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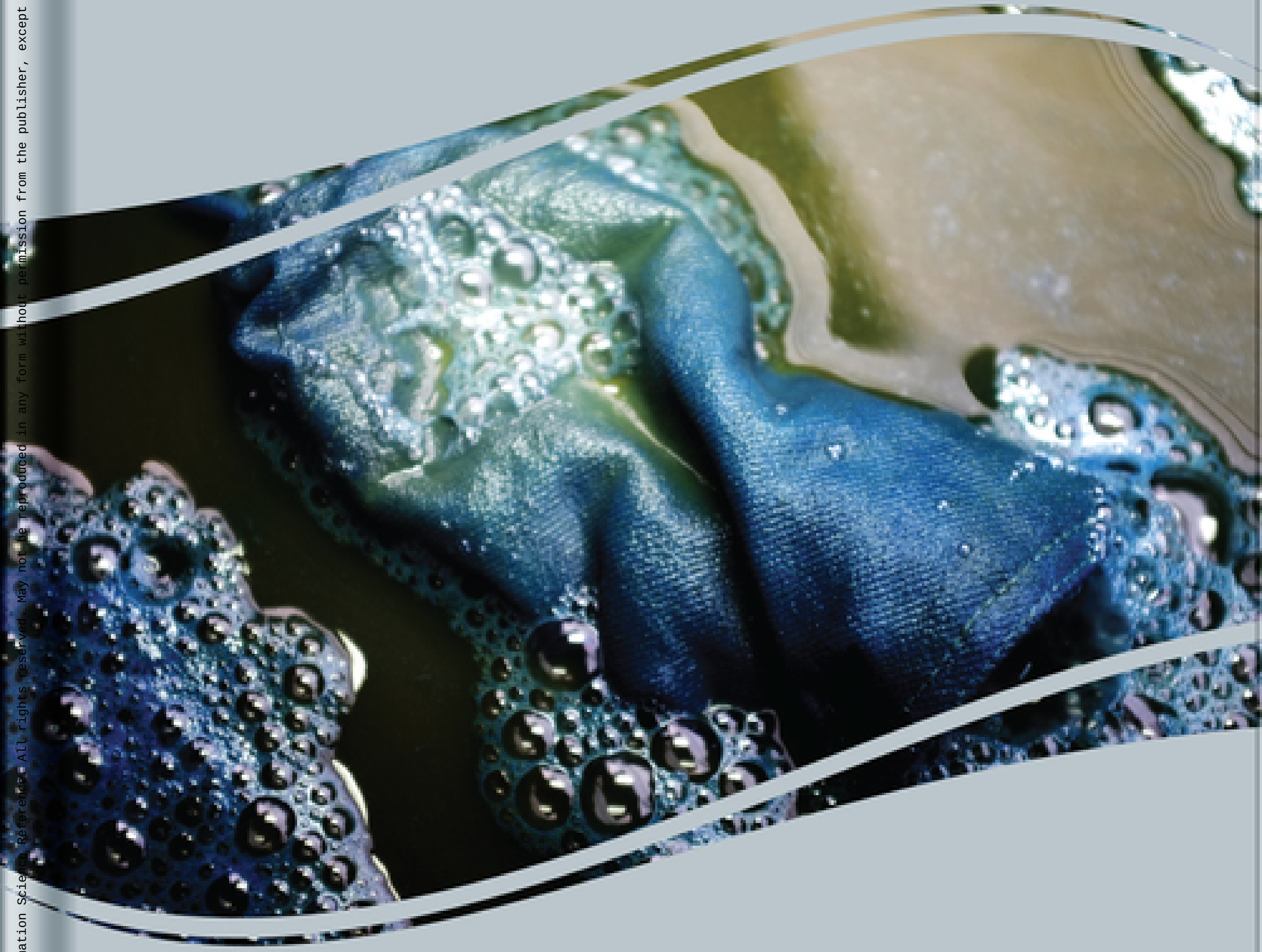
Impact of Textile Dyes on Public Health and the Environment



Khursheed Ahmad Wani, Nirmala Kumari Jangid,
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Impact of Textile Dyes on Public Health and the Environment

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Table of Contents

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 8

Chapter 9

Detailed Table of Contents

Chapter 1

The textile sector is 14% of total industrial production in India and contributes to about 4% of the gross domestic product and earns about 27% of India's total foreign exchange. Worldwide, up to 10,000 dyes are available and their annual production is above 7×105 metric tons, which are being used not only in textile sector but also applied in paper, food, and pharmaceutical industries. Textile industries in India have been consuming more than 100 L of water to process 1 kg of textiles and have contributed heavily in polluting surface and ground water resources in many regions of the country. The toxic and carcinogenic effect of untreated textile effluent is well understood. The decolorization and detoxification of industrial dye effluents is the most important aspect and is a major concern to meet environmental regulations. This chapter presents a review of literature on the significance of bioremediation technologies over other physicochemical methods for efficient removal of textile dyes from industrial waste effluents to improve the fragile ecosystems in different regions of the world.

Chapter 2
Classification, Chemistry, and Applications of Chemical Substances That Are Harmful to the Environment: Classification of Dyes 20
Sonika Jain, Banasthali Vidyapith, India
Pankaj Kumar Jain, Banasthali Vidyapith, India

A detailed classification of dyes has been discussed along with their chemical class and chemistry. International, regional, and national classification and labeling systems are already established and tested in practice. These hazardous chemicals can be liquid, solid, gas, aerosol, mists, vapors, semisolid, etc. Hazardous chemicals have wide applications (e.g., dyes, which are used for coloring purpose; pesticides, which are used for pest control; fertilizers are an essential part of the agriculture system; plastic and plastic waste; and e-waste to name a few). In this chapter, the authors deal with the identity, classification, and application of these harmful chemicals, especially dyes, which are mandatory to use. More emphasis is given to the natural and synthesized dyes about their use along with their modrants, which are a necessary part of the dyes without which they can't exhibit colors. Dyes have wide variety of applications, which have also been discussed along with their various harmful effects on environment, mankind, and aquatic life.

Chapter 3
Toxicology of Dyes 50
Aarti Singh, Indian Pharmacopoeia Commission, India
Anupama Mittal, Indian Pharmacopoeia Commission, India
Nirmala Kumari Jangid, Banasthali Vidyapith, India

Colours play a prominent and dominant role in human life. The dominating feature of any product has been found with its colours elevating the market of colouration in different sectors. Studies have shown that around 10,000 dyes are being circulated in market. Chemistry has been found to lead this industry of colours. Vast production of fabric colours include azo dyes, whereas anthroquinone is also one of the prevailing complexes for cotton and fabric dyeing. The toxic level of the dyes and pigments are not confined till manufacturing but also have after usage effect of the products. It has been found that the chemicals have a carcinogenic effect on human health. During the manufacturing procedure, around 50% of dye stuff gets along with the effluents of the industry leading to release of colourful water. Modification in choice of chemicals is being considered to lessen the toxic effects of existing complexes. This chapter is mainly focused on the toxicology of dyes.

This chapter highlights water quality parameters of Rajasthan state using satellite remote sensing and GIS technology. Water and soil quality indices have been applied to identify and assess the magnitude of contamination due to textile effluents in the surroundings of textile industries. In the resultant indices, variability caused due to presence of textile effluents is prominently visible and interpreted with geo-statistical representations. Visible change in soil and water quality has been observed in surroundings of textile industries all over the Rajasthan state. Significant variations have been observed in Pali, Sanganer, Bhilwara regions due to presence of textile industries. To conclude, remote sensing and GIS technologies along with natural resource parameters as utilized in the study can be performed for generating assessment reports for extended area at regional as well as national level and providing backgrounds in formulation of government policies for sustainable development and management of textile industries.

As the textile industries use aqueous method for dyeing processes, the color that is released in the environment is associated with the incomplete absorption of dyes on fibres. So, there is a strong need to reduce the amount of residual dye in textile effluent. Large amounts of liquid wastes are produced from textile industries that contain both organic and inorganic compounds. The degradation of azo dyes is difficult using the conventional processes. These complex azo dyes containing N=N bond have been found to show carcinogenic evidences on reductive cleavage. Azo dyes have capability to alter physical and chemical properties of soil, causing harm to the water bodies. Dyes are toxic in nature, which is lethal for microorganisms present in soil affecting agricultural productivity. The presence of azo dyes in water decreases its water transparency and water gas solubility. This reduces light penetration through water, decreases its photosynthesis activity, causing oxygen deficiency and de-regulating the biological cycles of aquatic system.

Among the different substances containing organic compounds, dyes are considered the most important class, and they are now an essential requirement in the modern world, mostly in the textile industries. In addition to the textile colouring, they are used in automobile, leather, paints, paper industries, etc., but their importance in the textile industries is maximum. Because of huge demand of dye, the production of a variety of dyes with advanced properties has drastically increased. Since dyes are complex aromatic organic compounds containing conjugated double bonds, they are highly toxic to the biological community of the world. In this chapter, more emphasis is given for synthesis technologies of various kinds of dyes, different kinds of hazardous pollutants generated from the dyeing industries, and their environmental impact along with the implementation of the technology developed to reduce the pollutant and its effect to our sustainable environment. Hence, more focus has to be given for manufacturing and application of dyes from renewable natural resources.

Colour is the most important part to make any fabric attractive, but its use for dying has become a major environmental hazard. Colloidal particles present with color increases the turbidity, gives bad appearance, foul odour, and obstructs the penetration of sunlight into water bodies required for the photosynthesis process, which interferes with the oxygen flow mechanism and hence marine life. So, it is essential to remove such pollutants from the waste water before its final disposal into water bodies. Photocatalysis is one of the advance oxidation processes, mainly carried out in the presence of light and suitable photocatalytic materials for the degradation of dyes. This chapter outlines the background of dye chemistry, the application areas, and the impact of dyeing effluents in the environment and on living beings.

Chapter 8

The textile industry is one of the important industries that generates a large amount of industrial effluents. Color is the main attraction of any fabric. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry. Synthetic dyes have provided a wide range of colorfast, bright hues. However, their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds, and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. These organic materials react with many disinfectants, especially chlorine, and form byproducts (DBPs) that are often carcinogenic and therefore undesirable. This effluent, if allowed to flow in the fields, clogs the pores of the soil resulting in loss of soil productivity. This chapter gives an overview on the health and environmental impact of dyes.

Chapter 9

Life of living or non-living being depends on water; in short, water is life. But these days, with the growing industrialization, it is spoiling a lot. Wastewater contains contaminants like acids, bases, toxic organic and inorganic dissolved solids, and colors. Out of them, the most undesirable are colors caused mainly by dyes. Color and other compounds present in water are always not desirable for domestic or industrial needs. The wastes of dyes are predominant amongst all the complex industrial wastewater. This water is dark in color and highly toxic, blocking the sunlight and affecting the ecosystem. Among all the dyes, azo dyes contribute to commercial dyes used widely in textile, plastic, leather, and paper industries as additives. The removal and degradation of azo dyes in aquatic environment is important because they are highly toxic to aquatic organisms. For every industry, clean technology has become an important concern. In this chapter, the authors discuss about existing processes as well as promising new technologies for textile wastewater decolorisation.

