90 minutes reaction time. 79% of NH_3-N removal has obtained under pH condition 11. The effect of pollutant strength toward this method also has been experimental by Zakaria et al. (2015). The result (Figure 9) shows that, oxidation by ozone/$ZrCl_4$ performed well in low COD (Pulau Burung) value compared to high COD (Alor Pongsu).

Based on preliminary study and experimental data obtained, ozonation with $ZrCl_4$ has a good potential in remediate recalcitrant pollutant. Improvement of biodegradability by using this method also give a good sight in stabilized landfill leachate treatment industry (Amr et al., 2016). In additional, elaboration details about several importance factors in oxidation i.e. the mechanism involve, the influence of pH, reaction time, by-product generated, the scale and operation costs may also help AOPs works efficient in landfill leachate treatment industry. Therefore, further study about this treatment is encouraged in order to understand more about this process and its suitability to be applied on site.

COMPARISON FOR CHEMICAL APPLICATIONS

In this section, the comparison performance of ozonation alone with combination ozone/chemical catalyst (H_2O_2, Fenton, $ZrCl_4$ and Persulfate) in term of improvement of biodegradability ratio, removal efficiencies (percentage removal) and treatment cost and benefits is discussed. The data is collected from the previous researcher records and the best combination among them is determined.

Figure 9. Performance of ozone/ZrCl$_4$ in landfill leachate from Alor Pongsu Landfill Site (COD = 2180 mg/L) and Pulau Burung Landfill Site (1123 mg/L)
(Zakaria et al., 2015)



Comparison Based on Biodegradability Improvement

Biodegradation value (BOD$_5$/COD) is the crucial indicator to determine the period phase of leachate and directly described the condition of the sample. There are three period phases to classify the condition of leachate, which are acid phase (young leachate), intermediate phase (partially stabilized leachate) and methanogenic phase (stabilized leachate) (Table 2). According to Kurniawan (2006), BOD$_5$/COD > 0.5 is categorized as young leachate, while BOD$_5$/COD between 0.1 – 0.5 is categorized as partially stabilized leachate and BOD$_5$/COD less than 0.1 is stabilized leachate. As explained in Table 2, the characteristic of landfill leachate itself will determine the suitability of the treatment. Besides, it is hard to treat the sample which has lower biodegradability ratio and certain method such as biological treatment is not functional on it. Therefore, another method such chemical treatment or physic-chemical treatment is more suitable to replace the biological process. Na et al. (2016) has successfully used Fenton as oxidative agent in improving BOD$_5$/COD value as well as the quality of leachate.

Methanogenic phase is the third phase (stabilized landfill leachate) in anaerobic degradation where accelerated by methanogenic bacteria and produce high methane gas concentration. In this stage, the concentration of volatile fatty acid is low, thus explains the reduction of BOD$_5$/COD value. As the volatile fatty acids fraction decreases with landfill age, the biological treatments become ineffective in organic matter disposal from stabilised landfill leachates (Aziz et al., 2010). The BOD$_5$/COD value for landfill leachate can present as low as 0.05 in aqueous (stabilized landfill leachate) as shown in Table 2. Therefore, intensive physico-chemical or chemical treatment technology i.e. ozonation, oxidation, adsorption and coagulation/flocculation process is needed in order to remediate and improve the biodegradability of the leachate sample.

Advance oxidation process has been proven by many scholars as effective in increased the biodegradability of leachate. The summary of experimental data for AOPs performance toward biodegradability is presented in Table 6.

Comparison between advance oxidation proses shown that the quality of leachate is improved by increased the value of biodegradability ratio. Small improvement of BOD_5/COD for ozonation alone (0.07 to 0.09) proved that O_3 alone was not powerful enough to remediate leachate pollutant by itself. However, after applying catalyst in ozonation process, the performance of AOPs has been improved and changes the phase of leachate from stabilized landfill leachate to intermediate or partially stabilized. This can be seen in the performance of ozone/H_2O_2, O_3/Fenton, $O_3/ZrCl_4$ and O_3/Persulfate. Moreover, this transaction has allowed leachate effluent from oxidation (by AOPs) undergoes the biological process as a post treatment. Biological treatment is more preferred in wastewater treatment industry because it is environment friendly and low operation cost.

Some of researcher found that BOD_5 value in effluent is increased after oxidation process. It is a normal situation in AOPs because the refractory of humic structure and aromatic substance into smaller makes more biodegradable organic matter appears after ozonation process. Oxidation process occurs in certain treatment only capable to oxidise complex organic substance into small particle. Thus, residual of organic matter from this process has increased the BOD_5 value (Fang et al., 2005; Sallanko and Okkonen, 2009).

Based on Table 6, the most effective treatment to oxidize recalcitrant pollutant is ozonation with zirconium tetrachloride. The BOD_5/COD has increased from 0.07 to 0.34 by using $ZrCl_4$ as catalyst.

Comparison Based on Removal Efficiencies and Treatment Cost and Benefits

In wastewater treatment industry, there are three crucial factors in selecting a good treatment method to be applied and develop on site which is the efficiency of treatment, operation costs and the safest of treatment (to human and environment). Suggested, the treatment must present high effectiveness in remediate sample and offer economic cost operation. In this section, the comparison of removal efficiencies and the rough cost operation of advanced oxidation proses are summarise and discussed.

According to Table 7, ozonation alone performed lower compared to others (ozonation with catalyst). This fact is also supported by Legube and Leitner (1999) which summarized that ozonation with catalyst is excellent oxidize organic substance (total organic compound) compared to ozonation alone. Strong

Table 6. Summary of biodegradability value before and after undergoes ozonation alone and ozonation with catalyst

AOPs	Biodegradability	
	Raw	After Treatment
O_3	0.07	0.09
O_3/H_2O_2	0.10	0.70
O_3/Fenton	0.09	0.27
$O_3/ZrCl_4$	0.07	0.34
O_3/Persulfate	0.034-0.05	0.29

(Amr et al., 2016; Tizaoui et al., 2007; Aziz and Amr, 2015; Amr et al., 2015)

Table 7. Summary of removal COD and color by advanced oxidation process in leachate treatment

AOPs	Experiment Condition	Percentage Removal		Reference
		COD	Color	
O_3	O_3: 80 g/m^3	27	87	Tizaoui et al., 2007
O_3/H_2O_2	O_3: 80 g/m^3, H_2O_2: 2 g/L	48	94	Tizaoui et al., 2007
O_3/Fenton	O_3: 80g/m^3, H_2O_2: 1700 mg/L, Fe^{2+}: 2800 mg/L	87	100	Aziz et al., 2015
$O_3/ZrCl_4$	O_3: 27 g/m^3, $ZrCl_4$ dosage ratio: 1:2 g (COD:$ZrCl_4$)	88	100	Amr et al., 2016
O_3/Persulfate	O_3: 80 g/m^3, persulfate: 25 g, pH: 10	72	93	Amr, 2013

pollutant concentration and complex organic composition in leachate required high oxidation activities. As discuss earlier, by adding catalyst in ozonation, the decomposition of ozone is improved and increased the production of hydroxyl radical. Some of catalyst such as Fenton has also helps generated hydroxyl radical as mention in equation 10. Continuously repeating production of radical and oxidise the organic matter makes reaction rate of ozone/catalyst method is higher than ozonation only.

Oxidation by using ozone/persulfate also demonstrated the high removal of COD and color. Theoretically, persulfate is behaviour as a strong oxidant agent with potential energy (E) 2.01 V, similar with Fenton. The application of sulfate as oxidative agent has been study on textile wastewater treatment (Kehinde & Aziz, 2015) and combination UV/persulfate was also tested in petrochemical wastewater (Babaei & Ghanbari, 2016). Moreover, the interaction persulfate with heat or pH adjustment can produce sulphate radical (E=2.6V). Therefore, both oxidative species is able to remediate the pollutant sample by oxidise organic matter. The formation of sulphate radical is explained in equation 19 (Deng, 2015).

$$S_2O_8^{2-} + thermal\,activation \rightarrow 2SO_4^{\bullet -} \tag{19}$$

Affinity of persulfate to generate sulphate radical ($SO_4^{\bullet -}$) has make Amr, (2013) used persulfate in sodium persulfate ($Na_2S_2O_8$) reagent with ozonation. In this study, combination of ozone/persulfate has been tested on landfill leachate sample under optimal condition of pH 10, reaction time 210 min and dosage persulfate 25g. The researcher also proudly report that this study has recorded high removal of COD and color such as 72% and 93% respectively (Table 7). Soubh and Mokhtarani (2016) also has agreed and used ozone/persulfate as post treatment in leachate study. The optimal percentage removal of COD and color obtained is 87% and 85% respectively at experiment condition; 0.79 g/h ozone dosage, 4500 mg/L $Na_2S_2O_8$, pH 9 and reaction time 210 minutes. The BOD_5/COD also has improved from 0.13 to 0.61 as well as the toxicity which is reduced by more than 80% under this experiment condition (Soubh & Mokhtarani, 2016).

The performance of ozone/[ersulfate in oxidise organic compound not only depend on sulfate radical, but the oxidation process is also happened by hydroxyl radical. Therefore, the present of both radical (hydroxyl radical and sulfate radical) has increased the efficiency of AOPs in remediate recalcitrant wastewater. The production of sulfate and hydroxyl radical is presents in equation 20 to 23 (Amr et al., 2015; Waldemer et al., 2007):

$$SO_4^{\bullet -} + H_2O \rightarrow OH^{\bullet} + SO_4^{2-} + H^{+} \tag{20}$$

$$SO_4^{\bullet -} + OH^{-} \rightarrow OH^{\bullet} + SO_4^{2-} \tag{21}$$

$$S_2O_8^{2-} + 2H^{+} + 2e^{-} \rightarrow 2HSO_4^{\bullet -} \tag{22}$$

$$SO_8^{2-} + HO^{\bullet} \rightarrow 2HSO_4^{\bullet -} \tag{23}$$

Among this advanced oxidation process, combination ozone with $ZrCl_4$ showed better performance in term of removal as well as ozone dosage used compared to others. Oxidation using ozone/$ZrCl_4$ process only required 27 g/m^3 to obtained optimum condition compared with other method (required 80 g/m^3 of ozone). This process also has efficiently remove 88% of COD and 100% of color from the sample. However, there are still more research and experimental needs to be done for this combination. It is important to have a good understanding of mechanism involved as well as realistic evaluation on the relative cost of operation. Thus, further experimental and study on these potential AOPs in landfill leachate treatment is encouraged.

After efficiency, the cost of operation is also an important factor to consider. The general estimation of operation cost includes: (Tizaoui et al., 2007; Mahamuni & Adewuyi, 2010):

1. Chemical cost: Including reagent prices and pH adjustment
2. Electrical/ energy cost
3. Analytical costs: Cost of sampling, labor to the sampling activities as well as cost of chemical for analysis.
4. Labor cost.
5. Maintenance or part replacement cost.

The summary of estimation costs for each AOPs treatment is summary in Table 8.

The lower price is better. Comparison between ozonation/catalyst processes with ozonation alone shows that ozonation with hydrogen peroxide gives lower operation costs. However, the performance of O_3/H_2O_2 is low especially on COD removal (Table 7). Therefore, the best method between those com-

Table 8. Summary of operation cost for several ozonation with catalyst in landfill leachate treatment

AOPs	Operating Cost	Reference
O_3	43.19 - 120.29 USD /m^3/g of leachate	Cortez et al., 2011b
$0_3/H_2O_2$	2.3 USD/ kg COD	Tizaoui et al., 2007
O_3/Fenton	15.92 USD/ m^3 stabilized leachate	Amr et al., 2013
O_3/Persulfate	105.37 USD/ m^3 stabilized leachate	Amr et al., 2013

binations is ozonation with Fenton. Although the operation prices for O_3/Fenton is slightly expensive then O_3/H_2O_2, but the performance presented by this method is acceptable and worth it to be selected as potential landfill leachate treatment applied on site. In previous section, combination of ozone with zirconium tetrachloride also shows an excellent performance. However, the operation cost was not reported in still in investigation.

The operation of ozonation with catalyst may require some budget but environmental and human health issue is more important than money. Concerning the cost of various ozonation with catalysts, others advance oxidation process i.e. electrochemical oxidation, and ultrasound oxidation are more expensive due to the high demand of electrical energy for devices UV lamps, ultrasounds (Li et al., 2010).

CONCLUSION

Leachate contains high pollutant concentration and complex organic substance. A strong treatment is needed to remediate leachate and preventing the environmental from contamination. Advance oxidation process is proven as effective method to treat recalcitrant pollutant. In order to make leachate effluent meet the standard limitation discharge, the performance of AOPs has been innovatively improved by combining catalyst in ozonation process and his technique has enhanced the efficiency of AOPs. In addition, homogeneous catalyst is commonly used because of its characteristic which is homogeneity and accelerates the reaction rate effectively. In short, oxidation using ozone/catalyst gives more advantageous compared to other AOPs such as (in the scope of leachate treatment):

1. Improving biodegradability of leachate
2. Increased the reaction rate.
3. Remove color and COD effectively.
4. Oxidise and mineralization the recalcitrant compound.
5. Fewer by-products produce.
6. Applicable to be applied on site.

The performance of this combination has increased the performance of pollutant removal especially COD and color. Ozonation with zirconium tetrachloride has achieved 88% and 100% of COD and color removal at ozone dosage 27 g/m^3 only compared to others combination. The higher percentage removal also obtained using others combination of ozone with hydrogen peroxide and Fenton (Table 7). The biggest achievement using this method is improving the biodegradability of leachate as well as the phase of leachate itself. It is also indicate that the biological treatment is able to be applied after the sample has undergoes AOPs. However, the major problem of this treatment method is the operation costs compared to conventional treatment. Therefore, an alternative to combine ozonation with natural catalyst can be considered in future research.

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Chapter 13

Advanced Oxidation Processes (AOPs) in Landfill Leachate Treatment

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ABSTRACT

Sanitary landfilling is the most acceptable method to eliminate solid urban wastes. However, it is known that sanitary landfill generates large amount of heavily polluted leachate. High concentrations of recalcitrant organics make its degradation more complicated and high concentration of organic material can be toxic and reduce bioremediation process. Landfill leachate treatment by advanced oxidation processes (AOPs) have been intensively studied with high successful rate for removing refractory pollutants (biological degradation) from leachate. Fenton reaction which is one basic AOPs is based on the addition of hydrogen peroxide to the leachate in the presence of ferrous salt as a catalyst. Because of that, many improvement and development of new Fenton-based methods have been reported in the literature. This review discussed the application of Fenton and related processes in terms of wide application in landfill leachate treatment. The effects of various operating parameters and their optimum ranges for organics contaminant removed were also discussed.

INTRODUCTION

Municipal solid waste (MSW) can be defined as the wastes arising from domestic, commercial, industrial, and institutional activities in urban areas (Bartone, 1990). Malaysian solid waste consists of an extremely high concentration of organic waste which leads to a high moisture content and a bulk density above 200 kg/m^3. The major components of Malaysian wastes are food, paper, and plastic which include about 80% of overall weight based on waste characterisation (Kamaruddin, Yusoff, Ibrahim, & Zawawi, 2017). Besides, a study done by **** also implied that organic waste components represent the most waste characteristics from a case study done in Kelantan, Malaysia as shown in Figure 1. These characteristics reveal the nature and lifestyle of the Malaysian population. Economic development and population grows

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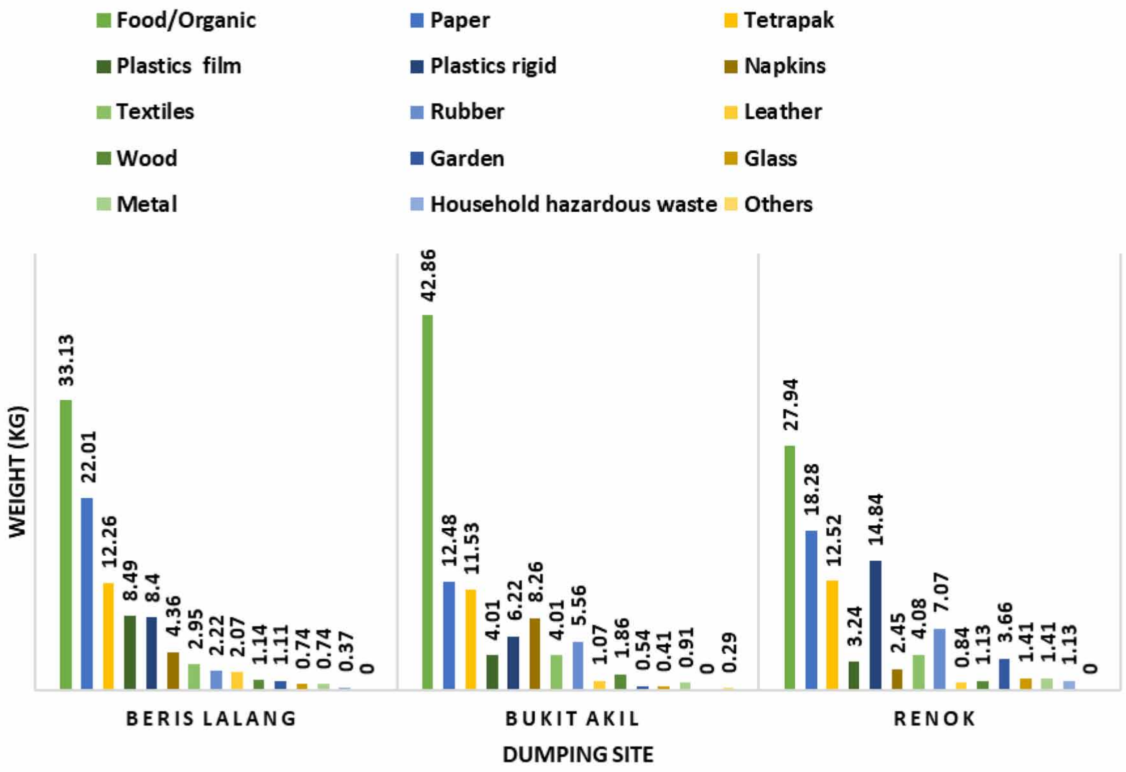
at a rapid rate, poor transportation and lack of expertise contributes to the management of municipal solid waste being one of Malaysia's most vital environmental problems (Manaf, Samah, & Zukki, 2009).

The waste components were determined after sorting a known weight of sample in to different waste streams (15 components) and divided from the total weight accumulated. Based on Figure 1, the major fractions of MSW component analysed consists of organics, papers and tetra Pak component. Meanwhile, plastics (film and rigid), napkins, textiles, rubber, leather, wood and garden wastes made up in the ranges of 0.4 to 14.84% of total MSW components. The results for organic components were in the range of 28 to 43% of total wastes and prevailed for all three-studied area. The waste is mostly dominated by kitchen and food waste (Periathamby, Hamid, & Khidzir, 2009). Such high organic waste in the study area could be due to the high consumption of edible products such as dairy, processed food, and unprocessed food. The fractions also indicated that residents of Kota Bharu produced the lowest organic fraction (33.13%) followed by Gua Musang (27.94%) and Kuala Krai (42.86).

As comparison, normal organic waste fraction for Malaysian according to the data from Ministry of Local Government and Housing stood at 45% of total MSW (Hamatschek, Entwicklungszentrum, Tee, & Faulstich, 2010). The results also indicated that paper waste was the second largest fraction in terms of weight which might be due to the increasing usage of paper in daily packaging including foods, hardware and dairy products. Besides, the main fractions of paper waste ascertained in the study were cardboards and other packaging papers. Tetra Pak waste was the third largest fraction in term of weight. This could be due to the increasing soft drink sold at cheaper price than conventional metal can drinks.

Figure 1. Typical waste composition of Malaysian wastes (as disposed)



Also, society in opinion that by drinking soft drink from tetra Pak containers gives a more lavish style than attractive perception towards metal can drinks which are also considered safer to them. As a result, there is a potential for tetra Pak recycling towards the waste minimization among society that can be nurtured and educated for sustainable waste minimization.

The data also revealed that more than 10% of the total MSW characterized can be diverted rather than be sent to the dump sites for final disposal. In terms of plastic waste, two different plastics types were distinguished which were plastic film and plastic rigid. Plastic film waste was found in the range of 3 to 8.5% of the total waste analysed. In this study, the plastic film was categorized into films, polystyrene and foam. Most of the plastic were derived from food and drinks packaging. Meanwhile, plastic rigid which further divided into PET bottles for bottling drinks and water, LDPEs, HDPEs, PVCs, and PSs which made up in the range of 6.2 to 14.8% of total waste. The accumulated weight percentage recorded was significantly lower than Penang (24%) (Ahmad Zamri, Yusoff, & Aziz), Selangor (18%) (Samah et al., 2013) and Malaysia (17%) (Agamuthu & Fauziah, 2011). A few other fractions such as napkins, rubber, textiles leather wood, garden waste, glass and metal ranged between 0.7 to 4% which were comparable with other studies (Ahmad Zamri et al.). In comparison, the figures demonstrated that combustible has the highest shared from the whole waste component in the range of 94 to 96% than incombustible fraction. The finding shows that there is a possibility of turning the combustible fraction into refused derived fuels (RDF) for thermal processing in general consideration.

Landfilling

Landfilling is currently, the only technology implemented for solid waste disposal in Malaysia, and the majority of the landfill sites are open dumping areas, which causes severe environmental and social risks (Kamaruddin, Yusoff, Aziz, & Alrozi, 2016; Manaf et al., 2009; Yunus & Kadir, 2003) Due to the growing population and development, volumes of waste generated continues to rise with only less than 5% of the waste being recycled. Rapid developments and industrialization in Malaysia necessitate more efficient waste management plan (Fauziah, Simon, & Agamuthu, 2004).

Landfill should be carefully designed to bury the waste with isolation from the surrounding such as groundwater and surface water. Landfills are considered the most attractive disposal route for municipal solid waste when it comes to economic considerations (Kamaruddin, Yusoff, Rui, et al., 2017). Other methods which can be an alternative to landfilling (incineration and composting) are actually considered as volume reduction processes because they produce waste fractions (ashes and slag) which ultimately must be landfilled (Foo & Hameed, 2009; Renou, Givaudan, Poulain, Dirassouyan, & Moulin, 2008).

Even though the landfill technology has evolved from an open, uncontrolled dumpsite to a highly engineered facility designed to eliminate or minimize the potential environmental impact of the waste on the surrounding environment, generation of contaminated leachate remains an inevitable consequence of the practice of waste disposal in landfills (Deng & Englehardt, 2006; Kurniawan & Lo, 2009). Landfill leachate is a runny fluid which moves through or leaches from a landfill. This liquid is either already present in the landfill or it may be produced after rain, picking up dissolved materials from the decomposing wastes and mix with them (Wisegeek, 2010).

Depending upon the characteristics of the substances that exists in the landfill, the landfill leachate can have an enormously unfortunate environmental impact (Hung et al., 2015). Landfill leachate is a complex organic liquid that is high in pollution capacity, is a recurrent source of groundwater contamination which may cause catastrophic consequences in regards to human health (Franchetti, 2009; Kocasoy & Murat, 2009).

ADVANCED OXIDATION PROCESSES IN LEACHATE TREATMENT

Leachate from MSW landfill is a high strength liquid and is very difficult to deal with. High concentrations of recalcitrant organics make its degradation more complicated; microorganisms have the ability to convert contaminants is different and high concentration of organic material is toxic thus hindering the bioremediation process (Zamri, Kamaruddin, Yusoff, Aziz, & Foo, 2015). Therefore, selecting the appropriate treatment strategy is often complicated. As the leachate ages and stabilizes, the biodegradable fraction of organic pollutant in leachate decreases and, consequently, conventional biological treatments are followed by classical physicochemical methods are no longer sufficient to attain the levels of decontamination required to reduce the negative effects of landfill leachate on environment. Therefore, in order to meet the standards, new treatment alternatives should be established (H.-s. Li, Zhou, Sun, & Feng, 2009).

It has been reported that AOPs are powerful technologies capable of degrading a wide variety of refractory compounds from old and stabilized leachates and are outstanding alternatives for the treatment of high-strength and non-biodegradable landfill leachate (Hermosilla, Cortijo, & Huang, 2009; Metcalf, Eddy, Burton, Stensel, & Tchobanoglous, 2003). In addition, they can also achieve a considerably high efficiency on the removal of organic compounds from leachates compared to other physiochemical technologies which brings about phase transfer of the contaminants in question and do not involve chemical destruction (Deng & Englehardt, 2006; Hermosilla et al., 2009)

Using AOPs for wastewater remediation is the most recent, modern direction, providing technically a feasible, economically acceptable, environmental friendly and sufficient method. Hence, in treating recalcitrant organic compounds which resist biological or classic physiochemical methods, AOPs presents itself as an alternative; and probably will represent one of the best options for wastewater treatment in the near future (Deng & Englehardt, 2006; Kurniawan & Lo, 2009)

AOP is the popular alternative when treating bio-refractory and recalcitrant compounds in wastewaters, involving the entire or partial destruction of pollutants to carbon dioxide and water or to other by-products which may be less dangerous to the environment or could be easier to degrade using other techniques (Hermosilla et al., 2009). Nowadays, AOP processes present the best solution, and has been proven to be the most efficient and flexible means of achieving high purification (Arslan-Alaton, Ayten, & Olmez-Hanci, 2010; Üstün, Solmaz, Morsünbül, & Azak, 2010) This includes some chemical treatment processes designed to eliminate or reduce organic and inorganic materials in wastewater by oxidation (Gogate & Pandit, 2004). Generally, chemical treatment methods involving the generation of hydroxyl radicals, has been applied successfully for the removal or degradation of recalcitrant and refractory compounds based on the high oxidative power of the OH radical (Canizares, Lobato, Paz, Rodrigo, & Sáez, 2007; Gogate & Pandit, 2004).

In recent years, some AOPs techniques were applied for the removal of refractory organics from wastewater samples but electro-Fenton were not well established in the literature. Furthermore, the application of the technique was not documented for degradation of stabilized landfill leachate. The optimized process conditions are unclear, which is another problem when the AOPs treatments are implemented. Additionally, the synergistic and antagonistic effect as well as the interaction among variables is unknown and it is a large gap in landfill leachate treatment knowledge. Indistinct catalytic mechanism of Fenton and electrochemically assisted Fenton (electro-Fenton) reagent is another lack of data. A further understanding of this may help improve the knowledge of landfill leachate treatment.

Fenton Treatment

Fenton

Among AOPs, the Fenton treatment (Fe^{2+}/H_2O_2) has become the most acceptable method for the treatment of landfill leachate with hazardous organics. This process employs catalytic based conjugate on the generation of hydroxyl radicals (OH●) from hydrogen peroxide with iron ions acting as homogeneous catalyst at acidic pH and ambient conditions (Pera-Titus, García-Molina, Baños, Giménez, & Esplugas, 2004). The catalytic decomposition of hydrogen peroxide by ferrous ion (i.e., Fenton's reagent) was first described by Fenton (1894) and is one of the most commonly used AOPs for wastewater treatment.

Fenton's reagent is made of hydrogen peroxide and an iron catalyst for oxidation and remediation of a wide variety of organic substrates (Zhang, Choi, & Huang, 2005). Some metals have a strong catalytic power to generate highly reactive hydroxyl radicals (OH·). Nowadays, the Fenton's reaction is used to treat large varieties of water pollution. One of the most common AOPs in wastewater treatments nowadays is the Fenton's reagent. This process involves the electron transfer among hydrogen peroxide and ferrous ion, which acts as a homogenous catalyst, resulting in hydroxyl radicals (OH●) capable of degrading and destroying organic pollutants (Hermosilla et al., 2009). Fenton process may be implemented in treating wastewater, soils that have been contaminated and sludge with the actions of organic pollutant removal, reducing toxic, improving biodegradability as well as the removal of BOD, COD and colour. Fenton chemistry includes reactions of hydrogen peroxide with soluble iron producing species such as the hydroxyl radical and possibly others, which are highly reactive, to oxidize organic or inorganic compounds when they are present (Brillas, Sirés, & Oturan, 2009; Pignatello, Oliveros, & MacKay, 2006).

There is no evidence of hydroxyl radical formation in the absence of iron, when, H_2O_2 is added to a landfill leachate (i.e., no reduction in the level of COD). The increased concentration of iron accelerates the removal of COD to a point where further addition of iron becomes inefficient. This characteristic of Fenton's Reagent is a feature (an optimal dose range for iron catalyst), although the range varies between wastewaters (Neyens & Baeyens, 2003). The decomposition of hydrogen peroxide can be catalysed by iron minerals and initiates Fenton-like oxidation of contaminants in leachate when supplying hydrogen peroxide. The main advantages of this method when compared to other oxidation processes in treating hazardous wastes are: 1) both iron and hydrogen peroxide are inexpensive and non-toxic; 2) because the reaction is homogeneous, there are no mass transfer limitations; 3) light is not required as a catalyst, therefore, the design is simpler than ultraviolet light system; 4) and, hydrogen peroxide can be generated in-situ, electrochemically which may further increase the economic feasibility and effectiveness of this process for treated contaminated sites (Sudarjanto, Keller-Lehmann, & Keller, 2006; Ting, Huang, & Lu, 2007).

The peroxide is broken down into a hydroxide ion and a hydroxyl free radical. The hydroxyl free, the primary oxidising species, can be used for oxidation and breaking down of organic molecules. The process is complicated, with numerous parallel reactions, but can be represented by the Equation 1:

$$Fe^{2+} + H2O2 \rightarrow Fe^{3+} + OH^{-} + OH\bullet \tag{1}$$

The mechanism of reaction is very complex and changes with conditions of the reaction. Hydroxyl radicals (OH●) resulting from the chain reaction between ferrous ion and hydrogen peroxide, and the oxidation of organic compounds (RH) by Fenton's reagent can proceed by the following chain reactions (Kang & Hwang, 2000; Lee & Shoda, 2008; Neyens & Baeyens, 2003; Pignatello et al., 2006; Zhang et al., 2005) Iron (III) is then reduced back to iron (II), a peroxide radical and a proton by the same hydrogen peroxide. In addition, hydroxyl radicals can rapidly destroy ferrous.

In the presence of organic substrate (RH), the primary product of the oxidation would be the organic radical, R●, which possesses mainly reducing properties of what and may be consumed through the reactions with H_2O_2, Fe^{3+}, and O_2. Organic matter would degrade due to the production of hydroxyl radicals through four pathways: radical addition, hydrogen abstraction, electron transfer, and radical combination. Generally, the reaction follows a mechanism similar to the one listed below (Zhang et al., 2005).

Even though it is environmental friendly and has a high oxidative efficiency, the application of Fenton's reagent for wastewater treatment is limited by the ferric iron sludge in its final disposal thus increasing the cost of waste disposal. In addition, Fenton's reagent is not supposed to oxidise some chemicals such acetic acid, oxalic acid and chloroform with ease. (Hermosilla et al., 2009; Sinha et al., 2007). Dealing with these challenges, modifications have been proposed to the Fenton, such as the combined application of electricity (electro-Fenton) and/or UV light (photo-Fenton). In detail, the most promising alternative is the combination of the Fenton's reagent with it because it allows the reduction of ferric to ferrous iron.

A major advantage of the Fenton's Reaction, with the absence of carbon in the peroxide, is that it does not produce further organic compounds or inorganic solids such as permanganate and dichromate. If the goal is to remove the organic compounds, it makes the Fenton's reaction more appealing than a biological process. However, there are organic species that show resistance to oxidation by the Fenton's Reaction. Small chlorinated alkanes, n- paraffin, and short-chain carboxylic acids, compounds that are typical oxidation products of larger molecules, seem to resist further fragmentation by the Fenton's Reaction.

Comparing with other AOPs, Fenton's reaction has its advantages. H_2O_2 is environmental friendly, since it slowly decomposes into oxygen and water. In addition, the lack of toxicity and the ease of removal from water makes Fe^{2+} the most commonly used transition metal for Fenton's reaction applications (Badawy & Ali, 2006). Moreover, harmful by-products produced associated with Fenton's reaction applications is noticeably lower compared to other AOPs (De Morais & Zamora, 2005). A summary of advantages and disadvantages of Fenton treatment is summarized in Table 1.

Electro-Fenton Treatment

Environmental application of the electro-Fenton process is a new topic and previous studies are limited. Among AOPs, oxidation with electrochemical and Fenton's reagent is considered as promising and attractive treatment technology for degradation and decolourisation of wastewaters. In recent years there has been an increased focus on the use of electrochemical methods which can produce OH● as the main oxidizing agent by different ways (Brillas, Calpe, & Casado, 2000; Kraft, Stadelmann, & Blaschke, 2003; Shao, He, Xue, & Li, 2006).

The Fenton process has also attracted great interest due to its high capacity to generate hydroxyl radicals through decomposition of H_2O_2 by Fe^{2+} in acidic conditions (Kang & Hwang, 2000; Lee & Shoda, 2008; Tekin et al., 2006; Zhang, Choi, Canazo, & Huang, 2009). Moreover, its application can

Table 1. Advantages and disadvantages of Fenton treatment

Advantages	Reference	Disadvantages	Reference
No energy input is necessary to activate hydrogen peroxide	Lücking, Köser, Jank, and Ritter (1998)	Additional water pollution caused by the homogeneous catalyst that added as an iron salt, cannot be retained in the process	(Lücking et al., 1998)
Fenton's reagent is relatively inexpensive and the process is easy to operate and maintain	Lu, Zhang, Huang, and Wang (2005)	Ferrous ions are consumed more rapidly than they are regenerated	(Zhang, Zhang, & Zhou, 2006)
Short reaction time among all advanced oxidation processes	Gotvajn and Zagorc-Konèan (2005)	Treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower	Ramirez et al. (2007)
There is no mass transfer limitation due to its homogeneous catalytic nature	W. Li, Zhou, and Hua (2010)	It is limited by a narrow pH range (pH 2–3) 16	J. Deng et al. (2008)
There is no form of energy involved as catalyst	(W. Li et al., 2010)	Iron ions may be deactivated due to complexion with some iron complexing reagents such as phosphate anions and intermediate oxidation products	J. Deng et al. (2008)

(Nidheesh & Gandhimathi, 2012)

be used in a vast range of organic pollutants, due to its simplicity and ease of implementation; ability to operate even under mild conditions of temperature and pressure. By using electricity (electro-Fenton), the efficiency of this process can be improved drastically, for the generation of additional hydroxyl radicals (Brillas et al., 2009).

Unlike the traditional process of electrochemical oxidation, which anodic oxidation accounts for organic pollutants degradation, the electro-Fenton process is characterized by the union of electrochemical oxidation and Fenton oxidation in one electrochemical cell. Besides anodic oxidation, the oxidation of OH● produced by Fenton reaction is also involved. The catalytic effect of Fe^{2+} in the Fenton process can be enhanced by electricity. Hence, it is called electro-Fenton process that can produce a large regeneration rate of $Fe^{2+.}$ Electro-Fenton process includes the combined advantages of electrochemical and Fenton treatment methods, and each of them is a powerful treatment method. Under electrically assisted Fenton reaction, more OH● radicals are produced and the oxidation of the organics to CO_2 can be enhanced in the same period (H. Liu, Li, Leng, & Wang, 2007a). Ferrous ions catalyse hydrogen peroxide which produces hydroxyl ions during the occurrence of the Fenton reaction. The oxidizing power of H_2O_2 can be strongly enhanced using Electro-Fenton method, in an acidic medium, where a small quantity of Fe^{2+} is added as a catalyst generating OH● and Fe^{3+} from Fenton's reaction, to the contaminated solution (Brillas et al., 2009).