Chapter 10

Advanced oxidation processes (AOPs), namely the Fenton oxidation, ozonation, electrochemical oxidation, and photocatalysis, are potential alternative techniques for dye removal from textile effluents. Their inherent ability to completely mineralize pollutants including those recalcitrant to biodegradation and to be compatibly integrated in conventional technologies present grounds for consideration of AOPs as alternative wastewater treatment options. Advanced oxidation involves generation and subsequent reaction of various radicals and reacting species with the target compounds. This chapter discusses the fundamentals and chemistry and efficiencies of the Fenton process, ozonation, electrochemical oxidation, and photocatalysis processes for complete dye removal from wastewater. The reaction mechanisms, performance, and factors affecting efficiency are discussed.

Chapter 11

This chapter describes an up-to-date critique of the use of adsorption as a wastewater treatment technique for the removal of dyes. The topics range from the classification of dyes, their occurrence in water and toxicity, various treatment methods, and dye adsorption dynamics onto agricultural wastes and inorganic adsorbents such as clay and metal oxides and adsorption onto microbial biomass under varying operational conditions. It is demonstrated that the discussed materials form alternative adsorbents for dye adsorption from aqueous solutions with comparable or better removal efficiencies relative to the non-renewable coal-based granular activated carbons; they are cheap and abundant. The relative performance of the adsorbents under different environmental parameters for dye removal has also presented. The deductions made and alluded to from various kinetic and adsorption isotherm models are also discussed. The chapter presents the past, present, and suggestions for future considerations in search of non-conventional adsorbents for dye sequestration from aqueous solution.

Remediation of environmental pollution has become a hot issue in the world. Environmental pollution, mainly caused by toxic chemicals, includes air, water, and soil pollution. This pollution results not only in the destruction of biodiversity, but also the degradation of human health. Textile industrial effluent often contains the significant amount of synthetic and toxic dyes. Some dyes are water-soluble, dyes such as azo dyes, sulfonated azo dyes, etc. Hazardous effect of dyes results in the formation of tumor, cancer, liver or kidney damage, insomnia, diarrhea, nausea, vomiting, dermatitis, chronic asthma, coughing, headaches, and allergies in humans and also inhibit growth of bacteria, protozoan, plants, and different animals. A range of wastewater treatment technologies have been proposed that can efficiently reduce toxic dyes to less toxic forms such as nanotechnology. In this chapter, the authors give an overview of the various aspects of nanotechnology to remediate industrial textile dye effluents.

Foreword

Dyes are organic substrates capable of imparting colors on various materials. Millions of tons of dyes are produced annually and used in different industries such as pharmaceutical, food, cosmetics, plastics, paper and textile industries. In the current scenario, the use of textile dyes has become the most serious threat to the environment and human health. About two million tons of dyes are released as effluents due to inefficiency in dyeing process of fabrics. Although, nowadays dyes are developed to meet the available standards of waste water treatments, unfortunately, most of the dyes continue to persist in the environment due to their high resistance and stability to light, temperature, water, microbes and certain chemicals.

The long term exposure to dyes and contamination of natural resources like water are also responsible for adverse effects on living organisms including humans. With the increasing demands of textile products, the use of dyes has increased considerably thereby compounding the severity of environmental pollution and human health issues. Thus, there is an urgent need to develop more stringent norms and regulations along with advanced and efficient chemical and biotechnological waste treatment techniques so as to minimize waste generation, re-use spent dye-bath and reduce harmful effects on environment and human health.

The chapters in this book provide an in-sight to the chemistry of dyes, the effects of dyes on abiotic components of environment such as water and soil, impact on human health and also describe the latest methods used to treat effluents from dye based industries.

The first chapter briefly describes the world of dyes and their importance in various industries. The second chapter deals with the classification and chemistry of dyes. The third chapter throws light on the toxicological effects of dyes. The impact of textile industries of Rajasthan on environment has been evaluated in the fourth chapter using Geo-spatial techniques. The fifth chapter highlights the adverse effects of dyes on water chemistry and biology and soil quality. The sixth chapter focuses on the harmful impact of effluents from dyeing and textile industries on the sustainability of environment. The health hazards caused by dyes have been discussed in the seventh chapter. The eighth, ninth and tenth chapters describe various chemical and biological treatments, advanced oxidation processes and use of low cost adsorbents, respectively, for removal of dyes from effluents or wastewaters. The eleventh chapter elucidates the applications, perspectives and regulatory measures for pharmaceutical colorants, pigments, dyes and lakes. The last chapter emphasizes the use of nanotechnology for the outdoor pollution management. Thus, the book covers not only the impact of textile dyes on environment and human health but it also offers various measures that can be adopted to minimize the menace caused by the use of dyes.

I congratulate the contributors of this book as it provides all the relevant information on dyes and their impact on environment and human health. I wish the book will be a reference source for all those researchers and manufacturers who are concerned with developing and designing of environmentally benign technologies for dyeing processes for sustainability of environment.

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Preface

Environmental pollution is an inevitable consequence of economic development and people's desire to improve their quality of life. With the increasing demand of textile industries in India discharge colored effluents is also increased. These colored effluents give undesirable perspective to the water streams where as some dyes and their metabolites pose toxic, carcinogenic and mutagenic effects. Out of various pollutants contained in industrial wastewaters, dye is considered to be very important from the aesthetic point of view and is stated as visible pollutant. Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade and are widely used in textiles, paper, plastic, leather, cosmetics and food industries to color their products. The extensive use of dyes often caused pollution problems in the form of colored wastewater discharged in to environmental water bodies. The synthetic dyes are cheap and offer a very wide vast range of new colors. The synthetic dyes are used in many spheres of life and their applications are continuously growing in various industries like textile, leather, cosmetics, paper, paint and food. Approximately 10,000 different dyes and pigments are used industrially, and over 0.7 million tones of synthetic dyes are produced annually. Tons of different dyestuffs are used per year thus making this industry as a major consumer of synthetic dyes and consequently cause water pollution. The dyes may cause disruption of biogeochemical cycles and irreversible damage to the aquatic environment. Dyes cause aesthetic problems and strongly absorb sunlight thus inhibiting the photosynthetic activity of aquatic plants and severely damage the whole ecosystem. Demand and necessity of synthetic dyes are continuously growing for dye manufacturing and dye utilizing companies all over the world. However, the major consumers of dyes are textile industries.

Wastewater effluent from cloth dyeing industries of Ludhiana used various dyes is one of the major water pollutants to aquatic ecosystem the water bodies also undergo chemical and biological changes thus after the physico chemical properties of water and most of the dyes possess toxicity that is hazardous to aquatic life. Dye effluents may contain toxic organic residues with the major compounds of phenol derivatives, aniline derivatives, organic acid and benzene derivatives. The dyes effluents are highly variable from day to day and hour to hour depending on the type and color of dye thus it may also using in between the month & seasons.

Workers in dye industry are exposed to an increasing number of chemicals and occupational hazards. Exposure to different types of dyes causes different types of diseases like skin allergies, respiratory diseases and musculoskeletal disorders among workers. The respiratory diseases may cause dry or productive cough of chronic or non-chronic nature, asthma and other respiratory symptoms among dye workers. Occupational dermatoses in dye industry account for a large number of occupational diseases in dye industry and could even exceed all other industrial diseases put together. Other organs such as the eyes, lungs, liver and urinary bladder may also be involved after chronic exposure. The common factors that predispose to the development of contact dermatitis are existing dermatoses, pressure, friction, sweating and prolonged immersion in water. Various investigations have been done everywhere throughout the world to identify and assess the wellbeing impacts specialists working in the coloring and printing industry. Be that as it may, such investigations are pitiful for Indian urban areas. It is important to safe protect the laborers of printing and coloring enterprises.

In this backdrop, the present book titled *Impact of Textile Dyes on the Public Health and the Environment* is an essential reference source that discusses the management of different types of dyes and provides relevant theoretical frameworks about new dye management technologies for control of water and soil pollution.. This book is ideally designed for environmentalists, policy makers, professionals, researchers, scientists, industrialists and environmental agencies.

This book included 12 chapters from different researchers across the world. These chapters have discussed the world of the dyes, classification, chemistry and applications of chemical substances, impact assessment of textile industries, effect of dyes on environment, effluent generated from dyeing and textile industries, impact of synthetic dyes on human health and environment, chemical & biological treatment of dyes, advanced oxidation processes and removal of dyes by adsorption, applications, perspectives, and regulatory aspects of and use of nanotechnology in detail.

Chapter 1 argues that the textile sector is 14% of total industrial production in India and contributes to about 4% of the gross domestic product and earns about 27% of India's total foreign exchange. Worldwide, up to 10,000 dyes are available and their annual production is above 7×10^5 metric tons, which are being used not only in textile sector but also applied in paper, food and pharmaceutical industries. This chapter also presents a review of literature on the significance of bioremediation technologies over other physicochemical methods for efficient removal of textile dyes from industrial waste effluents to improve the fragile ecosystems in different regions of the world.

A detailed classification of dyes has been discussed along with their chemical class and chemistry in Chapter 2. International, regional, and national classification and labeling systems are already established and tested in practice. These hazardous chemicals can be liquid, solid, gas, aerosol, mists, vapors, semisolid etc. Hazardous chemicals have wide applications e.g. dyes which are used for coloring purpose, pesticides which are used for pest control, fertilizers are essential part of the agriculture system, plastic and plastic waste, e-waste to name a few.

Chapter 3 is mainly focused on toxicology of dyes advocates that colours play a prominent and dominant role in human life. Dominating feature of any product has been found with its colours elevating the market of colouration in different sectors. During manufacturing procedure around 50% of dye stuff gets along with the effluents of the industry leading to release of colourful water. Modification in choice of chemicals is being considered to slow down the toxic effects of existing complexes.

Chapter 4 highlights water quality parameters of Rajasthan State using satellite remote sensing and GIS technology. Water and soil quality indices has been applied to identify and assess the magnitude of contamination due to textile effluents in the surroundings of textile industries. In the resultant indices variability caused due to presence of textile effluents is prominently visible and interpreted with geo-statistical representations. Visible Change in soil and water quality has been observed in surroundings of textile industries all over the Rajasthan state. Significant variations have been observed in Pali, Sanganer, Bhilwara regions due to presence of textile industries. Remote sensing and GIS technologies along with natural resource parameters as utilized in above study can be performed for generating assessment reports for extended area at regional as well as national level and providing backgrounds in formulation of government policies for sustainable development and management of textile industries.

Chapter 5 advocates that the degradation of azo dyes is difficult by using the conventional processes. These complex azo dyes containing N=N bond have found to show carcinogenic evidences on reductive cleavage. Azo dyes have capability to alter physical and chemical properties of soil, causing harm to the water bodies. Dyes are toxic in nature which is lethal for microorganisms present in soil affecting agricultural productivity. The presence of azo dyes in water decreases its water transparency and water gas solubility. This reduces light penetration as water decreases its photosynthesis activity, causing oxygen deficiency and de-regulating the biological cycles of aquatic system.

Chapter 6 emphasis that different kinds of hazardous pollutants generated from the dyeing industries has environmental impact. The implementation of the different technologies has been developed to reduce the pollutant and its effect to sustainable environment. Hence more focus has to be given for manufacturing and application of dyes from renewable natural resources.

Chapter 7 outlines the background of dye chemistry, the application areas and the impact of dyeing effluents in the environment and on living beings. So it is essential to remove such pollutants from the waste water before its final disposal into water bodies Photocatalysis is one of the advance oxidation processes, mainly carried out in presence of light and suitable photocatalytic materials for the degradation of dyes.

Chapter 8 gives an overview on the health and environmental impact of dyes. The textile industry is one of the important industries which generates large amount of industrial effluents. Color is the main attraction of any fabric. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry today. Synthetic dyes have provided a wide range of colorfast, bright hues. However their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic.