The electro-Fenton process involves the use of the Fenton reagent in an electrochemical system. This modification of using electro regeneration Fe^{2+} ions from Fe^{3+} at the cathodes and Fenton reagent utilization by directly producing H_2O_2 or Fe^{2+} or both through the electrochemical system, which reduces sludge production. The electro-Fenton process can proceed by the following chain reactions (Brillas et al., 2009; Deng & Englehardt, 2006; Guinea et al., 2008; Lee & Shoda, 2008; H. Liu et al., 2007b; Mohanty & Wei, 1993; Neyens & Baeyens, 2003). The decomposition of H_2O_2 is initiated and catalysed by ferrous iron (Fe^{2+}), resulting in the production of hydroxyl radicals in the solution. Hydroxyl radicals are also produced at the surface of a high-oxygen overvoltage anode from water oxidation:

The oxidative potential increases during the reaction of the process due to the increase of the OH● in the process. The hydroxyl radicals produced is the main oxidizing agent of organic matter which causes its mineralization, i.e., its conversion to CO_2, water and inorganic ions. Although HO_2●, a radical with much weaker oxidizing power than OH●, is also formed, organics are mainly destroyed by the action of OH● radicals produced in the medium. H_2O_2 may act as an OH● scavenger as well as an initiator. Also, the produced ferric ion from Equation 2 can be reduced to ferrous ion by electrochemical regeneration of Fe^{2+} ions on the cathode surface:

$$Fe^{3+} + e- \rightarrow Fe^{2+} \qquad (2)$$

In addition, ferrous ions can also be rapidly destroyed by hydroxyl radicals:

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH- \qquad (3)$$

The hydroxyl radicals produced would react rapidly with most of the organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules:

$$RH + OH\bullet \rightarrow H2O + R \qquad (4)$$

The resulting organic radicals then react with oxygen to initiate a series of oxidation reactions leading to mineralization of the organics to produce CO_2 and H_2O.

Electro-Fenton augments the oxidative power of Fenton's Reagent, by producing the ferrous ions in-situ, which minimizes free radical scavenging and consequently the amount of hydrogen peroxide required. It's also possible to electrochemically recycle the ferric ions, into ferrous ions which is much more efficient than with the conventional Fenton's Reagent process. This minimizes the amount of ferric hydroxide formed. As shown in the above reactions, electro-Fenton could improve the degradation efficiency. It seems that some additional organic compounds are treated or removed from leachate by the electro-Fenton process.

Photo-Fenton Treatment

The main mechanism of photo-Fenton are through the reduction of Fe^{3+} transformed to Fe^{2+} by producing more hydroxyl radicals in the present of photolysis (Deng & Englehardt, 2006) as shown in Equation 5:

$$(Fe\text{-}OH)2+ + h\nu \rightarrow Fe2+ + OH\bullet \qquad (5)$$

Meanwhile, photo-decarboxylation of ferric carboxylates (Hermosilla et al., 2009). i.e. occurred through:

$$\mathrm{Fe(III)(RHCO2)} + h\nu \rightarrow \mathrm{Fe2+} + \mathrm{OH}\bullet \tag{6}$$

$$^{\mathrm{RH}\bullet\,+\,\mathrm{O}}2 \rightarrow {}^{\mathrm{RHO}}2^{\bullet} \rightarrow \text{products} \tag{7}$$

The equations suggested that reduction content of catalytic iron is related to the amount of the final sludge volume. Besides, there will be some carboxylates or organic compounds appearing from this reaction that may be effectively treated (Deng & Englehardt, 2006). As a matter of fact, there is a very limited number of studies that have been conducted for this kind of treatment particularly for the landfill leachate treatment as compared to conventional Fenton. However, as many technological advancement and changes have been achieved lately, there have been quite a number of reports discussing the important of Photo-Fenton process in relation to leachate treatment as what has been summarized in Table 2 in the recent years.

Amor et al., (2015) performed coagulation/flocculation combined with solar photo-Fenton for mature leachate. They observed that higher DOC (75%) removal was achieved as compared than single solar photo-Fenton (54%). Further combination of these processes was able to reach a DOC removal of 50% after chemical oxidation with radiation energy of 110 Kj/L supported with H_2O_2 consumption of 116 mM. Meanwhile, (T. F. Silva, A. Fonseca, I. Saraiva, R. A. Boaventura, & V. J. Vilar, 2016) used a series of experimental conditions with total dissolved iron concentration in the range of 20–100 mg Fe^{2+}/L, initial pH ranges from 2.0–3.6, temperature between 10–50 °C. The acid used was individual H_2SO_4, HCl and a combination of H_2SO_4 + HCl. Meanwhile, the UV radiation was tested in the range of 22–68 W/m^2. They observed more than 72% reduction of DOC after 25 kJ/L of UV energy was supplied during a photo-Fenton leachate treatment. The leachate was submitted to aerated lagooning, followed with aerated activated sludge and coagulation as final step. (Chys, Declerck, Audenaert, & Van Hulle, 2015) tested photo-Fenton biologically treated leachate prior to granular activated carbon (GAC) adsorption. The results demonstrated that by using photo-Fenton treatment, the GAC filters were able to be reused multiple times (longer than 14 cycles). They revealed that Fenton treatment managed to reduce BOD

Table 2. Photo-Fenton of leachate studies

Leachate Type	Parameters	Removal Efficiencies (%)	Reference
Photo-Fenton > Fenton-like > Fenton > UV/H_2O_2 > UV	COD	49-78	(Primo, Rivero, & Ortiz, 2008)
Biologically treated leachate	DOC	34.7-71.4	(Vilar et al., 2012)
Biologically treated leachate	COD	20-30	(T. F. C. V. Silva, Fonseca, Saraiva, Vilar, & Boaventura, 2013)
Photo-Fenton alone	COD Turbidity Total Polyphenol	63 80 74	(Amor et al., 2015)
Combined coagulation with Photo-Fenton	COD Turbidity	89 75	(Amor et al., 2015)
Biologically treated leachate	Ammonium	95	(T. F. Silva, A. Fonseca, I. Saraiva, R. A. Boaventura, & V. J. Vilar, 2016)
Fenton/Photo-Fenton	COD Color	55.9/75.5 69.6/84.1	(Mahdad, Younesi, Bahramifar, & Hadavifar, 2016)

concentration, but a higher BOD/COD ratio (0.16) was attained due to higher removal of COD. However, they confirmed that ozone was responsible for the increase of the BOD/COD ratio up to 0.13. (T. F. C. V. Silva, A. Fonseca, I. Saraiva, R. A. R. Boaventura, & V. J. P. Vilar, 2016) studied scale up and cost analysis of a photo-Fenton process by using solar and/or artificial radiation. Because the target pollutants have different COD removals (1000 and 150 mg/L), they employed ranges variables and come out with specified objectives. The results have shown that the compound parabolic collectors (CPCS) in the ranges of 3836 and 6056 m^2, or 25 and 39 UV lamps to attain the target COD removal. Another plant setting which integrated natural and actual radiation requires 3862 m^2 of CPC, 19 and 30 UV lamps, respectively. (T. F. Silva et al., 2017) treated stabilized landfill leachate by using aerobic/anoxic biological treatment prior to photo-Fenton process. They observed that to achieve DOC concentration of 150 mg/L during photo-Fenton process, nitrites and nitrates presence requires:(i) 119, 49 and 50 mM of H_2O_2; (ii) 27.2, 8.8 and 11.1 mg of H_2O_2 per 1 mg of oxidized DOC; and (iii) 8.1, 7.9 and 9.3 kJUV/L of accumulated UV energy. Table 3 lists out several electro-Fenton processes applied on leachate treatment.

Effect of Operating Parameters

Effect of Reaction Time

According to Singh and Tang (2013), organic matter oxidation occurred within 10 minutes of Fenton reaction due to rapid production of OH by H_2O_2 and Fe^{2+}. Then, Fe^{3+} ion generated Fe^{2+} and OH. The authors further observed that a reaction time of 10 minutes to 2 days with a median of 60 minutes generally occurred and the different were due to second stage reactions. Wu, Zhou, Qin, Peng, et al. (2010) observed that the reduction amounts for COD, humic substance (HS) and TOC in the first 2 hours of Fenton process indicated 66.5%, 85.2% and 44.1% removal efficiency. It further increases to 76.5%, 95.8%, and 57.8% after completion of 24 reactions respectively. The fixed operation variables were initial pH of 4.0; $[H_2O_2] = 240mM$; $[F^{e2+}] = 40mM$; temperature = $30 \pm 0.2°C$, respectively. Biglarijoo, Mirbagheri, Ehteshami, and Ghaznavi (2016) used response surface methodology for leachate treatment by using Fenton as pretreatment. Based on optimization results which employed analytic hierarchy process (AHP), the best fitted preparation condition was found to be pH = 6, $[H_2O_2]/[Fe^{2+}]$= 20 mole ratio, $[Fe^{2+}]$

Table 3. Electro-Fenton treatment recent studies

Leachate type	Parameters	Optimum Condition	Reference
Mature leachate assisted with chemical coagulation	pH COD BOD	pH: 4, H_2O_2: 750 mg/L	Lin and Chang (2000)
High strength leachate	pH COD	pH: 3, H_2O_2: 0.34mol/L, Fe^2+: 0.038 mol/L, I: 2 A,d = 2.1 cm	Zhang, Zhang, et al. (2006)
Single treatment, high strength leachate	BOD COD pH	pH: 3, H_2O_2: 2000 mg/L, I: 2 A, reaction time: 20min	Atmaca (2009)
Stabilized leachate	Color COD	pH 3 and H_2O_2/Fe^{2+} molar ratio 1, while current density was 49 mA/cm^2	Mohajeri, Aziz, Isa, Zahed, and Adlan (2010)

= 170 mM, and reaction time = 105 minutes. In another study, in order to effectively remove organic matter, ammonia and toxic compound from leachate, combination of membrane separation process (MSP) and Fenton treatment were performed. This study suggested that high removal of COD (63%), true color (76%) and humic substances (50%) was observed during advance oxidation process/Fenton during optimum condition of 1.7 g H_2O_2/g COD raw leachate; $Fe_SO_4{\cdot}7H_2O{:}H_2O_2 = 1{:}5.3$; pH = 3.8; reaction conditions = 115 rpm/28 min). Authors observed that the presence of AOP with MPS accelerated the reaction process (Moravia, Amaral, & Lange, 2013). Meanwhile, Chen, Liu, Nie, Wu, and Wang (2014) observed that rapid reduction of COD (90 minutes) was attained when H_2O_2 concentration in the range 0.4 to 0.6 mol/L due to fast kinetics of Fenton's reagent that resulted in full consumption of Fe^{2+}. Meanwhile, pH 3 to 9 were found to be optimum for removal of COD and color from landfill leachate which has proportional relationship with oxidation process. Beyond 9, nonhomogeneous oxidation state is likely to form whereas inhibition of Fenton oxidation during high pH was not favorable because rapid oxidation of Fe^{2+} by dissolved oxygen might trigger (Kilic, Yonar, & Mert, 2014).

Effect of pH

In general, pH plays a significant role in Fenton and Fenton related processes as it directly influences removal efficiency of parameters. As pH related to bases and acidic concentration, speciation from iron and hydrogen peroxide is prerequisite. Until now, a lot of studies have been conducted to study the effect of pH in Fenton and Fenton related processes have been reported elsewhere. For example, Ertugay, Kocakaplan, and Malkoç (2017) employed zero valent iron (ZVI) process in the presence of Fenton process in leachate treatment. They observed that the highest color and COD removal attained at pH 2.0 with 88% and 74% efficiency. In another study, Gupta, Zhao, Novak, and Douglas Goldsmith (2014) employed H_2O_2 in Fenton process for matured leachate treatment. The results obtained suggested that TOC removal was to found increase as the pH of leachate was increased between 3 to 5 which results in 70% removal. They claimed that the drop of removal efficiency was due to precipitation of ferrous and ferric ions. This finding was also in accordance with the work done by Xu, Long, Shen, Feng, and Chen (2017) which revealed that pH has significant effects towards organics degradation because of HO production. In this case, optimized pH during Fenton of coagulated leachate was optimum at pH 2. In sequential treatment of landfill leachate by Fenton, coagulation and combination of both processes, results indicated that pH was optimum at 2.5 (63% COD removal) for Fenton. For coagulation, pH was optimum at 6 (64% COD removal). Finally, in combination of both methods (coagulation followed with Fenton) the optimum pH was found to be at 6 with 80% of COD removal. When Fenton is followed by coagulation treatment, lower COD removal was attained (63%). Apparently, the COD concentration from Fenton process is difficult to be removed by destabilization and crosslinking mechanisms (Boumechhour, Rabah, Lamine, & Said, 2013). Table 4 summarizes pH variables during Fenton and Fenton related processes as reported by previous researchers.

Effect of Temperature

Temperature is considered as the least significant factors to be considered in Fenton and related processes for leachate treatment. It is observed that by increasing temperature, it will lead to organic removal. This was evident when temperature of Fenton process was fixed below than 8.3°C, initial kinetics reaction would occur eventually (Umar, Aziz, & Yusoff, 2010). It then resulted in changes of reaction rate and

Table 4. pH values for Fenton and Fenton related processes

Leachate type	Optimum pH	pH control	Reference
Biologically treated	6.0	Initial	P. Wang, Lau, Fang, and Zhou (2000)
Stabilized	3.5	Initial	Kim, Kim, Won, and Kim (2001)
Mature	3.5 2.0-3.0	Constant Constant	Kim et al. (2001)
Pre-treated by coagulation step	2.5 – 3.0	Constant	Yoo, Cho, and Ko (2001)
Biologically treated	6.0	Initial	Lau, Wang, and Fang (2001)
Biologically treated	3.0-4.0	Initial	Lau, Wang, Chiu, and Fang (2002)
Biologically treated	2.5	Constant	Gulsen and Turan (2004)
Raw	3.0	Initial	Y. Deng (2007)
Biologically treated	5.0	Initial	X. Wang, Chen, Gu, and Wang (2009)
Raw	3.5	Initial	Guo et al. (2010)
Raw	3.0	Initial	Cotman and Gotvajn (2010)
Raw	2.5	Initial	Cortez, Teixeira, Oliveira, and Mota (2011)

removal performance was found to be affected. However, if the temperature is fixed higher than 50°C, COD removal from leachate is disturbed whereby flocs formation is destabilized beyond this temperature (Hermosilla et al., 2009). In terms of organics removal especially on COD parameter, many studies have been reported with respect to Fenton treatment. T. F. C. V. Silva, Silva, Cristina Cunha-Queda, et al. (2013) utilized photo-Fenton for landfill leachate treatment. In terms of temperature effect, the authors found that increased photo-Fenton reaction rate of more than three times were accounted due to Fenton thermal reaction from ferric ion reduction. In another report, Zhang et al. (2005) claimed that increase in temperature from 15 to 36°C increased COD removal from 25% to 33% which affects iron solubility. Faster reduction of Fe^{3+} to Fe^{2+} could be instantly achieved when temperature is raised to 42°C that allows Fe^{2+} formation for hydroxyl radicals generation. However, further increase of temperature is found to affect degradation significantly due to iron precipitation as claimed by Zapata et al. (2009).

Effect of Fenton and Hydrogen Peroxide Reagent Dosage

During Fenton and Fenton related processes, dosage of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) are crucial to evaluate their usage as it directly translate into the overall cost of operation of the treatment. Any excess or lack of these reagent will result in incomplete reaction that leads to scavenging. Accordingly, the rate of degradation may increase when the dosage of ferrous iron is increased. However, excess usage of ferrous ion makes it unutilized and leads to increase in the total dissolved solids (Babuponnusami & Muthukumar, 2014). Meanwhile, concentration of hydrogen peroxide also needs to be considered as overall efficiency of Fenton and Fenton related processes are depending on this reagent. It has been reported that an increase in hydrogen peroxide leads to an increase of degradation rate (Kang & Hwang, 2000). This was true when Fenton was selected as the primary treatment oxidation which caused hydrogen peroxide to scavenge generated hydroxyl radicals. Therefore, optimum hydrogen peroxide dosage needs to be adjusted in such a way that their amount is fully utilized. Furthermore, overdose of hydrogen peroxide could result in iron sludge formation that slow down the rate of sedimentation due to off-gassing of the oxygen as response to decomposition process (Kim, Kim, Won, & Kim, 2001). Furthermore, this observation is further confirmed from a study done by Gogate and Pandit (2004) which reported that excess amount of iron salt led to an increase in effluent with TDS and electrical conductivity as well as sludge production that needs further treatment. In terms of efficiency of biological treatment, it impedes overall system configuration. The role of hydrogen peroxide and ferric ion during the removal of organic compounds by Fenton needs to be well understood in determining the optimal reagent dosage. As a matter of fact, hydrogen peroxide is more vital as it affect mass of $^{\bullet}OH$ generated. Especially during initial COD content before degradation (Deng & Englehardt, 2006).

Generation of Fenton Sludge

The main disadvantage of using metal based catalyst during Fenton treatment is the generation of sludge and disposal of it requires secondary waste treatment which incurs appropriate handling as it is considered schedule waste. Sludge normally generated after neutralization step. In most study, copper and iron are two common metal catalysts used in Fenton (Primo, Rivero, & Ortiz, 2008). A study done by Hermosilla et al. (2009) observed that although Fenton was able to reduce COD concentration from leachate, iron sludge produced after neutralization needs appropriate disposal. Another study also revealed that slurry phase formed from photo-Fenton treatment was able to reduce heavy metals concentration through adsorption treatment provided that soluble species were carried together with slurry (Vedrenne, Vasquez-Medrano, Prato-Garcia, Frontana-Uribe, & Ibanez, 2012). Other than adsorption, precipitation may also be introduced as part of sludge treatment strategies from photo-Fenton treatment. For example, ferric precipitated as a result from neutralization process could be bonded and immobilized and trap metal species. Also, should the effluent carry silicates and aluminum oxides, proposed co-precipitate would retain their crystalline structure (Benatti, da Costa, & Tavares, 2009). In terms of metal speciation affinity, arsenic, should it be present in leachate during photo-Fenton treatment, could effectively adsorb onto iron (III) hydroxide. In terms of mechanism, arsenic may present as As^{3+}, photo Fenton reaction would oxidize into As^{5+} which exhibits higher affinities that leads to its uptake. In another study, Atlin (2008) applied photoelectron-Fenton (PEF) proposed to removed COD, color and phosphate from landfill leachate. He revealed that sludge volume index (SVI) decreased when the applied current increased which is caused by the rise the speed of the Fe ions and is directly proportional to the initial hydrogen peroxide concentration. As the amount of it increases, decomposing of $Fe(OH)_n$ occurred. The author further affirmed that a further increase in pH to 3 caused the SVI to increase as $Fe(OH)_n$ formed larger floc size and become stable in alkaline condition (Altin, 2008). When photo-Fenton process was applied after submitted to coagulation-flocculation step for mature leachate treatment, the authors reported that slurry produced was able to remove heavy metals by adsorption if the metal speciation was in soluble state (Vedrenne et al., 2012).

Optimization

Optimization step in determining the ideal preparation condition for Fenton and Fenton related processes are necessitated to ensure maximum treatability of leachate parameters. In the past, researchers preferred to employ classical optimization process by using one factor at a time approach. Based on this method, one variable is changed over specific range of studies while other variables are left constant. This method ensures the least uncontrolled factor although there are further treatment and replication required. In fact, this method is very time consuming and expensive as many repetition of experiment are needed to ensure consistent result (Umar et al., 2010). Besides, interaction between variables could not be established (Mohajeri, Aziz, Isa, Zahed, & Adlan, 2010). Thus, central composite design (CCD) approach has been widely used for Fenton optimization variables. For example, Wu, Zhou, Qin, Ye, and Zheng (2010) employed CCD and response surface method (RSM) to evaluate the interactive effects of operating variables such as initial pH, H_2O_2 dosage, and Fe^{2+} dosage. They demonstrated that initial pH, H_2O_2 dosage, and Fe^{2+} were optimum at 3.64, 240 mM and 100 mM, respectively. At this condition, COD was able to be removed at 46% efficiency. Meanwhile, Mohajeri et al. (2010) employed Fenton for landfill leachate treatment. They observed that the best preparation condition was: pH = 3, Fe = 560 mg/L, H_2O_2 = 1020 mg/L, H_2O_2/Fe^{2+} molar ratio = 3, agitation rate = 400 rpm and reaction time = 120 minutes. Under this condition, COD and color were removed with 58% and 78% efficiencies. In another study, (Mohajeri et al., 2011) utilized RSM for the determination of optimum variables preparation for leachate treatment by Fenton process. They revealed that pH and its quadratic effects were the main factors contributing to higher parameters removal. The optimum H_2O_2 concentration, Fe(II) concentration, pH ad reaction time were found to be optimum at 0.033 mol/L, 0.011 mol/L, 3 and 145 minutes, respectively. The optimized preparation condition result in 58%, 79% and 82% removal efficiencies for COD, color and iron contents, respectively.Yilmaz, Aygün, Berktay, and Nas (2010) observed that, under the optimum operation conditions (initial pH = 3, 2000 mg/L, Fe^{2+} and 5000 mg/L H_2O_2), 56% of COD and 89% color were effectively removed.

PRE-TREATMENT PROCESS

Landfill leachate carries a lot of concentrated parameters that needs in-depth knowledge before any treatment can be applied. This is true because different age of landfill produces different strength of leachate parameters. For example, (Kamaruddin, Yusoff, Aziz, & Basri, 2013) discussed three types of leachate depending on the landfill age. Young leachate is considered within 1 to 5 years of landfill operation, mature leachate refers to landfill that has been in operation for 5 to 10 years. Meanwhile, stabilized leachate is referred to any landfill that has surpassed the age of 10 years. Within this period, the most obvious parameter changes are COD, BOD, ammoniacal nitrogen and heavy metals (Kamaruddin, Abdullah, Yusoff, Alrozi, & Neculai, 2017). Therefore, considering different type of treatment strategies may be applied to treat leachate, pre-treatment is commonly applied in order to reduce certain target parameters so that precedent treatment will be able to further improve treatment efficiency. In the past, many Fenton and Fenton-related processes were supported with pretreatment post-treatment as complemented strategies. For example, Guo et al. (2010) employed combination process of air stripping, Fenton, sequencing batch reactor (SBR) and coagulation for leachate. They observed that air stripping at pH 11 and aeration time of 18 hours able to remove 9% of ammonia. When submitted to Fenton, the leachate was further treated with COD removal up to 61%. They claimed that combined processes effectively decreased the pollutant loading. Advanced treatment of mature leachate was applied by using combination of coagulation, Fenton oxidation and biological aerated filter processes. The study demonstrated that initial pH of 5, reaction time of 3 h, H_2O_2 dosage of 5.4 mmol/L were found optimum with COD removals of 67% and 56%, respectively (Wang, Chen, Gu, & Wang, 2009). While there are concerns on biodegradability of leachate, solar energy was found suitable to be incorporated with Fenton process combined with nitrification and denitrification processes. A study done by Vilar et al. (2011) revealed that complete removal of ammonium was achieved through denitrification and nitrification after previous neutralization of photo-Fenton reaction. They found that optimum C/N ratio for denitrification to be 2.8 mg CH_3OH per mg N-NO^{3-} which consumed 7.9 g/8.2 mL methanol of 1 L leachate. Whereby, optimum photo treatment applied was 29.2 kJ_{uv}/L and consumed 90 mM of H_2O_2 which reflects to 57% mineralization of leachate. This condition lead to 57% and 86% reduction of polyphenols and aromatic content. In order to improve biodegradability of organic matter removal, Fenton and ozone oxidation was applied after subsequent biological treatment of mature leachate. This study revealed that Fenton treatment alone removed 46% of COD and increased their BOD/COD ratio from 0.01 to 0.15. After tested toward ozone oxidation, the COD removal increased to 72% and BOD/COD ratio was also increased from 0.01 to 0.24 (Cortez, Teixeira, Oliveira, & Mota, 2011). In another study, leachate collected from waste disposal site was treated with selected oxidation processes which were ozonoation, ozonation/hydrogen peroxide, Fenton and combination of them. The study pointed out that combined Fenton and ozonation resulted with more than 70% COD removal (Goi, Veressinina, & Trapido, 2009). T. F. C. V. Silva, Silva, Cunha-Queda, et al. (2013) performed multistage treatment for mature landfill leachate. The treatment consists of activated sludge biological oxidation and photo-Fenton process. They reported that the first stage of biological step was found to remove over 95% of total nitrogen with 39% mineralization for DOC. Under this condition, nitrification rate was achieved at 8.2 mg NH4+-N/h/g of volatile suspended solids (VSS). Meanwhile, they observed that during anoxic conditions, the maximum denitrification rate was found to be 5.8 mg (NO_2^-–N + NO_3^-–N)/h/g VSS with a C/N ratio of 2.4 mg CH_3OH/mg (NO_2^-–N + NO_3^-–N). In addition, humic acid during this treatment was 37% of humic substance (HS). Then, when the leachate was involved in photo-Fenton, more than 80% of HS depletion was recorded with low molecular carboxylate anions of 70% and several other organic micropollutants resulting in more than 70% biodegradability. J. Li et al. (2016) performed combined treatment of landfill leachate by using Fenton oxidation-coagulation and photo-Fenton processes. The study showed that after precipitate separation, more than 90% COD and TOC reduction was achieved with H_2O_2/Fe^{2+} dosages of 35 mM/8 mM and 90 mM/10 mM. For Fenton-oxidative-coagulation process, more than 70% organic matters removal was achieved. When subjected to combined process, H_2O_2 efficiency was found to increase from 216 to 228%. They also claimed that more than 80% of phthalic acid esters and 90% of polycyclic aromatic hydrocarbon were removed based on combined treatment. In another in depth study, a combined treatment process that consists of air stripping, Fenton, sequencing batch reactor (SBR) and coagulation to determine the removal efficiency of COD, BOD and NH_3-N. The result demonstrated that about 93%, 88% and 98% of parameter removal efficiency were achieved (Z. Liu, Wu, Shi, Guo, & Cheng, 2015).

COMPARISON BETWEEN PROCESS

The comparison of different AOPs is of interest to determine the best COD and color removal performances and the most efficient process for the removal of recalcitrant compounds in leachate. The aim of this study was to evaluate the above-mentioned approaches in terms of reduced organic load, and decreased color for the treatment of landfill leachate. To investigate the synergistic effect of combined electrochemical method and Fenton's reagent, leachate solution was treated with Fenton reagent alone, the electrochemical method alone and the electro-Fenton method alone, respectively.

A comparison of various AOPs studied in terms of COD and color reduction are illustrated in Table 5. It. The obtained results from the comparative experiments revealed that the proposed electro-Fenton process is much more effective than the other treatment processes for the landfill leachate. Significant differences are seen between both COD and color removals, especially in the results obtained by the electro-Fenton process. However, the performance of the electro-Fenton process is much better than Fenton reagent and electrochemical oxidation.

Table 5 showed that the COD removal efficiencies were 58.3% in Fenton treatment, 49.3% in electrochemical oxidation treatment and 95.6% in electro-Fenton treatment. From the table, it can be inferred that electro-Fenton oxidation process demonstrated higher degradation and decolorization efficiencies than that by Fenton and electrochemical oxidation processes. The most effective mineralization and decolorization rate was obtained by electro-Fenton process and the ranking was in the order of electro-Fenton>Fenton > electrochemical oxidation.

It should also be noted that electro-Fenton process needs a shorter reaction time compared to Fenton and electrochemical oxidation processes. From the table, it is observed that the mineralization achieved by Fenton and Electrochemical oxidation are moderate (58.3% and 49.3% respectively) and a sizeable fraction of recalcitrant compounds remained in the solution. Electro-Fenton process on the other hand, has removal efficiency more than 95%. In the electro-Fenton process, COD and color were removed rapidly during the first 30 minutes, but both Fenton and electrochemical methods could only remove a much smaller fraction of COD and color from leachate solution after 2 and 4 hours of treatment respectively. The major differences observed in the three technologies can be explained in terms of the different mechanisms involved in each process. The oxidation mechanisms in the three technologies are not only based on the production and use of the hydroxyl radical, but also include other kinds of oxidation mechanisms specific to each technology.

Table 5. Comparison between processes

Method	COD removal	Color removal	Reference
Fenton oxidation	60%	74%	Lopez, Pagano, Volpe, and Di Pinto (2004)
	71%	99%	Meriç, Kaptan, and Ölmez (2004)
	61%	Not reported	Y. Deng and Englehardt (2007)
	88%	95%	Lee and Shoda (2008)
	58%	79%	Mohajeri (2010)
Electrochemical oxidation	73%	86%	Moraes and Bertazzoli (2005)
	56%	Not reported	Shao et al. (2006)
	68%	84%	Bashir et al. (2009)
	59%	Not reported	Ilhan, Kurt, Apaydin, and Gonullu (2008)
	49%	59%	Mohajeri (2010)
Electro-Fenton oxidation	81%	Not reported	Zhang, Choi, and Huang (2006)
	72%	90%	Atmaca (2009)
	96%	98%	Mohajeri (2010)

It is assumed that in these three processes, the hydroxyl radicals are implicated in the oxidation, but according to the results, these huge differences have to be explained by the action of other oxidants. In electrochemical oxidation, the influence of current density on the evolution of COD with specific electrical charge passed shows that both direct oxidation on the surface of the electrode, and mediated oxidation by hydroxyl radicals electro-generated from water decomposition and/or by other oxidants electro-generated from chlorides (hypoclorites and chloride anions), take place.

Unlike the traditional process of electrochemical oxidation in which anodic oxidation accounts for organic pollutants degradation, the electro-Fenton process is characterized by the union of electrochemical oxidation and Fenton oxidation in one electrochemical cell, so besides anodic oxidation, the oxidation of OH produced by Fenton reaction is also involved. Electro-Fenton process includes the combined advantages of electrochemical and Fenton treatment methods, and each of them is a powerful treatment method. Under electrically assisted Fenton reaction, more OH● radicals are produced and the oxidation of the organics to CO_2 can be enhanced in the same period.

In Fenton oxidation process, only hydroxyl radicals generated from the catalytic decomposition of H_2O_2 are able to oxidize organic carbons and its oxidation intermediates. It seems that Fe^{2+} is a powerful catalyst so that can produce huge amount of hydroxyl radicals and resulting more degradation than electrochemical oxidation. The electro-Fenton process had a significantly higher COD removal efficiency than the conventional Fenton process due to the production of more hydroxyl radicals when excess H_2O_2 reacts with the electro regenerated Fe^{2+}. Hydrogen peroxide can be electrochemically generated in-situ, which may further increase the effectiveness of this process for treating contaminated leachate. The final COD removal efficiency achieved by the electro-Fenton method was 95.6%, nearly 37% higher than Fenton's reagent alone and 46% higher than electrochemical oxidation alone. This indicates that electro-Fenton method had a synergistic effect for COD and color removal because the electro-Fenton reaction takes advantages of both the Fenton and electrochemical oxidation techniques.

A major advantage of electro-Fenton process is that the ferric ions can be recycled into ferrous ions, so that they behave like a catalyst. The electro-Fenton process had a significantly higher COD removal efficiency than the conventional Fenton process due to the production of more hydroxyl radicals when excess H_2O_2 reacted with the electro regenerated Fe^{2+} at the cathode. Another reason for higher efficiency is the oxidation is not only due to hydroxyl radicals but to other active oxidants. It can be attributed to electro-oxidation on the anode surface and the oxidation mediated by other electrochemically-formed compounds generated this electrode (due to the oxidation of salts present in the leachate).

The results obtained for electrochemical oxidation indicate that incomplete and very slow mineralization and decolorization of leachate were observed with electrochemical oxidation system (less than 49% of CO and 59% of color removals, respectively, after 4 hours). This implies that the electrochemical oxidation is not sufficient to produce efficient mineralization and decolorization of leachate. It is known that besides the formation of hydroxyl radicals (Deng & Englehardt, 2007), electrochemical oxidation combines direct electrooxidation on the anode surface and mediated oxidation by the other electrochemically formed compounds such as hypoclorites and chloride anions.

In electrochemical oxidation, to achieve satisfactory efficiency, high dosages of salt are needed to give sufficient supporting electrolyte. Such salt addition to the influent would raise the total dissolved solids in the effluent to levels potentially unacceptable for final disposal. It can also increase the conductivity of leachate. One major disadvantage of electrochemical oxidation is the formation of undesirable toxic chlorinated compounds as a byproduct during treatment while electro-Fenton process provides a simple, viable and promising AOP for the remediation of chloride-free effluents of leachate. As it can be observed, this technique is not able to achieve high mineralization of the waste, and more than 50% of COD and 40% of color remains at the end of the treatment.

In contrast, when Fenton and electrochemical oxidation combined was used as treatment method, more effective and rapid COD and color removal were observed. In the case of electro-Fenton, the higher efficiencies help to confirm that there are other important oxidation processes that complement the hydroxyl radicals mediated oxidation.

Electro-Fenton processes like electrochemical oxidation also involve direct electrooxidation on the anode surface and mediated oxidation by the other electrochemically formed compounds such as hypoclorites and chloride anions because of existing chloride salts in the leachate solution. As mentioned before, electro-Fenton process is pH dependent and pH influences the generation of hydroxyl radicals hence affecting mineralization and decolorization efficiency. This trend confirms that organics are more rapidly destroyed with OH formed from Fenton's reaction than with Cl- generated from NaCl reaction, since the rate of the first reaction depends on pH, whereas the second one is pH-independent.

Compared with the traditional electrochemical oxidation, the process with Fe(II) is more efficient with lower power consumption, and the removal efficiency of organic pollutant is much better when Fe(II) is used. It appears that the combined process is more effective because electricity promotes hydrogen peroxide decomposition, yielding additional hydroxyl radicals, thus increasing mineralization and decolorization. Numerous studies have indicated that electricity promotes Fenton reaction (Atmaca, 2009). It can therefore be assumed that electro-Fenton can compete favorably with electrochemical and Fenton oxidation due to the higher number of oxidants involved in the electro-Fenton process. It can also be seen that electro-Fenton is the only oxidation technique that is able to achieve outstanding COD and color removal close to 95%. Conversely, electrochemical and Fenton oxidation are only able to reduce the organic load by around 49% and 58%, respectively. Another disadvantage of Fenton process is the fact effluent pH subsequent to Fenton oxidation needs to be adjusted to satisfy requirements for discharge or following biological treatment and to convert dissolved iron to iron sludge since Fe^{3+} is least soluble at pH 8.0.

As far as the treatment cost is concerned, the conventional Fenton process requires a higher cost in chemicals, associated with higher hydrogen peroxide consumption levels (3 times more), and also has to deal with iron sludge disposal. In the presence of electricity and lower H_2O_2 dosage, more electro-regeneration cycles will be performed to produce the large amount of hydroxyl radicals in order to yield much more COD and color removals. So another advantage of electro-Fenton is the reduction of inorganic sludge production by electro regeneration of Fe^{2+} from ferric ions (Fe^{3+}).