Chapter 9 discuss about existing processes as well as promising new technologies for textile waste water decolorisation. The waste of dye is predominant amongst all the complex industrial wastewater. This water is dark in color and highly toxic blocking the sunlight and affecting ecosystem. Among all the dyes, azo dyes contribute maximum to commercial dyes used widely in textile, plastic, leather, and paper industries as additives. The removal and degradation of azo dyes in aquatic environment is important because they are highly toxic to aquatic organisms.

Chapter 10 discusses the fundamentals and chemistry and efficiencies of the Fenton process, ozonation, electrochemical oxidation and photocatalysis processes for complete dye removal from wastewater. The reaction mechanisms, performance, and factors affecting efficiency are discussed. Advanced oxidation processes (AOPs) namely the Fenton oxidation, ozonation, electrochemical oxidation and photocatalysis are potential alternative techniques for dye removal from textile effluents. Advanced oxidation involves generation and subsequent reaction of various radicals and reacting species with the target compounds.

Chapter 11 describes an up-to-date critique of the use of adsorption as a wastewater treatment technique for the removal of dyes. The topics range from the classification of dyes, their occurrence in water and toxicity, various treatment methods, and dye adsorption dynamics onto agricultural wastes and inorganic adsorbents such as clay and metal oxides and adsorption onto microbial biomass under varying operational conditions. The relative performance of the adsorbents under different environmental parameters for dye removal has also presented. The deductions made and alluded to from various kinetic and adsorption isotherm models are also discussed. The chapter presents the past, present, and suggestions for future considerations in search of non-conventional adsorbents for dye sequestration from aqueous solution.

Chapter 12 provides an overview of the various aspects of nanotechnology to remediate industrial textile dye effluents. Textile industrial effluent often contains the significant amount of synthetic and toxic dyes. Some dyes are water-soluble, dyes such as azo dyes, sulfonated azo dyes, etc. Hazardous effect of dyes result in the formation of tumor, cancer, liver or kidney damage, insomnia, diarrhea, nausea, vomiting, dermatitis, chronic asthma, coughing, headaches and allergies in human and also inhibit growth of bacteria, protozoan, plants, and different animals. A range of wastewater treatment technologies have been proposed which can efficiently reduce toxic dyes to less toxic form such as nanotechnology.

We firmly believe that this book will be quite helpful to all those who are directly and indirectly related with the world of dyes.

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Chapter 1

World of the Dye

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ABSTRACT

The textile sector is 14% of total industrial production in India and contributes to about 4% of the gross domestic product and earns about 27% of India's total foreign exchange. Worldwide, up to 10,000 dyes are available and their annual production is above 7×105 metric tons, which are being used not only in textile sector but also applied in paper, food, and pharmaceutical industries. Textile industries in India have been consuming more than 100 L of water to process 1 kg of textiles and have contributed heavily in polluting surface and ground water resources in many regions of the country. The toxic and carcinogenic effect of untreated textile effluent is well understood. The decolorization and detoxification of industrial dye effluents is the most important aspect and is a major concern to meet environmental regulations. This chapter presents a review of literature on the significance of bioremediation technologies over other physicochemical methods for efficient removal of textile dyes from industrial waste effluents to improve the fragile ecosystems in different regions of the world.

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INTRODUCTION

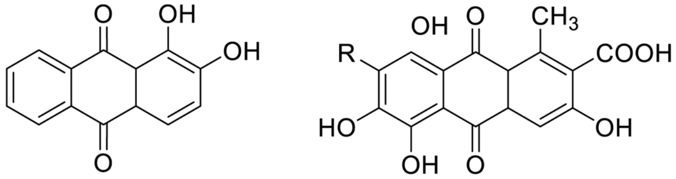
Indigo, the first known organic blue dye was used as a colorant and also found in mummies wrap 4000 years ago Commercially, there are 100,000 dyes available. Mainly they find application in textile industry, Silveira et al. (2009) followed by food, cosmetics and paper printing industry. To make the fabric more attractive and to provide the customer with variant shades, it becomes imperative to use variety of chemicals in dyes like direct dye, processing dye, reactive dye etc. But this variance and increasing use of chemicals marks a serious concern as its manufacturing and application are associated with several environmental issues, effecting textile industry.

In early 1856 it was Perkin who pioneered the synthetic organic dye, mauve. Later on in 1871, Wolfe prepared picric acid dye by nitration of indigo blue dye. Since then, many of other synthetic dyes have been introduced in the non-ending list of dyes (Mathur et. al (2006).

'Natural dye' includes all dyes that are derived from natural sources like plants, animal and minerals. Natural dyes are applied to the fiber by using mordent, which should attach with both, color and the fiber, and are mostly non-substantive. Synthetic dyes also find application in industries like paper, rubber, chemical, but has been majorly used in textile industry (Keharia & Madamwar (2003). It has been reported that textile industries are using more than 10,000 commercial dyes, which accounts for 10-15% of waste being discharged into the environment (Reisch, 1996).

To reduce its toxicity it is necessary to depolarize the effluent before it gets discharged into the water stream. Major problem associated with the treatment of these dyes from effluents includes its water solubility and presence of harmful chemicals, making it difficult to depolarize and poses a great challenge for environmental managers (Ho & Chiang, 2001). Sometimes it is obvious to use combinational methods to remove different kind of contaminant present in the dye (Hamza and Hamoda, 1980; Shaul, 1982; Shelley, 1976). Adsorption method may also be employed to remove color from the waste water of dying and textile industries (Mckay, 1980; Yeh, 1993; Mckay, et. al.1990). Different adsorbate used are (sludge) Zahangir Alam (1993), magnetically modified brewer's yeast, cassava peel activated carbon (Safarikova, 2005) tapioca peel activated carbon (Rajeshwari, 2001), soil (Chidambaram and Selvaraju, 2007, fly ash (Singh 2006), jack fruit peel activated carbon (Mall and Upadhyay, 1998), groundnut shell activated carbon activated with Zinc chloride solution (Inbaraj & Sulochana, 2006), neem leaf powder Inbaraj & Sulochana (2002), kaolinite, montmorillonite, hazelnut activated carbon (Malik et. al. 2006), bagasse pith, natural clay, maize cob, rice bran based activated carbon (Aydın & r Yavuz, 2004), guava seeds activated with Zinc chloride solution followed by pyrolysis (Nassar and Geundi, 2004) etc.

Figure 1.
(Edward Noah Abrahart and J.B. Stothers 2018)



Alizarin

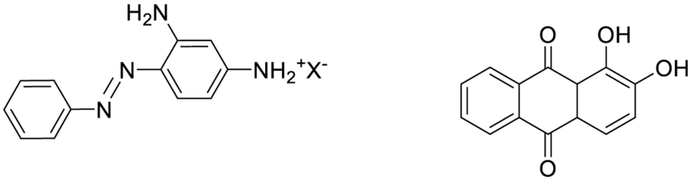
kermesic acid(R=H)
carminic acid (R=glycosyl)

Classification of Dyes

According to the source of material, nature of chromophore and methods of application, dyes have been classified as

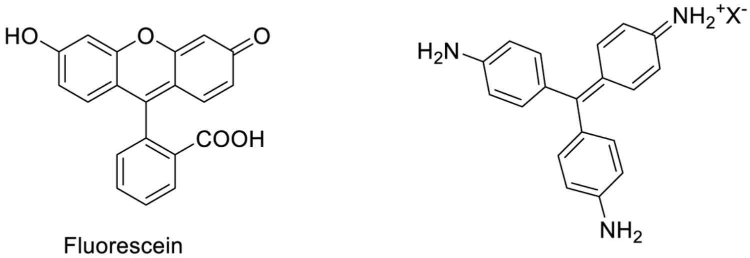
1. **On the basis of source:** Dyes are generally classified on the basis of their occurrence into two groups;
2. **Natural Dye:** Dyes derived from natural sources comes under this category. Most of natural dyes are those which are derived from plant sources. E.g. roots, bark, leaves,wood or berries. Examples include, alizarin and indigo, Alizarin and indigo being red and blue colored dye. T. Abrahart and Stothers (2018)
3. **Synthetic Dyes:** The British chemist, William H. Perkin, discovered the first commercial synthetic dye, mauve, in 1856 and from then the synthetic dyes started replacing all natural dyes in textile world. Then and now, many of the synthetic dyes have been introduced in the market.In today's scenario only one natural dyes, logwood is used commercially and that too to a small degree, for silk, leather, and nylon. Abrahart and Stothers (2018)
4. **On the basis of chromophore present:** Dyes are classified into four types according to the chromophore present in them as:
    a. **Nitro and Nitroso Dyes:**Dyes containing chromophore, nitro or nitroso group and auxochrome -OH, have been classified under this category. Examples: Naphthol yellow S Mordant green. Raue & Corbett (2000).
    b. **Triarylmethane Dyes:** These are intensely colored synthetic organic dye which contains triphenylmethane backbones, in which three aromatic ring is attached to a central carbon; one ring being in the quinoid form. It conatins amine, substituted amine and OH group as auxochome.Example includes, Malachite Green. Gessne. Thomas & Mayer(2000)

Figure 2.
(Edward Noah Abrahart and J.B. Stothers 2018)



Chrysoidine
(as azobenzene)

alizarin
(an anthroquinone)



Fluorescein
(a Xanthene)

parasafline
(a triphenylmethane)

c. **Anthraquinone Dyes:** These are rose colored organic dye having anthraquinone backbone. Example includes, Alizarin also known in the name of Rose madder and Alizarin crimson. Gordon & Gregory (1987).

d. **Indigo dyes:** These are blue colored organic dye, which was extracted from plants, but nowadays it has been synthesized. The main chromophore of indigo dye is carbonyl, and find application as dye in cotton yarn, wool and silk. Elmar Steingruber (2004)

5. **Classification based on methods of application**:on the basis of processes used in application of dye on fiber, which depends on their nature are classified as:

   a. **A substantive dye or direct dye**: These dyes contain acidic or basic auxochrome and employed in neutral or lightly alkaline medium.it is used to dye cotton, paper, leather, wool, silk and nylon.

   b. **Vat dyes:** These dyes are not soluble in water, but soluble in sodium hydrosulfide (Na-S-H) and is used to dye cotton fibers as it contains –OH group, which is resposnbile for getting bind to the cotton. Bamford & Dewar (1946)

   c. **Mordant dyes**:Mordant dyes find application in staining cell besides its application in textile field.This type of dye is known to form coordination bond with the fiber or tissue, which is responsible for holding the dye fast to the fiber. The resulting coordination complex of dye and ion is colloidal and can be either acidic or alkaline. Bryan (2005)

d. **Azo dyes:**These dyes are also water insoluble in which two components react to produce the dye which could be Phenol, Napththol or Aniline. This dye is used to dye cotton fibre but is highly toxic, associated with the chemicals. Klaus Hunger (2005)

e. **Disperse dyes:** These are water insoluble dyes and is used for dyeingpolyester and acetate fibers. Molecular size is smallest of all the type of dyes. A disperse dye molecule may further be divided into azobenzene (as Disperse Red 1 or Disperse Orange 37) anthraquinone, nitrodiphenylamine, heterocyclic ring type,depending upon the type of group attached to it. Heinrich Braun(1983).

6. **Effects of dyes and their metabolites:** textile dyes are always known for its harmfulness for environment besides human. Because of the carcinogenesis and mutageneis nature associated with azo dyes, it is considered to be the most harmful dye and therefore posses a threat to the environment and human health.