The main advantage showed by the electro-Fenton treatment of landfill leachate was that it consumed 3 times less hydrogen peroxide and 4 times less reaction time, yielding much more COD and color removal than a conventional Fenton treatment. Electro-Fenton process is also much more economic than electrochemical oxidation in terms of energy consumption and reaction time, resulting in much more COD and color removal efficiencies than electrochemical oxidation. Since the oxidation rate of the electrochemical process was extremely slow, it is expected that the energy cost will be very high. The treatment cost can be drastically reduced by the addition of a small amount of ferrous iron and hydrogen peroxide to the leachate to be treated with the application of electricity. Furthermore, since chlorinated organic carbons which are formed as a byproduct during electrochemical process; they have to be removed before discharge by using a suitable method and therefore it needs extra cost while treated leachate by electro-Fenton process is chlorinated organic free. Among all the AOPs studied, electro-Fenton process is found to be most efficient in COD removal i.e., in only 30 minutes, a maximum of 95% degradation was achieved.

In case of color reduction, a maximum of 97% was achieved while only 79% was reduced using Fenton oxidation and 58% using electrochemical oxidation. The electro-Fenton process was superior to the conventional Fenton process due to its higher treatment efficiency at low H_2O_2 concentration, low inorganic sludge production, low residual H_2O_2 after treatment, consuming shorter time and removing turbidity, suspended solids and Fe^{2+} ions completely. Moreover, in electro-Fenton process, effluent pH raised up to neutral pH (> 8), so effluent pH is normal, and accordingly no need for additional treatment and consequently additional cost. Fenton's chemistry seems to be beneficial if used as a supplement to enhance the rates of hydroxyl radicals and another active oxidant rather than using Fenton's reagent alone.

Electro-Fenton process was also found to be superior to the electrochemical oxidation due to its higher treatment efficiency at lower energy consumption, not consuming electrolyte, requiring shorter time, removing turbidity, suspended solids and Fe^{2+} ions completely and not producing toxic compounds while in electrochemical oxidation of leachate some chlorinated organic compounds are formed which are toxic and hazardous to the environment.

Electrochemical and Fenton oxidation lead to a significant removal but they are not able to reduce the COD below the discharge limits fixed typically by the municipal authority. With electrochemical and Fenton oxidation it is clear that a complementary treatment should be used to refine the quality of the effluent because the concentration of COD after the treatment is still high; additional treatment leads to additional cost. Hence, these two oxidation technologies should not be used as a final treatment but is better suited as a post or pre-treatment process. The result also indicates that electro-Fenton combines some powerful oxidation mechanisms that give this technology a clear advantage as compared with electrochemical or Fenton process. As hydroxyl radical are nonselective oxidizing agents, the electro-Fenton process can be generalized to the treatment of landfill leachate containing toxic and persistent organic pollutants. Indeed this process can be considered ecologically friendly, simple to handle and most importantly, economical.

Among the AOPs performed, electro-Fenton process should be the best candidate, not only because it can achieve above 95% of COD removal, but also because the process is cost-effective and simple in technological aspect and at the same time ensures rapid processing since it takes only 30–45 minutes for treatment compared to Fenton and electrochemical oxidation.

CONCLUSION

As a concluding remark, the results herein show the use of electro-Fenton to destroy organic pollutants in leachate provides an ecologically friendly water treatment technique which can therefore be considered as a serious alternative method for landfill leachate treatment methods such as Fenton and photo-Fenton. Treatment of the leachate by electro-Fenton process elevates its water quality to the standard for direct discharge. Hence, electro-Fenton is recommended as a powerful technique for the degradation and decolorization of landfill leachate owing to efficient removal of COD and color, providing an attractive, cost-effective, high efficiency and user-friendly treatment method for the degradation and decolorization of landfill leachate.

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Chapter 14

Application of UV-Based Advanced Oxidation Processes in Water and Wastewater Treatment

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ABSTRACT

The presence of hazardous micropollutants in water and wastewater is one of the main concerns in water management system. This micropollutant exists in a low concentration, but there are possible hazards to humans and organisms living in the water. Moreover, its character that is recalcitrant to microbiological degradation makes it difficult to deal with. Advanced oxidation processes (AOPs) are efficient methods to remove low concentration micropollutants. AOPs are a set of processes consisting the production of very reactive oxygen species which able to destroy a wide range of organic compounds. The main principal mechanism in UV-based radical AOP treatment processes is the use ultraviolet light to initiate generation of hydroxyl radicals used to destroy persistent organic pollutants. Therefore, this chapter presents an overview on the principle of radical oxidant species generation and degradation mechanism by various type of UV based AOP in treating contaminants present in water and wastewater. The current application and possible improvement of the technology is also presented in this chapter.

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INTRODUCTION

An escalation of refractory or recalcitrant contaminants in water and wastewater have led to various technologies being developed which includes the use of advanced oxidation processes (AOPs). These processes have shown great potential in treating wide range of pollutants from low to high concentration and has been applied for various types of water treatment such as groundwater (Molnar et al., 2012) wastewater (Babuponnusami & Muthukumar, 2014; Ebrahiem & Mohammednoor, 2017) and landfill leachate (Hassan et al., 2016; Palmer 2016). Photochemical is one of the technology used in AOPs. The technologies have gained more popularity over the past two decades because of its capability to give the dual benefits of contaminants treatment and disinfection (Parsons, 2004). Other than that, the simple and clean operation is also the factor that contributes to the selection of this technology for water and wastewater treatment.

UV irradiation is often used in AOPs since the exposure to the UV-light can enhance oxidizing agents such as hydrogen peroxide (H_2O_2), chlorine and ozone (O_3) to form free radicals (Kumar et al., 2012). Besides that, organic pollutants are oxidized to simpler, less refractory organic compounds or to carbon dioxide, water and mineral acids (Crittenden et al. 2012). Basically, Ultraviolet (UV) based radical AOPs generate powerful oxidizing species such as the hydroxyl radical ($OH^\bullet$) by direct photolysis of hydrogen peroxide (H_2O_2), photo-Fenton reactions or heterogeneous photocatalysis. In UV direct photolysis, degradation process through an absorption of incident radiation from the UV light is the main removal mechanism. Therefore, the application usually focusses on the contaminants that strongly absorb UV radiation. On the other hand, UV direct photolysis with H_2O_2 produces OH radical that can remove the contaminants by oxidation processes (Malato et al., 2003). Thus, contaminants in water can be treated by both UV radiation and OH radical induced processed. Most UV light absorber contains double bonds or conjugated double bonds which includes carbon, nitrogen or oxygen atoms and characterized by delocalised π-electrons (Parsons, 2004).

The growing interest in the application of UV-light based in water and wastewater treatment was driven by the concern of potentially carcinogenic and toxic contaminants present in the water and strict regulation set by the water authorities. Consequently, many studies were conducted to explore the UV-light induced degradation of different types of organic and inorganic compounds of environmental concern. OH radical-driven by UV-based AOPs such as photooxidation (UV/O_3, UV/ H_2O_2, UV/O3/ H_2O_2) and photocatalysis (photo-Fenton, UV/ TiO_2) reactions demonstrate significantly larger rates of pollutant removal than those of direct photolysis. This chapter aims to present an overview of the range of UV based radical AOPs available and discuss the principals or fundamentals behind the processes as well as the current applications and opportunities for this treatment to be used in the future.

UV Radiation With H_2O_2 (UV/ H_2O_2)

The basic principle of AOP involves the production of hydroxyl radicals ($OH^\bullet$), which can be generated from hydrogen peroxide (H_2O_2) with the presence of ultraviolet (UV) radiation. This process combines H_2O_2 and UV-light in a synergistic effect to degrade organic chemicals and pathogenic microorganisms in aqueous solutions. The generation of hydroxyl radicals are the fundamental to the process as the hydroxyl radicals are largely responsible for the success of this process.

Photolysis of H_2O_2 to Form Free Radical Species

Hydroxyl radicals are formed by the photolytic dissociation of H_2O_2 in water by UV irradiation at a wavelength of 254nm (Krishnan et al., 2016). The H_2O_2/UV process generates hydroxyl radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The mechanism most commonly accepted for the photolysis of H_2O_2 is presented by the Eqn (1):

$$H_2O_2 + hv \rightarrow 2\ HO^{\bullet}\ (\lambda \leq 254\ \text{nm}) \qquad (1)$$

*hv represents UV radiation.

UV radiation is usually produced by using low-pressure mercury vapor UV lamps with a 254 nm peak emission.

Cooper and Zika (1983) described the H_2O_2 as a powerful oxidizer which naturally decomposes to water and oxygen and created by the action of sunlight in natural surface water due to the natural organic element present. Thus, the direct photolysis of H_2O_2 leads to the formation of OH radicals. H_2O_2 has also been used for many years to degrade organics in industrial or municipal wastewater. It can also be used for the disinfection of wastewater treatment plants. When H_2O_2 is combined with UV light, catalyst or other oxidants, the resulting treatment is far more efficient in destroying organics present in high strength wastewaters. H_2O_2 may generate a wide variety of free radicals and other reactive species that can transform or decompose organic chemicals when combined with the catalyst. H_2O_2 reaction chemistry is complex, but it can be broken into several major concepts and reaction mechanisms, including free radical chain reactions such as (Benjamin et al., 2011):

- Initiation, propagation and termination steps,
- Radical scavenging,
- Oxidation of organic contaminants
- Competing and non-productive reactions.

Collivignarelli et al., (2017) elaborated that the efficacy of the UV/H_2O_2 process depends on various conditions that affect its ability to degrade organic molecules including the type and the concentration of the organic contaminants or dissolved inorganics (such as carbonates and metallic cations), light transmittance of the solutions, pH, temperature, and hydrogen peroxide dosage.

A series of simple reactions will occur when a free radical has been initiated by photolysis. A large number of reactions is a reason for the complexity of the chemistry. Hence, it is very difficult to predict all the products of oxidation according to the complicated mechanism (Parson, 2004). There are many factors that could affect the radical concentration which includes:

- pH
- Temperature
- The presence of ions
- The type of pollutant
- Presence of scavengers (bicarbonate ion)

It is important to emphasize the synergistic effect between the UV radiation and H_2O_2 which is beneficial only with contaminants that require a relatively aggressive oxidation conditions (high activation energies) while using the UV/H_2O_2 technique (Laura et al., 2014).

Mechanism of Decontamination

Mechanism of decontamination of UV radiation with H_2O_2 (UV/H_2O_2) involves:

H_2O_2 Oxidation

Generally, oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons (Grote, 2012). The electron transfers result in the chemical transformation of both the oxidant and the reductant, in some cases producing chemical species with an odd number of valence electrons which are known as radicals, which are inclined to highly unstable. Thus, the radicals are highly reactive because one of their electrons is unpaired. Oxidation of water contaminant is to 'mineralize' which turn the elements of contaminant organic into simple, relatively harmless and inorganic molecules (Parson, 2004; Laura et al., 2014)

Meanwhile, oxidation reactions that produce radicals have a propensity followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed (Grote, 2012). The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The most powerful oxidants are fluorine, hydroxyl radicals ($OH^\bullet$), ozone, and chlorine. Radical is also indicated as $OH^\bullet$ or OH'. Hence, the optimal H_2O_2 concentration depends on the amount of pollutants to be oxidized.

Hydroxyl radical ($OH^\bullet$) acts as a strong oxidizing agent which can destroy many organic and inorganic compounds in water. $OH^\bullet$ are non-selective in nature which can react without other additives with a wide range of contaminants (Brandon et al., 1997). Furthermore, $OH^\bullet$ attacks organic molecules either by abstracting a hydrogen atom or adding a hydrogen atom to the double bonds resulting in new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization.

UV Photolysis

The photolysis of hydrogen peroxide generates hydroxyl radicals, which oxidize target compounds. Photolysis is a process in which compounds absorb photons and the energy released drives oxidation processes induced by light. The photolysis rate of a compound can be estimated based on its light absorption rate and quantum yield. The extinction coefficient represents the phenomenon where as wavelength decreases, more photons are absorbed. It is the photolysis of hydrogen peroxide that generates the hydroxyl radicals that drives the UV/H_2O_2.

The UV light allows the production of an oxidizing agent (ROS) called hydroxyl radical ($OH^\bullet$) (Eqn. (2)) which is one of the strongest oxidants known, much more efficient than hydrogen peroxide alone (Amin et al., 2008) and is therefore much more efficient in killing microorganisms and degrading organics in water.

$$H_2O_2 + \text{UV light} \dashrightarrow 2\,OH^\bullet \qquad (2)$$

Organic substances are generally more sensitive to light than inorganic ones. It is subjected to degradation by direct absorption of photons of hard UV radiation or by reaction with water photolysis products, such as with OH●. These radicals serve as an important part in the mineralization of dissolved organic matter to carbon dioxide and water (Simonenko et al., 2015; Krishnan et al., 2016).

Application of H_2O_2 With UV (H_2O_2/UV)

The strong oxidizing power of H_2O_2 makes it suitable for the destruction of a variety of pollutants such as bacteria, toxic organic compounds and some metals. The process has many applications in drinking water production including taste and odor control, hydrogen sulphide removal, metal removal, ozone enhancement and disinfection. UV may be used in combination with hydrogen peroxide (indirect photolysis) to produce highly reactive and unselective H_2O_2 which has been proven to be effective for the removal of some organic pollutants. Table 1 shows the summary of the findings for application of H_2O_2 with UV (H_2O_2/UV).

UV Radiation With Ozone (UV/O_3)

Ozone has been studied in combination with ultraviolet (UV) radiation, which UV photons can activate ozone molecules. The combination of the ozone with UV light is expected to increase the efficiency of ozonation process by constructing more hydroxyl radicals in the treatment system. O_3/UV process is effective for oxidation and destruction of toxic and water-refractory organic compounds (Laura et al., 2014).

A simplified reaction sequence is shown as below (Eqns. (3) and (4)):

$$O_3 + H_2O \rightarrow O_2 + H_2O_2 \text{ (in the presence of UV light)} \tag{3}$$

$$2\ O_3 + H_2O_2 \rightarrow 2\ OH^{\bullet} + 3\ O_2 \tag{4}$$

Generation Oxidative Species

Most of the OH● is produced from ozone in the chain reaction where OH- (high pH) or H_2O_2 (hydrogen peroxide) act as starter. The combination of O_3/UV effectively destroys organic contaminants largely because of the very high oxidation potential of the hydroxyl radical. Brandon et al., (1997) described that the free radical constructed by decomposition of ozone is the principal reacting species involved in the destruction of organic toxicants. O_3/UV reactions (also known as photolytic ozonation) in aqueous solution, ozone is energized and combines with water to create OH●, which is stronger and less selective than either chemical oxidant. Meanwhile, ozone effectively reacts with the organic contaminants that influence with residual ozone converting into two hydroxyl radicals per ozone molecule which indicates oxidation targets to multiple attackers, dramatically changing the oxidation landscape. With the highly active and nonselective hydroxyls acting on many targets, the ability of the ozone molecules to work more effectively increase. Thus, ozone residuals are destroyed at UV light wavelengths ranging from 250 to 260 nm, while microorganism inactivation can be achieved at UV wavelengths ranging from 100

Table 1. Summary of finding for application of H_2O_2 with UV (H_2O_2/UV)

Target Contamination	Matrix	Experimental condition	Removal efficiency/Remarks	Source
Trichloroethene (TCE)	Through the presence of 10.4 mM H_2O_2 resulted in formic, oxalic, dichloroacetic (DCA) and monochloroacetic (MCA) acids as organic byproducts	Trichloroethene (TCE) degradation mechanism in the presence of H_2O_2 under irradiation with a 1 kW medium-pressure Hg lamp.	The degradation of trichloroethene was recently evaluated. TCE degraded primarily through hydroxyl radical-induced reactions and only to a low extent through direct UV photolysis and chlorine atom-induced chain reactions.TCE and its degradation products were completely mineralized in 30 min, under a volume averaged UV-C irradiant power of 35.7 W/L from a 1 kW medium-pressure mercury vapor arc lamp.	Li et al., 2007
Methylisoborneol (MIB) and geosmin	Raw source water and treated water.	Through direct ultraviolet (UV) photolysis and the UV/hydrogen peroxide (H_2O_2)	Low Pressure (LP) and Medium Pressure (MP) direct UV photolysis removed 10% and 25–50% of the compounds by 1000 mJ cm^{-2} UV fluence, respectively. The addition of H_2O_2 created advanced oxidation conditions, and oxidized greater than 70% of these compounds at a UV fluence of 1000 mJ cm^{-2}. MP UV + H_2O_2 was consistently faster than LP UV + H_2O_2 for MIB oxidation, but water quality affected both UV + H_2O_2 AOPs. The UV + H_2O_2 AOP oxidation of these taste and odour contaminants in natural waters was effectively modelled using the steady state OH radical concentration model.	Rosenfeldt et al., 2005
Meprobamate, carbamazepine, dilantin, atenolol, primidone and trimethoprim	Pharmaceuticals in wastewater effluents	A custom-made low pressure (LP) UV collimated beam system was used for all the irradiations. The system included two G15T8 germicidal lamps (General Electric, Fairfield, CT, USA), housed inside a wood box. The intensity was measured using a radiometer (International Light, Peabody, MA) model 1700 (probe model SEL 240). The petri factor for the LP system was determined to be greater than 0.9. The un-weighted doses were calculated from the product of the fluence rate and exposure time.	The efficacy of UV/H_2O_2 treatment for the removal of pharmaceuticals from wastewater was a function of not only the concentration of EfOM but also its inherent reactivity towards OH•. The removal of pharmaceuticals also correlated with reductions in ultraviolet absorbance at 254 nm (UV_{254}), which offers utilities a surrogate to assess pharmaceutical removal efficiency during UV/H_2O_2 treatment.	Fernando et al., 2010
N-nitrosodimethylamine (NDMA) and 8 other nitrosamines.	Raw water from the alluvial test well near Brighton.	UV AOP testing was performed using two side by side collimated beam devices, each utilizing a low pressure, mercury-vapor UV lamp. A collimated beam device directs UV light through a non-reflective collimating tube to a sample that is placed in a Petri dish or beaker, continuously-stirred, and exposed for a predetermined amount of time. The UV dose was then calculated as the product of the UV intensity (as measured by a calibrated radiometer) and the exposure time.	The results showed predictable and repeatable destruction of NDMA, and destruction of other tested nitrosamines exceeded NDMA destruction at the same collimated beam UV doses. UV/H_2O_2 obtained to be effective processes for the control and treatment of trace organic contaminants.	Swaim et al., 2008
Natural Organic Matter (NOM)	Raw surface water	Through the post-UV/H2O2 chlorination.	The UV/H_2O_2 partially oxidized NOM, reducing its degree of aromaticity and leading to an increase in the level of biodegradable species. When combined with a downstream biological activated carbon (BAC) filter, UV/H_2O_2 reduced the formation of DBPs by up to 60% for trihalomethanes and 75% for haloacetic acids. Biological activated carbon was also shown to effectively remove biodegradable by-products and residual H_2O_2	Siva et al., 2011
Cyanobacterial taste and odor compound	Water treatment plant	Through direct ultraviolet (UV) photolysis and the UV/hydrogen peroxide (H_2O_2).	The results of this study demonstrate that H_2O_2 quenching for the operational period of 6 months has no significant impact on GAC capacity to remove geosmin and MIB from water. The type of taste and odor compounds, concentration of compounds, ratio of intra/extracellular compound, producer species present and duration of bloom season, GAC type, EBCT, and other operational practices are the factors that influence GAC capacity to remove the studied taste and odor compounds.	Zamyadi et al., 2015

to 400 nm, although a wavelength of 254 nm is most effective (Steven, 2003). Organic oxidation occurs due to the reaction with OH● radicals, molecular ozone and direct photolysis.

Mechanism of the Decontamination

Mechanism of decontamination for UV radiation with ozone (UV/O_3) encloses UV photolysis. UV photolysis is a process in which compounds absorb photons and the energy released drives oxidation processes induced by light. The photolysis rate of a compound can be estimated based on the compound's light absorption rate and quantum yield. Some organic compounds, such as N-nitrosodimethylamine (NDMA) can be reduced by photolysis alone. The key parameters for the success of UV/O_3 system are ozone dosage, UV irradiation level and pH. A high dissolved ozone rate must be maintained with effective transfer of ozone gas into aqueous solution for proper ozone dosing. The oxidation of inorganic and organic compounds during ozonation can happen through molecular ozone (direct reaction, prevalent in an acidic medium) or by hydroxyl radicals (indirect reaction, prevalent in the alkaline medium) (Carla, et al., 2013).

Application of UV/O_3

Many research that has been done by using the combined treatment of UV radiation with ozone (additional to the ozone generated by the UV radiation) produced more effective and faster oxidation of polypropylene, polyethylene terephthalate and polyethylene surfaces than either ozone only or UV treatment (Maria et al.,2005).

The combined treatment of UV radiation with ozone (additional to the ozone generated by the UV radiation) produces more effective and faster oxidation of polypropylene, polyethylene terephthalate and polyethylene surfaces than either by ozone only or UV treatment. Different reaction mechanisms are implied for each treatment (Bhurke et al., 2000).

Photo Fenton Process (H_2O_2 /Fe^{3+}/UV)

Fenton was explored through Fenton's reagent by a mixture of Hydrogen Peroxide (H_2O_2) and ferrous iron, that produces hydroxyl radicals (Fenton, 1894). Decomposition of H_2O_2 using ferrous iron (Fe^{2+}) or Ferric iron (Fe^{3+}) under the extent of mineralization using Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2, reagents are improved by irradiation with UV radiation and visible light (Vincenzo et al., 2011). The ferrous iron (Fe^{2+}) begins and catalyzes the decomposition of H_2O_2, resulting in the production of hydroxyl radical (Ebrahiem et al., 2013; Oscar et al., 2008). The higher production of OH● through the combination of oxidant compounds and metallic catalysts in presence of UV radiation and the potential applicability of sunlight as UV light resource is an attractive matter of this system. Meanwhile, a combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion (photo-Fenton (PF) process) produces more hydroxyl radicals compared to the conventional Fenton method or photolysis and in turn increases the rate of degradation of organic pollutants (Sina and Mohsen, 2017). Fenton, (1894) showed that a mixture of H_2O_2 and Fe^{2+} in the acidic medium has very powerful oxidizing properties. The pure mechanism is a simple redox reaction in which Fe^{2+} is oxidized to Fe^{3+} and H_2O_2 is reduced to hydroxide ion and the hydroxyl radical (Eqn. (5)):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$ (5)

Meanwhile, the reaction can be improved by UV/V irradiation, called Fenton reaction, produces additional OH radicals and leads to the recycling of the Fe^{2+} catalysts (Eqn. (6)). This reaction acts as the primary forces of photochemical self-cleaning of the atmospheric environment (Bauer & Fallmann, 1997).

$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + OH^{\bullet}$ (6)

These sequences of reactions indicate a cycle of iron between Fe^{2+} and Fe^{3+} states. The overall stoichiometry of the system expresses the production of two moles of $OH^{\bullet}$ per mole of H_2O_2 consumed (Vincenzo et al., 2011). Jr. et al., (2010) mentioned that any reaction or process that increases the rate of conversion of Fe^{3+} back to Fe^{2+} will in principle accelerate the rate of the Fenton reaction. Deng and Zhao, (2015) described that in the photo-Fenton reaction was applied UV irradiation with the traditional Fenton system with a major purpose of enhancing the UV induced reduction of dissolved Fe^{3+} to Fe^{2+}. H_2O_2 concentration is a primary role to determine the effectiveness of the degradation process. It has been observed frequently that the percentage degradation of the pollutants increases the amount of H_2O_2 (Rivas et al., 2001). The concentration of hydrogen peroxide indicates an important element in deciding the overall efficiency of the degradation process (Babuponnusami & Muthukumar, 2014). It has been observed that the degradation percent of the pollutant increases with an increase in the dosage of hydrogen peroxide (Ma et al., 2000). Nevertheless, care should be taken whilst selecting the operating oxidant dosage. The unused portion of hydrogen peroxide during the Fenton process contributes to COD (Lin and Lo, 1997; Barbara et al., 2012) and hence any excess amount is not recommended. Also, the presence of hydrogen peroxide is harmful to many of the organisms (Ito, et al., 1998) and will affect the overall degradation efficiency significantly, where Fenton oxidation is used as a pretreatment to biological oxidation (Babuponnusami & Muthukumar, 2014).

Maha and Zeinab (2014) justified the factor in controlling the Fenton reaction process which indicates the amount of Fe^{2+} and H_2O_2 and the pH. Fenton process is strongly dependent on the solution pH mainly due to iron and hydrogen peroxide speciation factors. The optimum pH for the Fenton reaction was found to be around pH 3, regardless of the target substrate (Rivas et al., 2001; Jr. et al., 2010; Babuponnusami & Muthukumar, 2011). Higher pH reduced the activity of Fenton reagent towards the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate (Parson, 2004). This condition indicates, less hydroxyl radicals are generated due to the presence of less free iron ions. The oxidation potential of hydroxyl radicals decreases with increasing pH. Sara et al., (2006) mentioned that the degradation rate increases with an increase of the iron ions concentration, though the extent of increase is sometimes observed to be marginal above a certain concentration as reported by Rivas et al., (2001). An excess of ferrous ions can provoke inhibition of the photochemical degradation process due to the fact Fe^{2+} can compete with organic compounds by oxidant agents (hydroxyl radicals).

Application of Photo Fenton Process (H_2O_2 /Fe^{3+}/UV)

Fenton and photo Fenton processes have been used for the treatment of several types of wastewater including those produced in dye manufacture, pulp bleaching, agricultural processing and chemical manufacture. Photo-Fenton processes could be applied in treating many industrial wastewaters, i.e. wastewater from plastic industry, landfill leachate, dye house industry (Bauer & Fallmann, 1997), municipal wastewater

(Klamerth et al., 2010), pesticides (Gong et al., 2015), organic effluent (Modh et al, 2008), phenolic wastes (Hernández et al., 2017), and also wastewater from paper industry.

Heterogeneous Photocatalysis (TiO_2/UV)

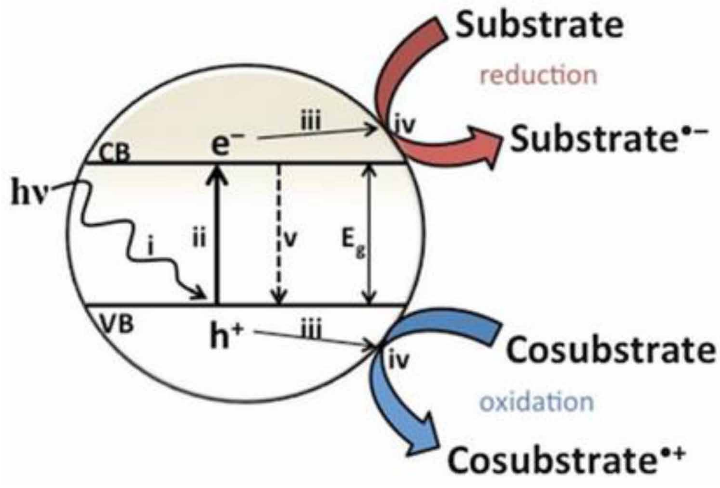
Photocatalysis is defined as the "change in the rate of chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance and the photocatalyst that absorbs light and is involved in the chemical transformation of the reaction partners" (IUPAC, 1997). Heterogeneous photocatalysis is also known as semiconductor photocatalysis where the process involves the semiconducting materials (photocatalyst) that is capable to absorb UV light and promotes a charge separation states that generate electron holes (sites on the semiconductor surface vacated by the electrons) (Quintero et al., 2015). The photocatalyst can be interpreted as a "catalyst able to produce, upon absorption of light, chemical transformation of the reaction partners. the excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of interaction" (IUPAC, 1997).

Solid semiconductors typically used as a photocatalyst. An example of the catalyst that can be used are titanium oxide (TiO_2), Zinc oxide (ZnO), Zirconium dioxide (ZrO_2) and Tungsten trioxide (WO_3) (Sud and Kaur, 2012). Yang et al, (2014) mentioned that heterogeneous catalysis with TiO_2 (UV/TiO_2) are amongst the most investigated AOPs system. This method is effective to degrade and mineralize toxic organic compounds in water and wastewater because of its inherent destructive nature and can be operated under ambient conditions (Sud and Kaur, 2012). At the same time, the method has been shown to be effective for the inactivation of various types of pathogenic microorganisms including some that are resistant to other method such as cholorination and ozonation (Malato et al., 2009; Robertson et al., 2012).

Generally, heterogeneous photocatalysis occurred at the surface of the photocatalyst (semiconductor materials), which is responsible to absorb the photon energy and provide the active site for the adsorption of the reactants (Byrne et al., 2015). The primary reactions that take place in the system are electrochemical oxidation or reduction reactions involving photogenerated hole and electron generated from the photo-excited semiconductor. Fundamentally, the electronic structure of most semiconductor materials are comprised of three parts which are highest occupied band full of electrons namely valance band (VB), a lowest unoccupied band called the conductance band (CB) and a region that is free of energy levels in between VB and CB called bandgap energy, E_g (Parsons, 2004). Figure 1 illustrated the electronic structure of semiconductor materials as well as the basic mechanism of heterogeneous photocatalysis.

In photocatalysis, adsorption of photons whose energy is equal or higher than the bandgap of semiconductor materials promotes excitation of the electron from VB to CB band, leaving a positive hole in the VB. The process is described as charge separation where electron–hole pairs of h_{VB}^{+} in the VB and e_{CB}^{-} in CB are generated (Parsons, 2004; Quintero et al., 2015). Typically, the fate of photogenerated electron/hole pairs is recombination as the energy is re-emitted as heat or light (Byrne et al., 2015). However, electrons that successfully migrate to the surface of the semiconductor during the charge separation states, act as oxidizing agent or reductant to the substrates/molecules adsorbed on catalyst surface producing intermediate products (Herman et al., 2010; Tolosana-Moranchel et al., 2017). The CB electron will be passed on to an electron acceptor (electrochemical reduction) while VB hole accepts electrons from donor species (electrochemical oxidation). Further treatment leads to mineralization of the intermediate products into CO_2.

Figure 1. Schematic of electronic structure and general steps of semiconductor photocatalysis or photocatalytic cycle: (i) light absorption, (ii) electron excitation, (iii) electron and hole migration, (iv) oxidation and reduction reaction and/or (v) recombination (Source: Quintero et al., 2015)



The most common semiconductor used as the photocatalyst in AOPs is titanium dioxide (TiO_2) because it is relatively inexpensive and readily available (Yang et al., 2014). According to Mattews, (1991), TiO_2 in the crystalline forms of anatase and brookite are the most effective for wastewater treatment. The oxidative degradation mechanism by TiO_2-Photocatalysed in aqueous system can be described by the following general equations (Spacek 1995):

$$\mathrm{TiO_2 + hv \rightarrow\ h_{VB}{}^{+} + e_{CB}{}^{-}} \tag{7}$$

$$\mathrm{h_{VB}{}^{+} + e_{CB}{}^{-} \rightarrow heat\,(recombination)} \tag{8}$$

$$\mathrm{TiO_2h_{VB}{}^{+} + compounds \rightarrow\ products_{0xidized}} \tag{9}$$

$$\mathrm{TiO_2h_{VB}{}^{+} + H_2O_{ad} \rightarrow\ TiO_2 +\ OH_{\ ad} + H^{+}} \tag{10}$$

$$\mathrm{TiO_2h_{VB}{}^{+} + OH^{-}{}_{ad} \rightarrow\ TiO_2 +\ OH_{\ ad} + TiO_2} \tag{11}$$

$$\mathrm{TiO_2e_{CB}{}^{-} + O_2 \rightarrow\ O_2{}^{-} + H^{+} + HO_2} \tag{12}$$

$$\mathrm{OH}\ _{\mathrm{ad}} + \mathrm{compounds} \rightarrow\ \mathrm{products}_{0\mathrm{xidized}} \tag{13}$$

Photocatalysis happened when the irradiation energy (hv) matched or exceeded the band-gap energy of TiO_2, electrons are promoted by UV-light or visible light and forms $h_{VB}{}^{+}$ and $e_{CB}{}^{-}$ electron pairs as showed by Eqn (7). Then, oxidation of organic compounds may occur directly on the semiconductor surface with electron holes (Eqn. (11)) or indirectly through a reaction with OH radical (Eqn. (13)). Equation (10) and Eqn. (11) represent the chemical reaction that produced OH radical in the aqueous system. The photogenerated holes that escape direct recombination (Eqn. (8)) also react with surface adsorbed hydroxyl groups or water to form OH radicals. The OH radicals that generated at the surface of TiO_2 leave the surface to a bulk solution to generate free OH radicals (Wang and Xu, 2012). Meanwhile, Eqn. (11) demonstrates the formation of superoxide radical anion ($O_2{}^{-}$) and hydroperoxyl radical (HO_2) on the surface of TiO_2. Overall, in the presence of oxygen and water, photocatalysis is able to produce a mixture of reactive oxygen species. The radical species is capable to inactivate microorganisms or degrade refractory organic compounds.

A study in UV/TiO_2 photocatalysis has been proven to remove a wide variety of organic pollutants from water and wastewater and deactivate a wide range of microorganisms (Robertson et al., 2012). Table 2 summarized the previous studies on the UV/TiO_2 processes.

There has been an argument on the degradation mechanism of pollutants by UV-TiO_2 as to whether photoreactions on the photocatalyst surface involved reactions with positive holes electron or surface bound OH● or in solution with free radicals (Li et al., 2007; He et al. 2008). For C.I. Reactive Black 5, Song et al, (2007) suggested that the degradation was mainly initiated by photolysis and/or $O_2{}^{-}$ in the bulk solution and then the cleavage of the naphthalene and benzene rings mainly attributed to the $h_{VB}{}^{+}$ pathway and OH radical reactions on the surface of the catalyst. Meanwhile, OH radical is the main species responsible for microorganism inactivation in water (Byrne et al., 2015). The full mechanism of photocatalytic inactivation is still unknown given the complexity or microorganisms. However, continuous attack by radical oxidant resulting in the damage of the cell wall, followed by compromise of the cytoplasmic membrane and direct attack of intracellular components as shown in Figure 2 (Sunada et al., 2003). Therefore, the radical oxidant produced during inactivation must be greater than that which the microorganism can protect against to ensure complete inactivation thereby preventing bacterial recovery and re-growth (Byrne et al., 2015).

Although TiO_2 photocatalysis showed good record in the decomposition of refractory contaminants and microorganism inactivation, there are still some drawbacks in the TiO_2 photocatalysis application. Bauer et al, (1999) stated that direct recombination of photogenerated electrons/holes and reduction of absorbed OH● by CB electrons are the reason for the low quantum efficiency in TiO_2-photocatalysis. Other than that, TiO_2 photocatalysts are unable to sufficiently absorb in the visible-light of the solar spectrum (Robertson et al., 2012).

In order to improve TiO_2 photocatalysis, more focus has been given to the enhancement of photocatalyst through doping metals, metals ions, semiconductor oxides, and nonmetal atoms such as Nitrogen, Sulfur, Iodine, and Cerium into TiO_2 to extend the absorption spectrum to visible light, slow the recombination rate of the electron-hole pairs and enhance the interfacial charge transfer efficiency (Zhao et al., 2005; Song et al., 2008). Through this method, the effectiveness of photocatalyst is highly improved whilst the electric power used as well as the operating cost can be significantly reduced (Wang and Xu, 2012).