It has been calculated that industry uses about about 10,000 different dyes and 700000 tons of synthetic dyes are produced owing to its high demand in textile as it could provide different shades of colour Zollinger, H. (1987) and Ogugbue C.J. and Sawidis T. (2011).Various proceses employed for dying textile material includes batch, continuous and semi-continuous processes.Batch process is the most common of all. Perkins W.S. (1991).

Due to the lack of efficient dying process Ogugbue CJ, Sawidis T. (2011), nearly 200,000 tons of the dyes goes out in the effluent and persists in the environment. The high stability of some dye make them resist toward the waste water treatment techniques and therefore known to cause serious environmental issues which are harmful for human health also Perkins W.S. (1991). Adding to this issue, antimicrobial agents have been increasingly used to dye cotton O’Neill C et al. (1999), which are not prone to undergo degradation,the presence of complex structure make them irresistible to biodegradation. It is however mandatory to eliminate the harmful dye from the effluent before it get discharged to the main stream. Ogugbue CJ, Sawidis T. (2011) & O’Neill C *et al.* (1999). Wastewater coming out of these dyeing industry are considered to be the most polluting among all industry. The composition of textile effluent comprises of chlorinated compound besides surfactant Ben Mansour H (2012).

Textile wastewater causes fluctuations in Ph level, color, taste, BOD and COD, by decreasing the penetration of light thereby effecting photosynthetic activity of aquatic life The composition of textile effluent will depend upon chemicals or dye used during the dyeing of fabrics Zollinger, H. (1987) and Talarposhti AM (2001), the presence of even little quantity (less than 1 mg/L for some dyes) in water makes it harmful for aquatic life Forgacs E. (2004), Przystaś W. (2012) and Hubbe M.A.((2012),and unfit for consumption by animal bodies and human Ibrahim M.B. (1996) and Wijetunga S.(2010). Of all organic dye produced nearly 60-70% of dye are constituted by azo dye alone,as concerned with production and consumption Carliell CM (1998). The high usage is owed to good fastnessSeesuriyachan P. (2007), easy to synthesis, inexpensiveness in comparison to natural dye. As already explained these dye also finds application in pharmaceutical and cosmetics industries besides leather, paint, food and paper industries Ben Mansour H.(2007) and Chung K.T.(1992).The disadvantage associated with azo dye is its carcinogenesis and mutagenesis activity Chung KT(1992) and Pinheiro H.M.(2004).

The enzymes, azoreductases and nitroreductase present in the intestine and liver of mammalian, metabolize the azo and nitro dyes to amines Umbuzeiro GA (2005). Azo dyes being polar in nature get easily assimilated in body.The toxicity is due to azo dye itself or due to the metabolized product Rajaguru P (1999), which causes damage to DNA.

The most common problem associated with the treatment of effluents from textile industries is to remove the dyesfrom it. The dyes manufactured or synthesized in such a way so as to resist degradation, so that it can last for long time on fiber. This property makes the treatment process highly tedious and challenging .For example, under standard condition (25°C, pH7), the half life of reactive blue was found to be 46 years.

For monitoring certain dyes like C.I. Disperse Blue 373 (DB373), C.I. Disperse Orange 37 (DO37) and C.I. Disperse Violet 93 (DV93) Carneiro et al. (2010) designed an analytical method, Whose results indicated the presence of all the dyes under investigation in treated and untreated effluents. Mutagenic activity further confirmed the results. Proving the methods employed for treatment of effluents like pre-chlorination, flocculation, coagulation and flotation to be ineffective. Mutagenic activity further confirmed the results.

It becomes imperative therefore, to optimize the processes involved during its manufacture, keeping the objective of reducing its impact on environment, like economizing energy. For example, liposome used for encapsulating certain dye reduces the process temperature employed for its manufacture Barani H. *et al.* (2008). Other alternative is the use of ultrasonic energy, which reduces both energy and water consumption.Khatri Z *et al.* (2011).

It has become clear that dying industries consumes maximum water and the resulting effluent contains harmful chemical and colored substance,which harms not only environment but also human. Therefore it is important to have an idea of

Table 1. Treatment methods for textile effluents

Physical Methods	Chemical Methods	Biological Methods
Adsorption	Fenton reagent Technique	Aerobic degradation
Ion exchange	Ozonisation	Anaerobic degradation
Filtration	Photocatalytic methods	
Coagulation/flocculation		

the processes involved during dyeing and also about the alternatives, that could be adopted.

Treatment Methods for Textile Effluents

The main concern associated with the effluents is to protect the aquatic life, as the effluent is directly discharged into the land and water bodies, thereby effecting water and aquatic life. To make the treatment effective, number of methods could be employed like physical, chemical, biological or a combinational method. The use of physical and chemical methods however is considered to be ineffcetice as it is highly economical besides ineffective in eliminating the contaminants completely. (Table-1)

Of all the methods involved for treating as per the table, the best suited method is biological, which is effective, inexpensive, bio degradable and does not involve or generate any chemicals. some of the bacterium were found to be effective in removing the colors completely from the effluent, under optimum temperature and pH.

Adsorbent

Physical methods used for treatment of effluents of textile industries however do not possess serious concern to the environment like that of chemical methods. Various adsorbent employed are activated carbon, seed of avocado pear, teak tree bark powder, natural clay, bentoniteclay,shell fiber of coconut, ash of fly (i.e., pearl millet husk, wheat straw, coconut straw etc.), corn rope, included to waste of wood and agriculture etc. the use of activated clay nowadays is not employed as its generation is highly tedious. However it has certain advantages also, like specificity, regeneracity and high adsorption capacity. However some of the researchers have proposed adsorption process which is cost effective and efficient too (Sabino *et al.* 2016) (Table 2 & Table 3)

Table 2. Various researchers observations about the differences in adsorption capacity with metal hydroxide sludge at different pH

S. N.	Dye	Absorption Capacity	pH
1.	Reactive Blue 4	4.48 mg/g	7
2.	Reactive Blue 4	7.99 mg/g	7
3.	Rhodamine B	42.19 mg/g	7
4.	Reactive Red 120	45.87 mg/g	8
5.	Reactive Red 2	61.73 mg/g	9
6.	Reactive Dyes	85.81 mg/g	7
7.	Remazol Brilliant Blue	91.0 mg/g	7
8.	Congo red	513 mg/g	3
9.	Direct Blue 85 dye	600 mg/g	4

Table 3. Adsorption capacity of various dyes by researchers using waste red mud as adsorbent

S. N.	Dye	Absorption Capacity
1.	Rhodamine B	1.16 × 10-5 mol/g
2.	Methylene Blue	7.8 × 10-6 mol/g
3.	Congo red	4.05 mg/g
4.	Remazol Brilliant Blue	27.8 mg/ g
5.	Reactive Black 5	35.58 mg/g
6.	Lead (Pb)	38.2 mg/g
7.	Acid Blue 113	83.33 mg/g
8.	Safranin-O	89.4 mg/g
9.	Phosphate	205.13 mg/g

Physical Method

Several methods involved in physical methods are;

- Sedimentation
- Screening
- Nano filtration
- Reverse osmosis
- Electro dialysis

Physical method like sedimentation involves the removal of heavier impurity due to gravity feel. Aeration method can also be adopted besides sedimentation, which involves air to be bubbled in the waste water, causing an oxidation of contaminant. Major disadvantage of the physical process is limited lifetime of membrane filtration, fouling and need for replacing the membrane periodically, making it cost effective. The best physical process is considered to be adsorbent. Monika Kharub (2012).

Biological Method

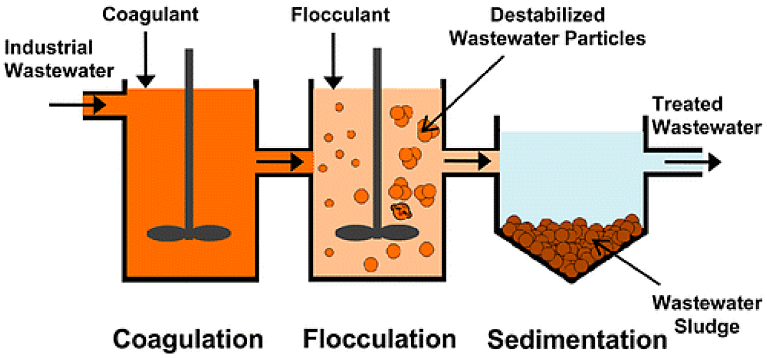
Biological method is considered to be the most economical method for treating the effluent of textile industries, because of its flexibility in design and operation large area consumption and toxicity makes even this processes slightly disadvantageous But it also has certain limitations associated with it. In addition, the effluents of textile industry are found in complexation with some metals. And low degradation of effluent makes this method unfit. In biological method certain processes like, bioaccumulation, bio colorization, and biosorption are more beneficial, as it is effective, economical and possess no threat to environment and is considered to be most important of all the treatment processes. However there is further need to improvise this method to make it even more effective.

Chemical Method

There are several methods associated with chemical methods which includes

- **Coagulation / flocculation:** these methods are employed for removing dye colour, turbidity or any suspended algae or micro-organism.When chemical

Figure 3.
(Chee Yang Teh et al. 2016)



coagulant is added to the effluent, precipitation or coagulation occurs, which is even effective for precipitation of iron and aluminium.these precipitates can further be removed by filtration, floatation or sedimentation.

- **Chemical Precipitation:** Chemical precipitation is a pH adjustment process mainly used for removal of dissolved metals from aqueous wastes. An acid or base is added to a solution to adjust the pH to a point where the constituents to be removed reach their lowest solubility. The solubility of metals decreases as pH increases and the metal ions precipitate out of the solution as hydroxide. Metals can be precipitated by adding alkaline agents, such as lime or caustic soda to raise pH. To remove chromium to Sodium bisulfate, cyanide to sulfates, including zinc sulfate or ferrous sulfate and metals to carbonates, especially calcium carbonate are used. M.N. Rao and Sri Harsha Kota (2017)
- **Electrokinetic Coagulation:** for removing minerals, metals, organic matter and colour from the textile industries effluent electro coagulation method is employed and is highly efficient.for example, chromium removal from textile effluent is done by employing aluminum electrode. Mouna Cherifi *et al.* (2016)
- **Advanced Oxidation Process (AOP):** of all the conventional processes employed for purification, Chemical oxidation processes is also effective for removing organic matter, Krishnan et. al. (2017), reducing chemical oxidation demand, also known as advanced oxidation process. Mohajerani et. al. 2009. This process being expensive, besides accumulation of sludge are not in regular use. Liakou (1997), Karahan *et al.* (2002), Moraes *et al.* (2000) ozonization process can be used to bring out oxidation, even in acidic medium at particular pH.
- **Photo Fenton and Fenton Reagents:** These reagents are a good example for advanced oxidation process, and is emerging field in treating the effluents. The effectiveness of these reagents employed for removing different dyes have been depicted in the Table 5.