Figure 2. Schematic illustration of the inactivation process of E. coli on photo-excited TiO_2 (Adopted from: Sunada et al., 2003)

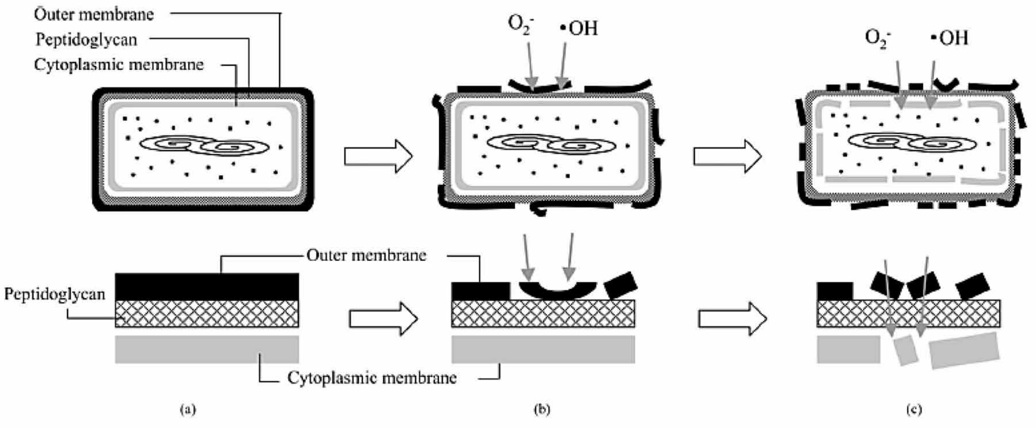


Table 2. Summary of the related studies of UV/TiO_2 photocatalysis for the removal of variety contaminants

Target contaminants	Matrix	Experimental condition	Removal efficiency/ remarks	References
Antibiotic Moxifloxacin (MOX)	Hospital effluent and demineralized water	UV-A, 4.0m W/cm2, 300 – 400 nm with mean peak at 365 nm TiO_2 loading at 1.0 g/L, Stirred at 13.2 rps and sparged with dry air (20 ± 1% O_2) at a flow of 60 ml/min, Temp, 25 ± 1 °C	The degradation rate of MOX in hospital effluent water during photocatalysis is 2 times lower than in demineralized water as a result of organic (humic and fulvic acid) and inorganic constituents (chloride anions and bicarbonate).	Van Doorslaer et al., 2015
Phenol	Synthetic water	UV-A 38 W/m2, 306-383 nm TiO^2 loading at 25 – 150 mg/L Atmospheric pressure Continuous oxygen flow of 75 Ncm^3/min	Hydrodynamic particle size of TiO_2 play an important role in the rate of photon absorption	Tolosana-Moranchel et al., 2017
Herbicide bentazon	Synthetic water	UV-A, 365 – 450 nm TiO_2 loading at 0.5 g/L,	Degradation of bentazon follows pseudo-first order kinetics and complete mineralization of ecotoxicity intermediated product achieved within 120 min of irradiation in the presence of 0.5 g/L TiO_2	Berberidou et al., 2017
Antibiotic Dicloxacillin (DXC)	Synthetic water	30-150 W, maximum emission at 365 nm TiO_2 loading at 0.-5 g/L Reactor temperature was controlled using mechanical ventilation	Degradation of DXC was carried out via hydroxyl radical attack following Langmuir–Hinshelwood kinetic behaviour	Villegas-Guzman et al., 2015
Pathogenic microorganism (*E. coli*)	Bacteria were grown under defined culture conditions to promote the expression of type 1 Fimbriae (filamentous, proteinaceous cell surface structures expressed by many enterobacteria)	UV-A, 2.86 mW/cm², 311 – 415 nm with mean peak at 368 nm) TiO_2 loading at 1.0 g/L, Bacterial suspensions containing TiO_2 was magnetically stirred throughout the experimental period and were kept in the dark,	*Escherichia coli* grown under conditions to express type 1 fimbriae demonstrated more resistance behaviour to photocatalytic destruction than control cultures, taking 75 min longer to be destroyed	Robertson et al., 2015

Other than that, the use of UV radiation lamps in AOPs for wastewater treatment is expensive (Malato et al., 2003). Thus, researchers have been leaning towards solar irradiation (e.g. light with a $\lambda > 300$ nm). The reduction in operating cost can be achieved when sunlight is used as the source of irradiation instead of UV-lamp (Sud and Kaur, 2012). However, three main conditions in the UV/TiO_2 system must be improved for its possible useful application which is 1) the depth of penetration of excitation light into aqueous TiO_2 suspension should be increased, 2) additional cost for catalyst recycling must be avoided and 3) an increase of the low quantum efficiency of the decomposition process on the excited photocatalyst should be attained (Bauer et al., 1999; Saein et al., 2009). Hofstadler et al, (1994) have proposed immobilization of TiO_2 on quartz glass fibres in the photoreactor as the solution to the two first issues while doping of TiO_2 with different materials can help to solve the third problem (Hoffmann et al., 1995).

Hybrid Method

Advanced oxidation processes (AOPs) for water and wastewater treatment continues to progress with better alternative and improvement. In AOPs treatment processes, one of the most important elements that need to be considered is the quantity of oxidant required to destroy target contaminants (Crittenden et al., 2012). Consequently, many efforts have been put in improving the efficiency of AOPs as oxidative decontamination method by enhancing the production rate of $OH^•$. Hybrid method has been studied to improve and overcome the shortcomings or weaknesses in AOPs technologies to achieve this purpose. Hybrid technique of AOPs can be described as a combination of individual AOPs techniques that can accelerate production of $OH^•$ to affect water treatment (Kumar et al., 2012). The production of $OH^•$ can be obtained through various alternatives way which makes AOPs versatile technologies. The combination of AOPs typically involves individual techniques such as UV/O_3 and O_3/H_2O_2 or H_2O_2/Fe^{3+}/UV, and TiO_2. Combining different AOPs usually causes interesting synergistic effects that significantly reduce the reaction time and cost.

UV/O_3/H_2O_2

A hybrid AOP of UV/O_3/H_2O_2 is a combination of AOP technique or system that consist of UV, O_3 and H_2O_2. This combination was claimed to be more effective than individual AOP such as UV/O_3, UV/H_2O_2 and O_3/H_2O_2. Previous studies (Wu, 2008; Cardoso et al., 2016) stated that pH plays an important role in H_2O_2 and ozone related processes. A more hybrid system involving H_2O_2 will perform better under acidic conditions. Oppositely, ozone related AOPs achieved better pollutants degradation efficiency in alkaline condition. Therefore, pH must be adjusted accordingly when H_2O_2 or ozone based treatment is used and change to neutral pH at the end of the treatment. Hence, AOPs system with better efficiency under the neutral condition is preferable and more economical (Wu, 2008).

According to Wu et al, (2008), UV/O_3/H_2O_2 demonstrated better decolourization efficiency of C.I. Reactive Red 2 (RR2) than UV/O_3 and O_3/H_2O_2 at pH 4 (acidic) and pH 7 (neutral) indicating H_2O_2 is the dominant oxidant in the system. Combining UV with O_3/H_2O system overcome the inhibitive effects of O_3/H_2O_2 such as low oxidation ability of H_2O_2 and OH radical scavenging by H_2O_2 which help to accelerate decolourization. In contrary, O_3/H_2O_2 system gives better efficiency than UV/O_3/H_2O_2 under alkaline condition (pH >7). It was suggested that O_3 is the dominant oxidant instead of H_2O_2 for the O_3/H_2O_2 system. The combined system of UV/O_3/H_2O_2 is more effective than O_3/H_2O_2 under neutral pH (pH 7), make it more economical treatment option.

Similarly, adding O_3 to UV/H_2O_2 can enhance decolorization efficiency of the system. The finding by Wu, (2008) revealed that UV/O_3/H_2O_2 performed better than UV/H_2O_2 system under neutral pH. In the UV/O_3/H_2O_2 system, the reaction of contaminants degradation are explained by combining Eqns. (14), (15) and (16), which shows hybrid system has a higher decolorization rate than the UV/O_3, UV/H_2O_2 and O_3/H_2O_2 systems.

$$H_2O_2 + hv \rightarrow 2OH \tag{14}$$

$$O_3 + H_2O + hv \rightarrow O_2 + H_2O_2 \tag{15}$$

$$O_3 + H_2O_2 + hv \rightarrow O_2 + HO_2 \tag{16}$$

Under alkaline conditions, H_2O_2 can react with O_3, producing hydroxyl and hydroperoxyl radicals (Eq. (16)) (Brillas et al., 2004). However, the same reaction (Eq. (16)) does not apply when the system is under acidic and neutral condition.

Photo-Fenton Processes Combined With TiO_2

Photo-Fenton processes involve a very complex photocatalytic reaction but is among the most effective AOP method to produce OH radicals. In photo-Fenton processes, two types of reaction involved in a generation of OH radicals. Apart from Fenton reaction, photo-Fenton continuously generated OH● through a reaction presented by Eqn. (17) to (20) (Kavitha and Palanivela, 2004). The simplified reaction of the photo-Fenton process is already shown by Eqns. (5) and (6). The photo-generated Fe^{2+} participate in the photo-Fenton reaction (Eqn. (6)) producing additional OH● that increases the oxidation rate in the system (Kavitha and Palanivela, 2004). Other than that, iron complexes play an important role in the degradation of compounds. The irradiated Fe(III) complexes undergo ligand-to-metal charge transfer which represents by Equation. (17) (Bauer et al., 1999).

$$\mathrm{Fe(III)\text{-}L} + hv \rightarrow [\mathrm{Fe(III)\text{-}L}]^+ \rightarrow \mathrm{Fe(II)} + L^{\bullet} \tag{17}$$

The possible ligands L include OH^-, H_2O, HO_2^- and carbohydrates. As an example, irradiation of ferric ions produced in aqueous solution leads to the formation of ferrous ion and OH● from reduction process as shown in Eqn. (18) (Faust and Hoigne, 1990). Meanwhile, the photo-decarboxylation of ferric carboxylate can be described using Equations (19) and (20) (Safarzadeh-Amiri et al., 1997).

$$\mathrm{Fe(III)OH_2}+ + hv \rightarrow \mathrm{Fe(II)} + OH^{\bullet} \tag{18}$$

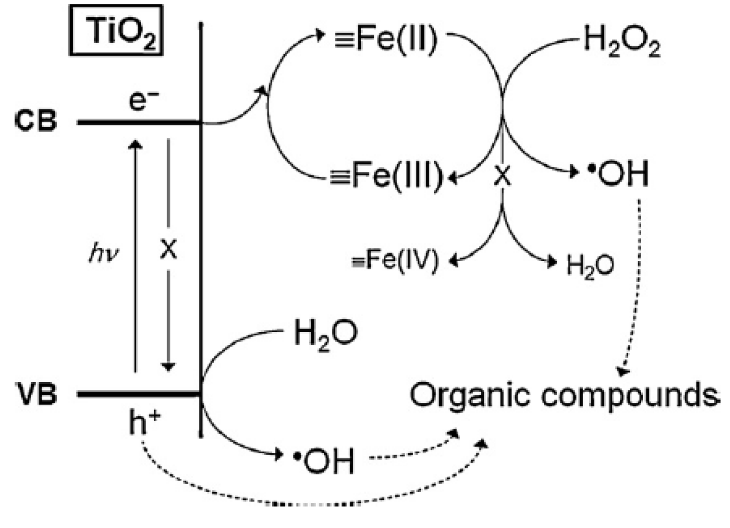
$$\mathrm{Fe(III)(RCO_2)}^{2+} + hv \rightarrow \mathrm{Fe(II)} + CO_2 + R^{\bullet} \tag{19}$$

$$OH^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow \text{Products} \quad (20)$$

Integration of two different AOPs often provides synergistic reaction routes for the generation of $OH^{\bullet}$. Several studies also reported an enhancement in oxidation of contaminants by UV/TiO_2 system with an addition of Fe(III) (Choi et al., 1994; Tryba et al., 2006) or simultaneous addition of Fe(III) and H_2O_2 (Mbaye et al., 2012). Kim et al, (2012) have investigated synergistic production of $OH^{\bullet}$ in the combined system of TiO_2 photocatalysis (UV/TiO_2 system) and Fenton system. Based on the finding, the combination of both systems can lead to acceleration in the production of $OH^{\bullet}$ even under circumneutral pH condition which is unfavorable for Fenton oxidation. The addition of Fe(III) significantly accelerated H_2O_2 decay which would likely enhance generation of oxidizing species and increase the degradation rate by 3.4-4 times. The reaction routes of oxidation in UV/TiO_2/Fe(III)/H_2O_2 is presented in Figure 3.

The presence of iron in the UV/TiO_2/Fe(III)/H_2O_2 system offers two reaction pathways for synergistic production of $OH^{\bullet}$ under neutral pH conditions. Firstly, Fe(III) absorbed onto TiO_2 surface was reduced to ferrous ion (Fe(II)) by CB electron whilst preventing recombination of electron-hole pairs. At the same time, VB holes are ready for oxidation of adsorbed organic compounds and for oxidation of surface-bound hydroxyl groups as well as adsorbed water molecules into $OH^{\bullet}$. In this system, reoxidation of Fe(II) by H_2O_2 and reduction by CB electron enables the catalytic cycle of Fe(II)/Fe(III) which helps in maintaining the level of Fe(III) as an electron acceptor. This cycle does not occur in other Fenton processes such as TiO_2/Fe(III)/H_2O_2, UV/Fe(III)/H_2O_2 and Fe(III)/H_2O_2. As a result, Fe(II) accumulated on TiO_2 surface and hindering electron-scavenging by iron leads to inefficient H_2O_2 decomposition (i.e. reoxidation of Fe(II)) did not occur) as reported by Lee et al, (2009) and Pham et al, (2009) in Fe(III)/H_2O_2 (or UV/Fe(III)/H_2O_2) system. The second pathway is where the Fe(II) species bound to the photo-excited TiO_2 surface converting H_2O_2 into reactive oxidant (e.g. $OH^{\bullet}$) which is typically produced by the Fenton reaction under neutral pH.

Figure 3. Schematic diagram representing the reaction pathway in UV/TiO_2/Fe(III)/H_2O_2 system (Kim et al., 2012)



Intensive studies have been conducted in relation to photocatalytic water and air purification using TiO_2-based photocatalyst with 75% of articles published in between 2009 to 2012 were associated with this treatment (Di-Paola et al, (2012). It was found that a major drawback to TiO_2 photocatalysts is its inability to sufficiently absorb in the visible-light of the solar spectrum (Robertson et al., 2012). Thus, artificial UV-light is required in the treatment. However, the use of artificial UV-light causes the treatment to become less economical as a large amount of energy must be used. A different alternative was sought to overcome this problem. In the attempts to enhanced TiO_2 photocatalytic efficiency, a combination of TiO_2 with other catalyst or oxidizing agents only give a small difference compared to TiO_2 alone (Di-Paola et al, (2012). However, modified TiO_2 (calcinated or implanted with other materials) demonstrates great changes in effectiveness to absorb in the visible region (Jack et al., 2015).

In a study conducted by Tryba et al, (2006), photo-Fenton process was combined with carbon coated TiO_2 for phenol degradation. It was reported that the degradation rate of phenol was significantly improved through this technique and complete mineralization of phenol is achieved in a very short time. The mechanism of phenol decomposition by photo-Fenton C-TiO_2 was governed by the complex reaction with iron and intermediate of phenol decomposition instead of radical reaction. As a result, the combined system is able to broaden the range of degradable contaminants through the reactivity of the oxidant produced from the complexes reaction. In a different study (Asiltürk et al., 2009), Fe doping of TiO_2 also exhibits excellent performance for removal malachite green dye. It was believed that the improvement was contributed by the shift in the optical absorption and increase of the surface area as a result of TiO_2 modification.

The iron based photocatalyst is one of the promising treatment technique in AOP since it has the potential to provide energy efficient photocatalyst for decomposition of toxic and refractory organic pollutants due to good visible light photoactivity. Moreover, iron characteristics such as non-toxic, inexpensive and easily acquired make it more appealing as catalyst. Photo-Fenton process has emerged as one of prominent technique to treat chemical contaminants but the number of studies focusing on microorganisms is significantly inferior (Giannakis et al., 2017). Combination of photo-Fenton with TiO_2 may further improve the inactivation of the harmful bacteria since TiO_2 photocatalysis known as one of most effective treatment for killing microbial pathogens. According to Jack et al, (2015), Fe-TiO_2 and FeO_2-TiO_2 are among the promising iron-based photocatalysts for future investigation.

Photocatalytic Ozonation (O_3/UV/TiO_2)

Generally, O_3 is a powerful oxidant than other agents such as H_2O_2 with some application in potable water and wastewater treatment. The organic compounds degradation by ozonation can be attained through direct or indirect reactions and is claimed to be more powerful than photocatalysis. It is also better in treating concentrated contaminants (Augugliaro et al., 2006). However selective behavior of O_3 and slow mineralization of organic compounds give a limitation in O_3 application (Hoigné, 1998). Meanwhile, photocatalysis is known to be adequate for the destruction of a wide variety of compounds but mineralization of intermediate products is slowly attained because of the low oxidation rate. Additionally, the technique is advantageous only for low concentration of solutes (Augugliaro et al., 2006). Thus, O_3 sometimes combined with catalyst that can convert O_3 into secondary oxidants (mainly $OH^\bullet$) which is more reactive and unselective by nature that are capable to react with various types of compounds (Hoigné, 1998).

The combination of heterogeneous photocatalysis with ozonation is carried out with the aim to enhance the overall mineralization of refractory organics (Xiao et al., 2015). In relation to inactivation of waterborne pathogens, photocatalytic ozonation is found to substantially reduce the contact time required to completely inactivate the pathogens by 50 – 75% compared to individual treatment process (Mecha et al., 2017). Combining individual AOPs usually generates interesting synergistic effects that can significantly increase the reaction rate (Wu and Ng 2008). It was revealed that this combination gives a dramatic synergistic effect which leads to an increase in treatment efficiency, shorter reaction time and cost reduction (Augugliaro et al., 2006; Wng and Xu, 2012). Therefore, the combined system of heterogeneous photocatalysis with ozonation has great potential for the reduction of recalcitrant pollutant and pathogenic microorganisms (Xiao et al., 2015; Mecha et al., 2017).