Table 4. Advantages and disadvantages of some methods of chemical technique

Methods	Advantages	Disadvantages
Ozonation	Volume is unchanged, stayed in vapor-state	Life duration is short(20 min)
Photochemical	Production of silt is off	Metals, acids, halides Produced as by-product
Electrochemical	Disruption of non-haphazard compounds	Price of power supply is high
Oxidative processes	Ease to use and simple	Activation of H_2O_2 agent

Table 5. Dyes and methods of treatment

S.N.	Dyes	Method	Procedure	Conclusion
1.	Amaranth	Photo Fenton and Fenton Reagents	Advanced oxidation processes	The % colour removal of amaranth dye by photo-Fenton reagent and Fenton reagent were 85% and 59% in 11 minutes and 22 minutes
2.	Reactive Black 5 (RB5), Reactive Blue 13 (RB13), & Acid Orange 7 (AO7)	Fenton's oxidation and aerobic biological treatment	Two stage sequential Fenton's oxidation followed by aerobic biological treatment train	In overall treatment train 81.95, 85.57, and 77.83% of COD reduction was achieved in RB5, RB13, and AO7 dyes, respectively. In the Fenton's oxidation process 56, 24.5, and 80% reduction in naphthalene group was observed in RB5, RB13, and AO7, respectively, which further increased to 81.34, 68.73, and 92% after aerobic treatment.
3.	Reactive red 198 (RR198) and blue reactive 19 (RB 19)	Fenton and Modified Fenton Processes	Standard jar tests	In the Fenton reaction the maximum efficiency was obtained at 94.70% and 99.31% for reactive red 198 and reactive blue 19, respectively.Moreover, by the modified Fenton method the maximum removal efficiency for reactive red 198 and reactive blue 19 was 94.8% and 99.43%.
4.	Blue 71 azo dye	Fenton's oxidation: Kinetic study	Oxidation process	94% color and 50.7% COD removal efficiency of the dye in 100 mg L^{-1} aqueous solution were achieved after 20 min of reaction. Results indicated that the removal efficiency was strongly dependent on initial pH, initial concentration of Fenton's reagents, initial DB71 concentration and reaction temperature
5.	Reactive Black 5	Fenton, Fenton-Like, Photo-Fenton and Photo-Fenton-Like	Advanced Oxidation Processes	RB5 can be effectively decolorized using Fenton and photo-Fenton processes with a little difference between the two processes, 97.5% and 98.1%, respectively, for optimal conditions.
6.	C.I. Acid Orange 8 (AO8) and C.I. Acid Red 17 (AR17)	Fenton, Fenton-Like, Photo-Fenton and Photo-Fenton-Like	Advanced Oxidation Processes	Decolorization efficiency observed in the order of photo-Fenton>photo-Fenton-like>Fenton>Fenton-like for the two azo dyes.
7.	Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN	Fenton Reaction	Color Removal and COD Reduction of Dye	Disperse Yellow 23, Disperse red 167 and Disperse Blue 2BLN was 84.66%, 77.19% and 79.63% respectively after retention time 160 minutes.
8.	Basic Yellow 2	Photo-Fenton	Advanced Oxidation Processes	The results show that the photo-Fenton method completely oxidizes and degrades Basic Yellow 2 into CO and HO.

Table 6. Methods, applications, advantages and disadvantages of different absorbents

S.N.	Method	Application	Advantage	Disadvantage
1.	Adsorption Carbon nanotubes as adsorbent	Point-of-use, heavily degradable contaminants (pharmaceuticals, antibiotics)	Highly accessible sorption sides, bactericidal, reusable	High production costs, possibly health risk
2.	Peat as adsorbent	Peat's ability of cationic exchange is its exclusive property	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
3.	Silica gel as adsorbent	The high surface area, good sedimentation ability and great adsorption of SiO_2 particles facilitates significant dye degradation	Effective for basic dye removal	prevent Side reactions
4.	Wood chips as adsorbent	Wood chips had positive effects for degradation of the dyes from wastewater as they provide are natural environment for living microorganisms	Good sorption capacity for acid dyes	Requires long retention times
5.	Zeolites as adsorbent	Disinfection processes	Controlled release of nanosilver, bactericidal	Reduced active surface through immobilization of nanosilver particles
6.	Nanoparticles (Ag, ZnO, TiO_2, coated ceramic filters) as adsorbent	Large surface area, small diffusion resistance, high adsorption capacity, fast adsorption equilibrium	Offers an effective and economic way to environmental bioremediation protection	Leaching problem
7.	Nano- adsorbents	Point-of-use, removal of organics, heavy metals, bacteria	high specific surface, higher adsorption rates, small footprint	high production costs
8.	Nanometals and nanometal oxides	Removal of heavy metals (arsenic) and radionuclides, media filters, slurry reactors, powders, pellets	short intraparticle diffusion distance compressible, abrasion-resistant, magnetic photocatalytic (WO_3, TiO_2)	less reusable
9.	Polymeric Nano adsorbents (dendrimers)	Removal of organics and heavy metals	Bi-functional (inner shell adsorbs organics, outer branches adsorb heavy metals), reusable	Complex multistage production process
10.	Magnetic Nanoparticles	Wastewater Treatment	Provides stability, Protection from oxidation, provides surface to which contaminant specific ligands are attached.	In vitro cytotoxicity
11.	Electrochemical destruction	Environmental compatible, as its main reagent, the electron, is a clean reagent	Breakdown compounds are nonhazardous	High cost of electricity
12.	Electrokinetic coagulation	It sends an electric current through electrodes resulting in different chemical reactions. The reducing agent, is replaced by an innovative cathodic electron transfer.	Economically feasible	High sludge formation

- **Physicochemical method:** This method is employed for the removal of heavy metals, oil, grease, organic matter, colloidal particles etc.efficiency depends on type of metals and their concentration. The disadvantages are sludge generation and generation of secondary pollutant.

CONCLUSION

Book chapter deals about various methods available for wastewater treatment of dyes effluent obtained from textile industries by using cost effective adsorbents which are easily available. Different techniques have been used for removal of toxic organic compounds from waste water such as filtration, coagulation/ flocculation, ion exchange, adsorption, fenton reagent technique, ionization, photocatalytic methods, aerobic degradation, anaerobic degradation etc. Chemical and biological methods are found to be limited because of high investment and functional costs. On the other hand physical methods like ion exchange and reverse osmosis are interesting methods because of their effective removal process of pollutants from industrial waste water. Among all the methods available for separation of pollutants from waste waters, the adsorption shows possible method for treatment and removal of organic pollutants in waste water treatment. Adsorption follows surface phenomenon and more advantageous over the other available methods because of its low capital, operation costs and simple design. Adsorption material available from various sources such as natural sources, agricultural, and industrial wastes. Dye removal from wastewater using activated carbon is effective method but in industrial processes it was restricted due to its high operational and investment costs.

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KEY TERMS AND DEFINITIONS

Chromophores: Functional group that imparts colour to the dyes.
Natural Dye: Dyes derived from natural source like plant animals and minerals.
Synthetic Dyes: Dyes manufactured chemically.

Chapter 2

Classification, Chemistry, and Applications of Chemical Substances That Are Harmful to the Environment:

Classification of Dyes

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ABSTRACT

A detailed classification of dyes has been discussed along with their chemical class and chemistry. International, regional, and national classification and labeling systems are already established and tested in practice. These hazardous chemicals can be liquid, solid, gas, aerosol, mists, vapors, semisolid, etc. Hazardous chemicals have wide applications (e.g., dyes, which are used for coloring purpose; pesticides, which are used for pest control; fertilizers are an essential part of the agriculture system; plastic and plastic waste; and e-waste to name a few). In this chapter, the authors deal with the identity, classification, and application of these harmful chemicals, especially dyes, which are mandatory to use. More emphasis is given to the natural and synthesized dyes about their use along with their modrants, which are a necessary part of the dyes without which they can't exhibit colors. Dyes have wide variety of applications, which have also been discussed along with their various harmful effects on environment, mankind, and aquatic life.

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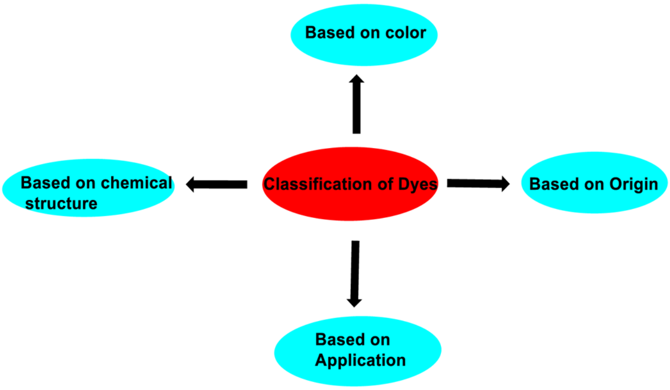
INTRODUCTION

Today's era is known as chemical era. Life without chemicals would be life without liveliness. Chemicals are the essential building blocks that create up all living and non-living things on Earth. In ancient time the ancestors used these chemicals directly from nature unknowingly about their effects and side effects. But today human have explored them exponentially and exhaustively. He has imitated these chemicals and has created their lots of isomers to see whether these chemicals have some impact or not. Some of these chemical entities are essential for us and found in air, food, water. Many synthetic chemicals which are being synthesized by human in uncontrolled way are used in every day products from medicines to computers to fabrics and fuels. Other chemicals are not made deliberately but are by-products of chemical processes. Many chemicals are used to improve the quality of lives and most are not harmful to the environment or human health. However, some chemicals have the potential to cause harm, in certain amounts, and should only be used when the potential risks are appropriately managed. Chemicals can enter the air, water, and soil when they are produced, used or disposed. Through these means like air, water and food they can interfere to the biological system also. Their impact on the environment and human health is determined by the amount of the chemical that is released, the type and concentration of the chemical, and where it is found. Initiatives should be taken for the safe guard of chemicals for this purpose one should know their identity, environmental hazards, and the corrective majors to check them. These methods should be organized, available at free of cost and should be very easy to understand.

Dyes are organic or inorganic substances obtained from plant or animal products without any chemical treatment. They are obtained from sources like leaves, flowers, bark roots, insects, etc.; however, they are obtained by exhaustive extraction process and not readily available. In ancient times, peoples used natural colorants for their various purposes which were generally obtained from blossoms, berries, roots and barks (Saxena & Raja, 2014). They were used for various purposes application to the thread without any pretreatment of the dye-material or the cloth. In the near the beginning stages of the nineteenth century, introduction of synthetic dyes manifest the decline in the use of natural dyes. However, there are certain ancient art forms such as Kalmkari, which continue to use the natural dyes.

Figure 1. Classification of dyes



CLASSIFICATION OF DYES

Dyes can be classified in a variety of ways (Agarwal & Patel 2000). Early methods of classification were based simply on the alphabetical arrangement of dyes. Later on, numerous other methods of classification were adopted, which are as follows:

Classification Based on Origin

Dyes are classified on the basis of their foundation from which they are obtained. This method is very broad and very old method of classification. This covers most of the dyes and very important method of classification.

Plant Origin

This category includes dyes from plant origin e.g:-

Harda (Black Myrobalan)

Fruits of Harda are used for the preparation of such dye. It gives grey and yellow shades with aluminum and ferrous mordants respectively. Cotton, wool and silk fibers are dyed with these types of colors.

Himalayan Rhubard

Himalayan shrub is used for their preparation. The roots and fruit both can be used. It gives bright shades orange, yellow. Botanical name is Rheumemodin. It can be used directly and alum can be used as mordant on wool and silk fiber base fabrics. The colors obtained reveal good light, wash & rubbing fortress (Das & Kalita, 2016)

Indigo Blue

This dye is obtained by fermentation of leaves of *Indigoferra tinctoria*. It is blue color dye used for coloring of wool cotton and silk fibers. This is one of the most ancient natural dyes used by humans in textile.

Kamala Dye

Kamala dye is prepared from the deposits or residues on the flowers of this tree. This can act as direct or in combination with mordant to give yellow shades to silk and wool fibers fabrics. The colors obtained reveal usual wash, light & rubbing fastness.