Generally, photocatalytic processes are referring to the use of semiconductor metal oxide as catalyst and oxygen as oxidizing agent (Ollis and El-Ekabi., 1993). According to several studies, the degradation efficiency of organic compounds by some catalytic ozonation systems such as O_3/Mn^{2+}, O_3/Co^{2+} (Raady et al., 2005), O_3/MnO_2 (Wu et al., 2007) and $O_3/UV/TiO_2$ (Domínguez et al., 2005; Yang et al., 2007) exceeds ozonation alone. Typically, the effectiveness of catalytic ozonation applied is strongly dependent on the catalyst.

Photocatalytic ozonation combined the photolysis ozonation with Titanium (TiO_2) as catalyst. In photocatalysis, TiO_2 is the catalyst of choice since it is less expensive, chemically stable, high photocatalytically active and non-toxic (Mills et al., 1997). During the treatment process, contaminants in water and wastewater can be degraded either by $OH^\bullet$ radicals produce fromTiO_2 photolysis or OH radicals generated from a sequence of reactions when O_3 captures an electron of CB (Cardoso et al., 2016). The use of electron from CB prevents the recombination of electron/hole pairs and improves the production of $OH^\bullet$ through oxidation by photogenerated hole at TiO_2 VB. These reactions link to the resulting synergistic effects which are seen as a promising technique for degradation of refractory microorganism and unbiodegradable contaminants in water (Cardoso et al., 2016). Figure 4 shows the proposed routes to the formation of radical oxygen species, organic compounds degradation and intermediates products mineralization.

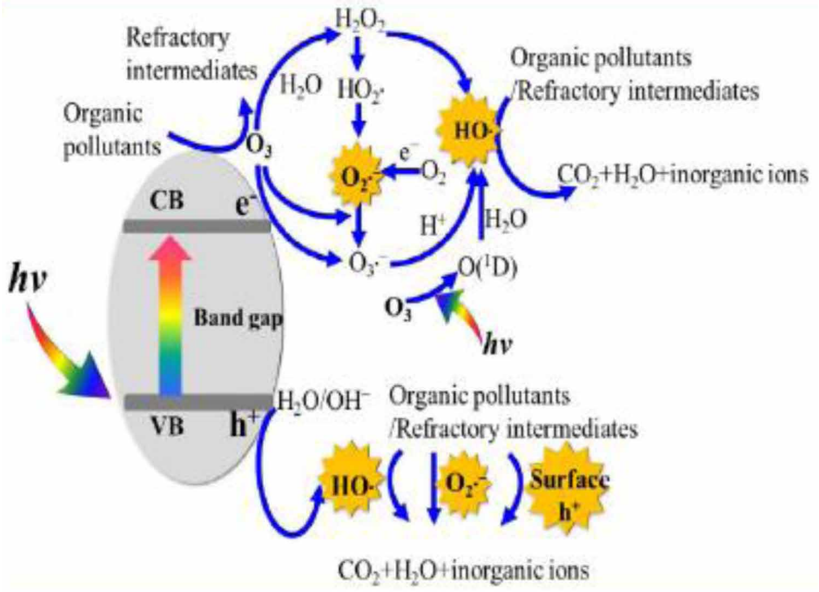
Wu and Ng, (2008) investigated the decolourization efficiency of $O_3/UV/TiO_2$ system and the possible reaction pathway of this AOP system. The possible pathway of $O_3/UV/TiO_2$ system can be described using several equations from TiO_2-Photocatalysis reaction and ozonation (Cardoso et al., 2016). The experimental finding by Wu and Ng, (2008) suggested that OH radical plays a major role in RR2 decolourization by $O_3/UV/TiO_2$ system. Meanwhile, photogenerated holes are the minor oxidants. A similar finding was also presented by other studies (So et al., 2002; Daneshvar et al., 2003).

$$\mathrm{TiO_2 + hv \rightarrow\ h_{VB}{}^{+} + e_{CB}{}^{-}} \tag{21}$$

$$\mathrm{TiO_2h_{VB}{}^{+} + H_2O_{ad} \rightarrow\ TiO_2 +\ OH\ _{ad} + H^{+}} \tag{22}$$

$$\mathrm{O_3 + TiO_2e_{CB}{}^{-} \rightarrow\ O_3{}^{-}} \tag{23}$$

Figure 4. Schematic illustration of photocatalytic ozonation pathway (Adopted from Xiao et al., 2012)



$$O_3^{\ -} + H^+ \rightarrow \ HO_3 \tag{24}$$

$$HO_3^{\ -} + H^+ \rightarrow \ OH \ \ + O_2 \tag{25}$$

$$O_3 + H_2O_2 + hv \rightarrow H_2O_2 + O_2 \tag{26}$$

$$Dye + OH \ \ \rightarrow \ products \tag{27}$$

$$TiO_2h_{VB}^{\ \ +} + Dye \rightarrow \ products \tag{28}$$

According to Hernández-Alonso et al, (2002), O_3 strongly reacts with TiO_2 electron holes to form ozonide radicals ($O_3^{\ -}$) (Eqn. 23). Then, hydroxyl radicals are formed on the TiO_2 surface through the reaction between $O_3^{\ -}$ with hydrogen (Eqns. (24) and (25)). The formation of hydroxyl ($OH^\bullet$) on irradiated TiO_2 surface is more active in the presence of O_3 than oxygen (Addamo et al., 2005). This is because O_3 capable of trapping and suppressing the recombination of photogenerated electron and holes which increases the production of $OH^\bullet$ (Wu & Ng, 2008). Moreover, under UV irradiation, O_3 can react with H_2O generating H_2O_2 (Eqn. (26)) which is another strong oxidizing agent. The reaction involved have improved decolourization and reduce the treatment time.

However, the right amount of ozone to TiO_2 dose must be applied. Several studies (Yang et al., 2007; Mehrjouei et al., 2015) reported that large amount of TiO_2 does not significantly increase the oxidation rate. Contrarily, adding large amount of TiO_2 may reduce UV penetration and subsequently declines the yield of photogenerated holes and hydroxyl radical production. Other factors that influence photocatalysis performance and ozonation are pH and amount of by-products in solution and catalyst surface area. In ozonation, Cardoso et al, (2016) mentioned that alkaline pH is able to increase O_3 decomposition for OH radicals while under acidic pH (pH < 3) direct O_3 attack namely ozonolysis occur. Typically, reactions of ozone with organic compounds lead to the formation of aldehydes and carboxylic acids. Both compounds do not react with O_3 which make it critical limitation in ozonation as complete mineralization of intermediate products could not be achieved. Consequently, radical degradation by $OH^\bullet$ is needed to obtain good compounds degradation as well as mineralization of intermediates products. A synergistic effect formed when O_3 is combined with photocatalysis. As a result, the efficiency of contaminants degradation is remarkably accelerated compare to when the treatment conducted separately (Bassegato et al., 2016).

In more recent years, combination of photo electrocatalyst and ozone gain more attention. The hybrid techniques are promising AOP system that could significantly enhance charge separation of TiO_2 electron/hole pairs which lead to more OH radicals produce (Bessegato et al., 2016; Cardoso et al., 2016; Segura & Brillas, 2017).

Vacuum UV (VUV) Oxidation

Vacuum UV (VUV) light application is closely related to water photolysis. In contrast to photooxidation and photocatalysis, the generation of reactive species such as OH radicals, $H^\bullet$, e_{aq}^-, $HO_2^\bullet$, and $O_2^{\bullet -}$ in this system requires no additional chemicals. The reactive oxidation species were generated through the homolysis of water by VUV irradiation during water photolysis (Schulze-Hennings et al., 2016). The radiation wavelength of VUV which is between 100 to 200 nm is used because water strongly absorbs UV light lower than 200 nm especially at 172 nm. There are two common ways for VUV photons generation, which are either by using excimer lamps or ozone generating low-pressure lamps (VUV-Hg lamps) (Duca et al., 2017). The two important reactions pathway for OH radical formation during VUV radiation/water system are: 1) photochemical homolysis of water (Eqn. (29)) and 2) photochemical ionization of water (Eqn. (30)). Due to the direct formation of OH radicals, VUV-radiation is counted as one of AOP technique. The formed products also include hydrogen atom and solvated electrons.

$$H_2O + hv_{<200nm} \rightarrow HO^\bullet + H^\bullet \quad (29)$$

$$H_2O + hv_{<200nm} \rightarrow HO^\bullet + e^- + H^+ \quad (30)$$

Degradation of contaminants by VUV oxidation can take place in several ways. Like other UV-based AOPs, the primary process in this system is governed by the reaction between OH radicals with the contaminants. Intermediate products are generated from this reaction (Eqn. (31)).

$$\text{Pollutants} + HO^\bullet \rightarrow \text{Products} \quad (31)$$

Direct photolysis of organic compounds by 254 and 185 nm irradiation is another possible reaction that may occur in the system. Equation (32) and (33) represents the direct photolysis reactions.

$$\text{Pollutants} + hv_{254\text{nm}} \rightarrow \text{Products} \tag{32}$$

$$\text{Pollutants} + hv_{185\text{nm}} \rightarrow \text{Products} \tag{33}$$

According to Oppenländer, (2007), the main drawback of water photolysis with VUV is short light penetration depth which prevents its employment for large scale application. Therefore, in a study conducted by Schulze-Hennings et al, (2016), light with higher penetration depth (light irradiation at 193 nm) than 172 nm was used for water photolysis. It was proved that the degradation of micropollutants was improved. This result makes for an interesting finding to overcome the weakness of VUV oxidation and can be the basis for further improvement of the system.

Besides that, an existence of various inorganic ions in water can affect the performance of VUV in many ways. These ions can influence the processes by (Duca et al., 2017):

- Absorbing the incident radiation, causing the process to be less efficient since fewer photons are available for the reaction with water
- Scavenge $OH^{\bullet}$, resulting in low $OH^{\bullet}$ concentration for oxidation
- Generate radicals when photolyzed

It is also well known that common inorganic ions in water such as nitrous acid/nitrite, nitrate and bicarbonate/carbonate can react with OH radicals. The reaction between these ions and OH radicals will produce another radical species. Equation (34) to (37) is used to describe the reactions.

$$NO_2^- + OH \rightarrow NO_3H \tag{34}$$

$$NO_2^- + OH \rightarrow OH^- + NO_3H \tag{35}$$

$$OH + CO_3^{2-} \rightarrow OH^- + CO_3^- \tag{36}$$

$$OH + HCO_3^- \rightarrow H_2O + CO_3^- \tag{37}$$

Radical species like CO_3^- is less reactive than OH but can still react with organic compounds in water and provide some degree of decontamination. Duca et al, (2017) have investigated the effect of the scavenging ions in atrazine degradation by VUV oxidation. The finding demonstrated that the presence of nitrate, carbonate and bicarbonate gives detrimental effect to the VUV system. For disinfection purposes, OH radical produced from VUV-radiation plays the main role in the microorganism destruction.

Comparison of Performance

Basically, all UV-based AOPs operated by means of photochemical reactions. The main principal mechanism in this treatment processes is the use ultraviolet light to initiate generation of hydroxyl radicals or other radical oxidant species used to destroy persistent organic pollutants and inactivate pathogenic microorganisms present in water and wastewater. Thus, there are differences in the degradation and mineralization rate of each treatment depending on the oxidizing agent or catalyst applied. Combining two or more AOPs techniques alter the reaction pathways which enhance free radical generation and eventually leads to higher oxidation rates. Therefore, hybrid AOP method is usually more efficient and possibly capable of attained complete oxidation of organic matter present in the aqueous system. Although combined system demonstrated greater pollutants oxidation, there are still some inherent disadvantages of this system. The major advantages and disadvantages of UV-based AOPs discussed in this chapter are summarized in Table 3

CONCLUSION

Advanced oxidation processes are a versatile treatment technique that make use of different reacting systems for the degradation of refractory organic compounds or inactivation of microorganism in water and wastewater treatment. Among various AOPs techniques, UV-based AOPs gain high recognition due to the effectiveness in destroying target micropollutants as well as inactivation of pathogens. The most important feature in the UV-based AOPs is production of OH radicals. It's non-selectivity behavior and extraordinarily reactivity is a useful attribute as an oxidant for destroying wide range recalcitrant pollutants. Similarly, pathogens microbial inactivation also depends mainly on the OH radicals. Although the disinfectant source changes, the equation remains similar. To date, an application of AOPs are still challenging given the pollutants in potable water and wastewater appeared extremely complex because of the revolution of chemical industries. The presence of various compounds and substances in the water pose underlying challenge that remains on the development of systems for treating large volumes of water. Among UV-based AOPs, the hybrid method seems to be more promising than an individual UV-AOPs. The combination of AOPs overcome some of the inherent problems in the individual AOPs and at the same time improving the performance of the treatment system. Complete mineralization of

Table 3. Advantages and disadvantages of UV-based Advanced Oxidation Process (AOP)

AOP process	Advantages	Disadvantages	References
H_2O_2/UV	● UV irradiation serve as disinfectant ● Existing of full-scale drinking water treatment. ● Efficient in mineralizing organic pollutants H_2O_2/UV treatment was more efficient than the Photo-Fenton process in the overall TOC removal efficiencies of the nonylphenol polyethoxylate surfactant. This is supported by studies conducted by Antonopoulou et al., (2014).	● Turbidity can interfere with UV light penetration ● Less stoichiometrically efficient at generating $OH^\bullet$ than O_3/UV process. ● H_2O_2 has poor UV absorption characteristics. ● If the water matrix absorbs a lot of UV light energy, most of the light input to the reactor will be wasted.	Krishnan et al, 2016; Laura et al., 2014; Grote, 2012.
O_3/UV	● High efficiency in water treatment. ● More efficacy than O_3 and UV ● More efficient at generating OH than H_2O_2/UV process for equal oxidant concentrations. ● Disinfection action.	● More energy consuming and cost is high enough. ● Turbidity can impede with UV light penetration ● Ozone diffusion can result in mass transfer limitations.	Krishnan et al, 2016; Grote, 2012
Photo Fenton H_2O_2/Fe^{3+}/UV	● Eco-friendly to aqueous environment ● Cycle regeneration of the consumed Fe^{2+} ions on illumination ● The reactions can convert toxic compounds into non-toxic or less hazardous products ● high efficiency and cost-effective	● Produce high concentration of anions in the treated wastewater. ● May produce large amounts of ferrous iron sludge. ● Need for acidic conditions	Krishnan et al, 2016; Wang and Xu 2012; Babuponnusami, 2011; Babuponnusami and Muthukumar, 2014.
TiO_2/UV	● Activated with near UV-light, consequently greater light transmission is achievable ● Destruction of a wide variety of compounds by hydroxyl radical formed ● high efficiency in inactivation of pathogens	● Fouling of the catalyst may occur ● TiO_2 residual must be recovered ● Mineralization is slowly attained due to its low oxidation rate ● Advantageous only for very dilute solutions ● Disinfection, using TiO_2 as photocatalyst, is limited by slow oxidation rate, which results from low quantum efficiency values ● Possibility of bacteria regrowth	Crittenden et al., 2012 Byrne et al., 2015 Robertson et al., 2012 Mecha et al., 2017
photo-Fenton processes combined with TiO_2 ($H_2O_2/Fe^{3+}/UV/TiO_2$)	● Drastic enhancement of $OH^\bullet$ production even under neutral pH condition ● Increase the degradation rate by 3.5-4 times compare to individual AOP ● Enhanced charge separation by H_2O_2 as an electron acceptor and the reductive conversion of H_2O_2 to $^\bullet OH$	● Not effective under alkaline condition ● H_2O_2 decomposition via a nonradical mechanism, which possible involves the formation of Fe(IV), which has a weaker oxidation power relative to ●OH	Tryba et al., 2006 Kim et al., 2012
$O_3/UV/TiO_2$	● Decompose organic substances more quickly and thoroughly ● High mineralisation rates ● Can increase the treating efficiency and shorten the reaction time ● Simple process and lower operating cost ● Reduced contact time required for inactivation of pathogenic microorganisms ● Overcome the bacterial regrowth problem	● Required to choose suitable photocatalyst ● The right ratio of ozone to catalyst must be applied ● More attention should be focused on the immobilisation of photocatalyst particles onto inert substrates, ● Need for acidic conditions	Mehrjouei et al., 2015 Cardoso et al., 2016 Bassegato et al., 2016 Mecha et al., 2017
VUV oxidation	● Chemical free process ● Excimer lamps can emit high-power quasi-monochromatic radiation at various wavelengths	● Short light penetration depth brings about a significant mass transfer issue, which lowers the efficacy of the process.	Duca et al., 2017 Oppenländer, 2007

bio recalcitrant compounds present in water and wastewater is possible to be achieved through these techniques. However, the ability of each AOPs system in dealing with multiple compounds is rarely discussed. This is because most of the previous studies reported AOP performance that deals with single compounds solution. Thus, there is a need to develop predictive models for system with multiple substrates. Aside from that, operating cost is often seen as an important factor that is usually considered in the selection of method for treatment. UV-based AOPs are driven by external energy sources such as electric power, ultraviolet radiation (UV) or solar light. Thus, these processes are often more expensive than conventional biological or chemical in water and wastewater treatment. The costs of UV-based AOPs are closely related to the efficiency and operational time of the processes. For example, heterogeneous photocatalytic or hybrid photocatalytic processes snown to be very effective in killing the pathogenic microorganisms but longer exposure time is required. There is also a risk of bacterial regrowth in the system after the treatment. Therefore, treatment processes with better techniques which are faster, more efficient and simpler are necessary to ensure high water quality treatment can be achieved whilst protecting the environment and reduce the operational cost.

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