Manju Phal

Manju Phal tree's nut galls are used to obtain creamy and grey shades dye to color wool and silk base fibers. It can act as direct or along with mordant. Botanical name is *Quercus infectoria*oliver.

Catechu (Kikar, Babul)

The bark of Indian gum Arabic tree is main source. It is used for dyeing of cotton fabrics with mordants. It shows yellow, black, brown and grey shade. It is having very superior fastness.

Madder

Botanical name is *Rubia cardifolia* (Indian madder), *Rubia tinctoria* (European madder).It gives orange, pink and red shades. The colors obtained demonstrate good fastness to washing rubbing and light. Local names are Madder, Manjistha.

Alizarin

Ground up roots of Indian Madder (*Rubiatinctorum*) are used to obtain this dye. It yields pink, purple and red shades with good color fastness. It is also one of the oldest natural dyes.

Walnut (Akhrot)

Bark of walnut tree is used for the dye. This yields brown shade with good fastness. It is used for dyeing of silk and wool fiber base fabrics. Botanical name is *juglanoregia*.

Al (Ali ki Lakdi)

Botanical name is *morinda tinctoria* roxb. The dye is extracted from root bark and roots of the al tree. It gives pink/red shades. Locally known as al ki lakdi.

Mali (Tamarind Tree)

Mali tree also known as tamarind tree botanically it is known as *tamarinddus indica* available in india abundantly. Leaves wood ash and fruit of this plant used for the preparation of this dye. It is used as dye fixer.

Arjun (White Murtha)

Bihar, Jharkhand, west Bengal and Chattisgarh are the major exporting center of the dye.

Bark of the Arjuna tree is exploited to obtain dye which gives Red /Pink shades with average fastness. Botanical name is *Terminali aarjuna*.

Dhaura ka Fool

The dye is extracted from flower of the dhaura tree. It yields pink / brown / red shades with good fastness. Botanical name is *woodfordia floribunda* (Shiva, 2007).

Animal Origin

LAC

It is extracted from *Lacifer lacca* insects. It is used for dyeing of silk, wool and cotton fiber base fabric. It gives purplish shades with copper mordant and reddish shades with tin mordant. Different shades like olive green, amethyst, ruby red, yellow, black, purple, steel grey etc can be obtained by using various mordants. (Kongkachuichaya, Shitangkoonb & Chinwongamorna, 2002).

Cochineal

It is a brilliant red dye produced from insects known as coccus cacti. It come in the market in the form of little dark colored grains which, when ground up in hot water, gives a red solution called carmine, containing a considerable amount of a coloring matter known as caraminic acid.

Kermes

Kermes consists of dried bodies of a variety of insects which lives on a species of oak. Lac another important animal source also gives red colour. The dye is obtained from the body of a small insect called coccus laccac. Tyrian purple is another dye from mollusks. Tyrian purple is the most highly prized ancient dye stuff, obtained from the juices of certain species of snails found in the waters of the Mediterranean Sea.

Dyes Derived From Mineral Sources

Natural dyes produced from mineral resources include chrome orange, chrome yellow, chrome green, Prussian blue, iron buff, manganese brown, mineral khaki, etc. Mineral colors are not dyes but inorganic compounds, insoluble in water and precipitated onto the fiber by double decomposition. Certain important minerals widely used as natural dyes are Red Lead (Sindur), Cinebor (Sangraj), Laminated Red earth (Gem), Ultramarine (Lajerd), Zinc white (Sajeda), etc.

CLASSIFICATION BASED ON COLOR

Natural dyes are frequently categorized on the basis of the color that they impart to the fiber substrate (Paul *et al*, 1996).

Natural Yellow Dyes

Yellow symbolizes growth and happiness and is perhaps the most abundant hue in nature. The number of plants that yield yellow dyes is much higher than the number that yield other colors, and the Color Index lists a total of 28 natural yellow dyes.

Natural Red Dyes

The Color Index lists 32 natural red dyes: some are extracted from the roots or bark of plants, while others, such as cochineal, are camouflaged in the bodies dull grey insects. However, the sources of these dyes are limited. Throughout history, natural red dyes have been of significant and in some cases legendary importance. Almost all natural red dyes have a basic quinone structure. They are mainly comprised of anthraquinones (alizarin, purpurin, munjistin, laccaic, etc.) or naphthoquinones (alkannin and shikonin); there is also one benzoquinone dye (carthamin). (Mohanty, Naik & Chandramouli, 1987)

Natural Blue Dyes

The Color Index lists only three natural blue dyes, namely natural indigo, sulphated natural indigo and the flowers of the Japanese *Tsuyukusa*, used mainly for paper making. The most brilliant and the fastest blue shades are obtained from indigo on all fibers. The principal coloring matter is indigotin, whose main sources are Indigo (*Indigo feratinctoria*) and wood (*Isatistinctoria*) (Tiedemann & Yang, 1995).

Natural Black Dyes

One important black natural dye is Logwood (*Haematoxylum campechianum*) which is also known as Cam peachy wood because it was discovered by the Spaniards on the bay of Campeche in Mexico. It is still used today for dyeing silk in deep shades on an iron tannate mordant. It also gives excellent depth and fastness on most natural and synthetic fibers (Knecht, Rawson & Loewenthal, 1933).

Natural Brown Dyes

The majority of natural brown dyes are obtained from quinone-based dyes, naphthoquinones and anthraquinones. Generally, copper and iron salts are used as mordants and they tend to turn the color to dull and deep shades, particularly browns. (Forrester, 1975).

CLASSIFICATION BASED ON CHEMICAL STRUCTURE

Natural organic dyes and pigments belong to a wide range of chemical classes, such as indigoid, anthraquinonoids, naphthoquinones, ketones, polymethines quinones, imines, flavones, flavanones, flavanols and chlorophyll (Glover, 1998).

Chemistry of Dyes

Direct Dyes

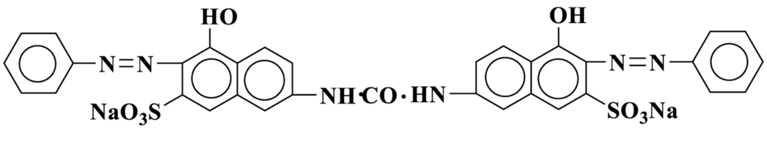
Their synonym is salt dye or colors which are used for the coloring of cotton fabrics, viscose rayon and other vegetable fibers. An electrolyte, salt, is added to the dye bath to control the absorption rate of the dye by the fiber. These (substantive) dyes are soluble and have an affinity for cellulose fibers. Direct dyes are easy to apply and cheap, but of poor fastness quality. They are applied to Cellulose fibers from aqueous liquor in which an electrolyte is added, which is usually Sodium Chloride as it accelerates the rate at which the dye is picked up by the fiber. They generally bleed. To make them fast on fabric add Sodium Bicarbonate for warm colors and Copper Sulphate for cool colors. They are also used as pH indicators and as biological stains. Direct orange 26 is a typical direct dye. (Aspland, 1997)

Chemistry of Direct Dyes

Chemically they are salts of complex sulfonic acids.

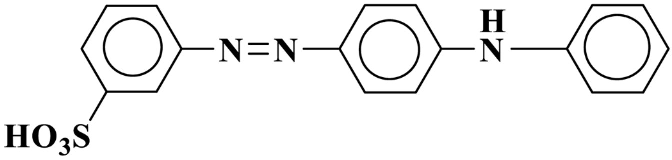
- Structure: More than 75% of all direct dyes are disazo or polyazo types and unmetallised azo structures.
- Ionic Nature: They are anionic in nature
- Solubility: Water soluble.
- Affinity: They have an affinity for a wide variety of fibers such as viscose, cotton, linen, silk, jute. Their planar shape and their length enable them to lie along-side cellulose fibers and maximize the Van-der-Waals, dipole and hydrogen bonds. They do not make any permanent chemical bond with the cellulosic fibers but are attached to it with very week hydrogen bonding as well as vander waals forces.

Figure 2.



Direct Orange 26

Figure 3. Acid yello36



Acid Dyes

Acid dyes are anionic in nature which are water-soluble and used to color wool, silk, nylon, rayon, certain modified acrylic, and polyester fibers. These dyes are prepared by using acid bath may vary in their chemical composition. These dyes are not fit for cellulosic fibers, chemistry of this dye revealed that there is salt formation between anionic groups in the dyes and cationic groups in the fiber. Bright colors are produced by these dyes but their fastness may be more or less. Most synthetic food colors fall in this category. Examples of acid dye are Pure Blue B, Acid red 88, Alizarine, Acid Yellow 3 (Perkins, 1996)

Mechanism of Dyeing With Acid Dyes

Basic mechanism involves reaction between anions and cations. Cations are generated by protein and polyamide fibers whereas anions are given by dyes in its aqueous solvent. Production of cations depend on acidity of the solution as acidity increased cation concentration also increases.

These cationic sites are thus available for the acid dye anions to combine with through hydrogen bonding, vander waals forces or ionic bonding. These linkages are strong enough to break, and thus dyeing produced are fast.

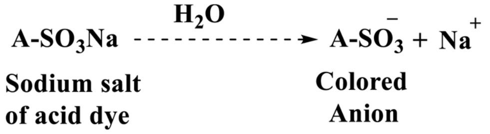
Basic Dye

Salts of organic bases are basic dyes which are water soluble also known as cationic dyes. Cationic dyes were originally used to color wool, linen, silk, hemp, etc., without the use of a mordant, or using agent. Their mechanism also involves formation of

Figure 4.

$$\mathbf{Dye^{-} + H^{+} + Fiber \rightleftharpoons Dye^{-}\ H^{+}{-}Fiber}$$

Figure 5.



$$A\text{-}SO_3Na \xrightarrow{H_2O} A\text{-}SO_3^- + Na^+$$

salt as cations are given by dyes as color component. With a mordant like tannic acid they were used on rayon and cotton. Basic dyes give brilliant colors with exceptional fastness to acrylic fibers. They can be used on basic dye able variants of polyester and nylon. Basic Brown 1 is an example of a cationic dye that is readily protonated under the pH 2 to 5 conditions of dyeing (Malik, Grohman & Akhtar, 2012).

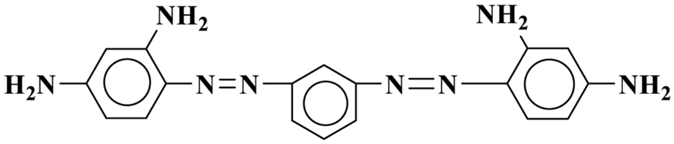
Reactive Dye

These dyes as their name indicate contains a reactive group which reacts with the amino or hydroxyl present on fiber. They have very high color fastness because they form covalent bond with the reactive groups. Because of the chemical reaction the color is fast and has a very long life. Cotton, wool or silk can be dyed with this type of dyeing of Fabrics. With some reactive dyes, the dyeing can be carried out at room temperature. However with most reactive dyes, the dyeing is carried out at high temperatures. Example: This type is the Reactive Blue 5 dye shown below (Tam et al, 1997).

Chemistry Behind Reactive Dyeing

The Four structural feature of typical reactive dyes molecule are: (1) The chromophoric group contributing the color, (2) The reactive system, enabling the dye to react with the hydroxyl group in cellulose, (3) A bridging group that links the reactive system to the chromophore, (4) One or more solubilizing group, usually sulphuric acid substituent attached to the chromophoric group for their color, although the azo chromophore –N=N- is by itself the most important. The dyeing principle is based

Figure 6.



Basic Brown 1

Figure 7. Chemical structure of reactive dyes

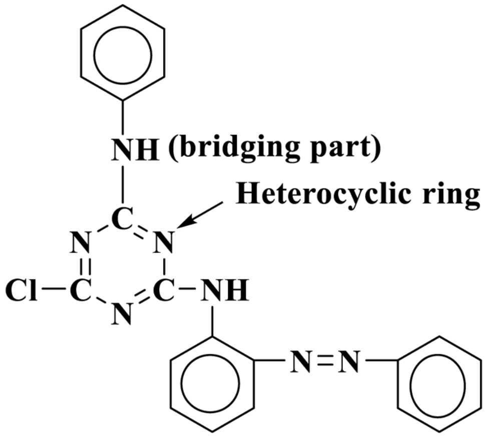
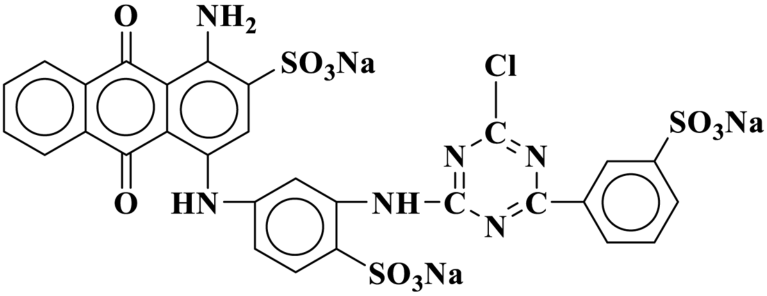


Figure 8.



Reactive Blue 5

on fiber reactivity and involves the reaction of a functional group of the dyestuff with a site on the fiber to form a covalent link between the dye molecule and the substance. All the reactive dyes contain sodium sulphonate group for solubility and dissolve in water to give colored sulphonate anions and sodium cations. Most reactive dyes have one to four of these sulphonate group, General form of the reactive dye is as follows:

S——R—-B—-X

Where, S = Water solubility group, R = Chromophore, X = Reactive System,B = Bond between reactive system and Chromophore.

Premetallized Dyes

Metal-complex dyes (also called premetallised dyes) may be broadly divided into two classes namely: 1:1 metal complexes and 1:2 metal complexes. 1:1 metal complex dyes must be applied in a strongly acid bath. The 1:1 means that one dye molecule is combined with one metal molecule. 2:1 metal complex dyes are to be dyed in a neutral to weakly acid bath. The 2:1 means that two dye molecules are combined with one metal ion (Chakraborty, 2011). The dye molecule will be typically a monoazo structure containing additional groups such as hydroxyl, carboxyl or amino groups, which are capable of forming strong coordination complexes with transition metal ions. Typically, chromium, cobalt, nickel and copper are used. Metal-complex dyes have good affinity for protein fibers. 1:2 metal-complex dyes are also suitable for polyamide fibers. Dyeing with metal-complex dyes requires the use of the following chemicals and auxiliaries:

- pH regulators – formic, sulphuric, acetic acid
- Electrolytes – ammonium acetate, sodium sulphate,
- Levelling agents – mixtures of anionic and non-ionic surfactants.

Figure 9. Structures of the metal complex dye 1

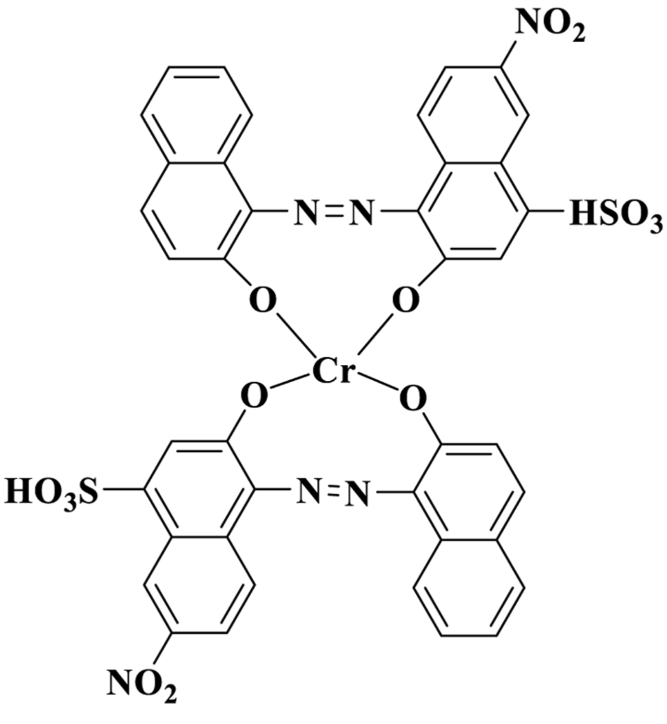
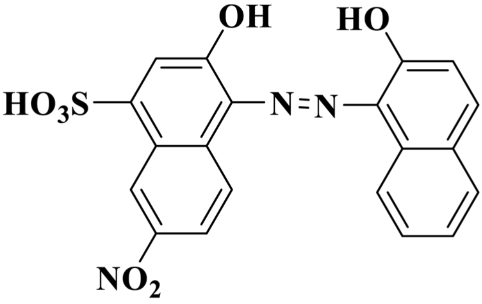


Figure 10. The non-metallized dye 2



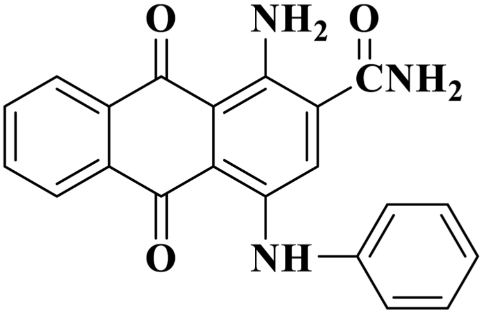
Disperse Dyes

These dyes are most favorably fitted for the coloring of hydrophobic fibers, such as polyester, nylon and acetate. Their nature is covalent very less soluble in water but good soluble in other solvents. For the sake of efficient diffusion into textiles, the particles of disperse dye should be as fine as possible comprising low molecular weight molecules in the range of 400 – 600. It is essential for disperse dyes to be able to withstand various dyeing conditions, temperature and pH resulting in negligible changes in shade and fastness (Aspland, 1992, Aspland, 1993). Disperse dyes are often substituted anthraquinone, azo or diphenylamine compounds which are non-ionic and contain no water solubilising groups. The dyes particles are thus detained in diffusion by the surface-active mediator and the dyes themselves are called disperse dyes. These dyes were originally developed for the dyeing of cellulose acetate but now they are used to dye nylon, cellulose triacetate, and acrylic fibers too. The dyeing rate can be significantly subjective by the choice of dispersing agent used during the grinding.

Disperse dyes have short solubility in water, but they can interact with the polyester chains by forming dispersed particles. Their main use is the dyeing of polyesters, and they find minor use dyeing cellulose acetates and polyamides. The general structure of disperse dyes is planar, small and non-ionic, with attached polar functional groups like nitro and cyano. The shape makes it easier for the dye to slide between the tightly-packed polymer chains, and the polar groups improve the water solubility, improve the dipolar bonding between dye and polymer and affect the color of the dye. However, their small size means that disperse dyes are quite volatile, and tend to sublime out of the polymer at sufficiently high temperatures.

Working principle of this dye involves Van-der-Waals and dipole forces between polymer and dye molecules. The dye is generally applied under pressure, at high temperatures of about 130°C. At this temperature, thermal agitation causes the

Figure 11.



Disperse Blue 6

polymer's structure to become looser and less crystalline, opening gaps for the dye molecules to enter. (Singha, 2013).

Mordant Dye

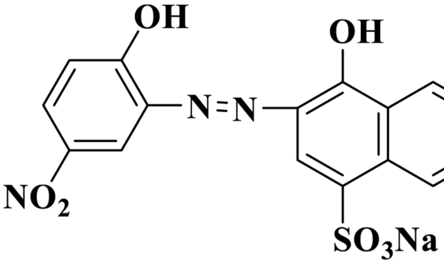
These dyes are named on the basis of working techniques that they require binding agent between the fiber and the dye known as mordant. Some dyes combine with metal salts (mordanting) to form insoluble colored complexes (lakes). These materials are usually used for the dyeing of cotton, wool or other protein fiber. The metallic precipitate is formed in the fiber producing very fast colors highly resistant to both washing and light. The mordant potassium dichromate is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them (Saxena & Raja, 2014).

These are a special class of acid dyes, which are soluble in water and applied to the fiber from an acidic bath. When a solution of an acid mordant dye is mixed with a solution of potassium dichromate in the presence of sulfuric acid, chromium ion from dichromate forms a complex with the dyes, this complex is insoluble in water, and hence precipitates on the fiber.

There are three different methods of application of chrome dyes on the fiber,

1. Chrome – Mordant method
2. After chrome method
3. Meta chrome method

Figure 12.



Mordant Brown 35

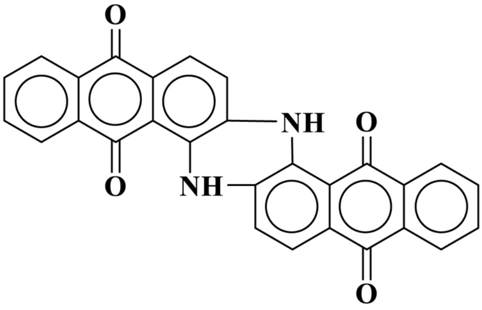
Vat Dye

The vat dyes are insoluble in water and complex polycyclic molecules based on the quinone structure (ketoforms). The term vat comes from the old indigo method dyeing in a vat: indigo had to be reduced to light form. Vat dyes are made from indigo, anthraquinone and carbazole. They are successfully used on cotton, linen, rayon, wool, silk, and sometimes nylon. Vat dyes are also used in the continuous piece of dyeing process sometimes called the pigment application process. The dyeings produced in this way have high wash and light fastness.

Sulfur Dye

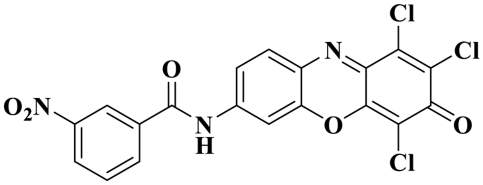
The sulphur dyes provide very deep shades, which have excellent resistance to washing but poor resistance to sunlight. They will dye cotton, linen, and rayon, but not brightly. A problem with sulphur dyes especially the black colors is that they make the fabric tender, or weaken its structure, so that it breaks easily. Sulfur dyes

Figure 13.



Vat Blue 4

Figure 14. Sulfur red 7



are applied to cotton from an alkaline reducing bath with sodium sulfide as the reducing agent. They are low cost and have good fastness to light, washings and acids.

An example is shown in Figure 14.

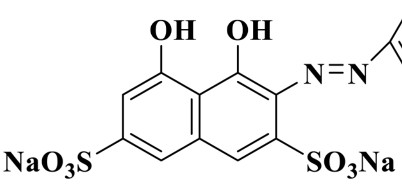
Sulfur dye, a class of dye containing sulfur, has more complex molecular structure. Sulfur dye is generally heated sulfur or sodium sulfide together with certain aromatic amines, amino phenols and other organic compounds, namely vulcanization. Most sulfur dyes are insoluble in water. In dyeing, sulfur dye needs to be dissolved in a sodium sulfide solution or alkaline hydrosulfite solution to reduce to its hidden color, and then absorbed and oxidized by fiber to show color. According to the desired dyeing conditions, sulfur dye can be divided into sulfur dye and sulfide vat dye. The former use sodium sulfide as reducing agent; the latter hydrosulfite as reducing agent, and its fastness and properties is between sulfur dye and sulfide vat dye, so that it is a higher sulfur dye.

Sulfur dye began to be produced in our country, mainly used for plant fiber dyeing. Sulfur dye is characterized by containing a sulfur atom in the molecule, becoming into water-soluble hydrocolloid after the reaction with a reducing agent such as sodium sulfide, dyeing the fibers, and then the dye turns insoluble through the air oxidation. The sulfur dye is not very bright, but generally washable and light fast, enables the fiber brittle. There is also soluble sulfur, which is soluble in water, and more convenient to use. The sulfur dye is a mixture generating from every reaction stage. In 1950, the continuous dyeing method of fine particles of sulfur appeared, but it occurred unsalable after the 1950s, because of the successive appearance of reactive dyes and advanced direct dyes, light fastness direct dye especially. Still, owe to its budget and other factors, it is still in use.

Azo Dyes

Azo dye is produced directly or within the fiber during the dying process. This can be achieved by reacting fiber with diazoic and coupling component. By monitoring the reaction conditions one can adjust bath criteria to produce required insoluble azo dye. In this dying process final color is given by the selection of diazoic and coupling components. This is outstanding feature of this dye. This method of dyeing

Figure 15. Acid red 29 (AR29) azo dye



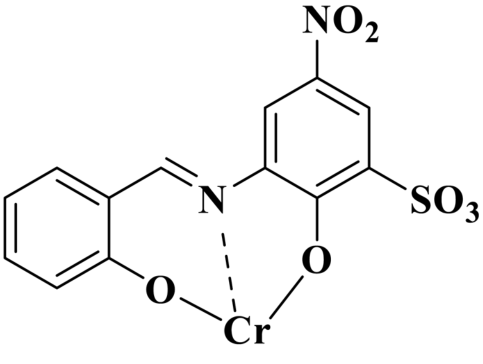
cotton is declining in importance due to the toxic nature of the chemicals used. Azoic dyes also known as Naphthols in the industry are actually manufactured in the fabric by applying one half of the dye. The other half is then put on and they combine to form the finished color. Unless they are carefully applied and well washed, they have poor fastness to rubbing or crocking.

Solvent Dye

These dyes are hydrophobic but soluble in alcohols, chloroforms or liquid ammonia. These colors are applied by dissolving in the target, which is invariably a lipid or non-polar solvent. The Color Index uses this as a classification and naming system. Each dye is named according to the pattern: – solvent + base colour + number .They are used for coloring, plastics, gasoline, synthetics, oils and waxes.

An example is shown in Figure 16.

Figure 16. Solvent yellow32



APPLICATION OF DYE IN VARIOUS FIELDS

Polymer linked synthetic dyes are of growing interest for medical and technical applications due to their multipurpose properties and increasing environmental awareness. The advantages over low-molecular compounds seem to be not only the condensed toxicity or the possibility of better upturn and reusability but also improved quality characteristics such as high color fastness in textile dyeing. Herewith some useful application of dye containing polymers are collected and discussed in consideration of their properties and linkage to the polymer.

Waste Water Treatment

The environment is being more and more affected by the steadily increasing frequency of dye pollutants, which induce unwanted color contaminations and sometimes have toxic effects to humans and animals (Azmi, Sani & Banerjee, 1998; Robinson, McMullan, Marchant & Nigam, 2001). Dyes are valuable materials not only in the textile industry but also in the manufacturing of plastics, paper, cosmetics, medicine and biology. Thus, effective dye removal from waste water is becoming more important. Plenty of chemical, physical and biological methods such as fungal decolorization, ozonation, and degradation, activated carbon usage, membrane-filtration or electrochemical techniques like coagulation have been developed and optimized in recent years (Alinsafi *et al*, 2005; Forgacs, Cserhati & Oros, 2004). Regardless, adsorption and the formation of inclusion complexes still seem to be the most effective and cost effective methods for the purification of effluents.

1. Polysaccharide-based materials which are non-toxic, stable and renewable can be a cheap and effective alternative to commonly used systems (Crini, 2005; Babel & Kurniawan, 2003). They exhibit a high binding capacity and specificity. Most popular example is represent by calix[4]arenes which have a high elimination ability for preferred water-soluble azo dyes (Yilmaz, Yilmaz, Yilmaz & Bartsch, 2007).
2. Biopolymers like chitin and starch are abundant and also modifiable to produce selective and biodegradable compounds like cyclodextrin and chitosan. The latter compound is a linear polycation with high affinity to reactive dyes like the anthraquinone and azo derivatives reactive blue 2 and reactive red 2 that are commonly used in textile dyeing and chemical research.
3. Chitosan can also be used for the adsorption of indigo carmine, an indigo derivative which is used as food additive and redox indicator, pH indicator (Prado, Torres, Faria &Dias, 2004).

4. Polymers can also be used not only used for waste water purification processes with dye pollutants. Due to the dyes' affinity to polymers and several low-molecular compounds, or rather metal ions, dye-containing polymers can be used anthraquinone based poly(vinyl chloride) (PVC) membranes in which the anthraquinone is covalently attached to the polymer are of great value for lead determination in waste water

Paintings and Textiles

The best-known applications of dyes for hundreds of years are painting and to provide beautiful color to textiles. Most dyeing processes are restricted to non-covalent attachment to textile fibers like nylon, wool, silk and cotton. Covalent dye-polymer systems are also known, often offering even better characteristics. The most important dye-polymer systems in textile industry and paintings are described below

1. Polymeric indigo derivatives are known that show a high resistance towards heat and solvents due to their low solubility and stability. Therefore, they can be used as high quality fibers and films (Voss et al, 2009).
2. Anthraquinone derivatives like β-thio or β-phenol substituted 1,8-dihydroxy-4,5-diaminoanthraquinone exhibited a high affinity for polymer fibers like polyesters and produce a blue-greenish color (Peters, 1990)
3. Anthraquinone sulfonic acid derivatives, in some cases bearing further amino groups, are important compounds for dyeing processes due to their high affinity towards silk and wool while cellulose fibers leave unaffected

Medicine

Dyes play an important role in medical applications because of both their physicochemical properties and color impression. Since this often involves applications inside the human body, it is quite important to use non-toxic derivatives. There has also been an increasing usage of dyes in the medical sector. Here, dyes act as an important ingredient in many of the medical tests conducted on humans. These dyes in coordination with latest diagnosis equipment allow flawless handling and high accuracy in tests that are carried out on patients.

1. Fluorescein angiography that derives its name from fluorescein. This dye is successfully used for carrying out tests like Angiogram which provides valuable information about the circulatory system.
2. Polymers are a good alternative to low-molecular dyes for in vivo applications like polymer-linked water-soluble rylene dyes for cell Polymers staining

3. *In vivo* application of polymer-attached dyes in medicine could be the therapy of rheumatoid arthritis.
4. Polymers in medicine are artificial iris implants, which are used to treat iris defects by improving vision and reducing glare.
5. Color tablets (coated/uncoated)
6. Staining on shell capsules
7. Syrup coloring
8. Providing color to drug that enhances the aesthetics as well as aids product identification

Electronic Devices

Organic dyes play an important role as fluorescence markers in spectroscopy and microscopy and as chromophores in sensory proteins and light-driven enzymes. Furthermore they have a great potential for application in the field of photovoltaics and in organic LEDs. Polymers used for the preparation of nonlinear optical azopolymers are amongst others polyacrylates, polyesters and polysilanes.

1. New copolymers with pendant azo-benzene chromophores that can be used as memory devices
2. The azo dye was functionalized with a polymerizable maleimide group and copolymerized with styrene to yield an active layer with rewritable flash memory performance (Liu, Li, Xia, Ge, Xu & Lu, 2011).
3. Aromatic azobenzene compounds have quite good stabilities in the cis-configuration and are able to store light energy as a chemical structure change. The optical storage can be either holographic or digital
4. Azo dye doped polymers like poly(methyl methacrylate) can also be used as optical data storage media
5. Azo polymers is their nonlinear optical behavior. Therefore, they can be used as modulators or optical frequency doublers and switches while showing good mechanical characteristics and processability

Optical Sensors

1. Polymer-attached dyes, which refer to the optical characteristics of the dye, is polymer-attached phenolphthalein that can be used as pH-sensitive material for analytical purposes.
2. The diacrylated phenolphthalein derivative can be used as a cross-linker to form superabsorbent and insoluble polymers while still being pH-sensitive. Therefore, these polymers are suggested for reusable materials for analytical

purposes to indicate basic medium (Fleischmann, Cheng, Tabatabai & Ritter, 2012).

3. Potential applications for mechanochromic blends are data storage devices, security plastics and papers, or mechanosensors and pressure sensors (Pucci & Ruggeri, 2011).

Electrochemical and Optoelectronic Applications

Nowadays, also electrochemistry is more and more affected by the polymer chemistry since high molecular structures offer good processability and modifiability, while giving the opportunity to combine the advantages of polymeric compounds and the properties of low molecular substances.

1. Anthraquinone-based polymers are excellent candidates for high-performance cathode materials
2. Another application of dye-containing polymers in electrochemistry is the coating of electrodes with polypyrrole films and use of indigo carmine as the counter ion.
3. Polypyrrole is a conducting polymer with the advantages of good stability and simple preparation. Therefore, it can be used as a modified electrode for a biosensor, electrocatalyst or electrochemically controlled release device
4. A quite new field of interest in polymers combined with dyes is organic light-emitting diodes (OLEDs) or rather polymer light-emitting diodes (PLEDs), which can be used as a full-color, high-efficiency and low-drive voltage material for flat-panel displays (Shirota *et al*, 2007).

HEALTH AND ENVIRONMENTAL IMPACT OF DYES

Chemical industries are distributed worldwide and dyes manufacturing industries constitutes its very small part. Nearly about 8 lakhs tons per year dyes are produced out of which almost 20% dyes are gone during different procedures of textile industries. Synthetic dyes are cherished in several industries such as paper printing, textile, food, leather, pharmaceutical and cosmetics. As we have already discussed about the classification of dyes viz: acid, direct, reactive, basic, vat, disperse, mordant, metal complex and sulfur dyes and many more. Azo dye constitutes major part of the textile manufacturing dyes out of 10,000 dyes due to its complex and synthetic nature. A major source of color release into the environment is associated with the incomplete enervation of dyes onto textile fiber from an aqueous dyeing process and the need to reduce the amount of residual dye in textile sewage has become a major alarm in recent years.

The workers who work in textile industry are the major sufferer who at the most risk and their health is affected most. However, with prolonged or accidental over exposure, there can be likely health hazards and all dyes and chemicals must therefore be treated with attention. Respiratory tract is affected in most of the cases due to inhalation of minute dust particles of dyes. Sometimes they can affect a person's immune system and in dangerous cases this can mean that when the person next inhales the dye their body can react intensely. Respiratory sensitization can be caused which includes symptoms like watery eyes, sneezing, itching and coughing, wheezing asthma like symptoms.

Perchance the biggest health problems related to dyeing and finishing processes arise from acquaintance to chemicals acting as aggravations. These may cause skin irritation, itchy or sneezing, blocked noses, and sore eyes. They include formaldehyde-based resins, ammonia, acetic acid, some shrink-resist chemicals, some optical whiteners, caustic soda, soda ash and bleach. Certain vat, reactive and disperse dyes are also recognized as skin sensitive. Textile industries produce large amounts of liquid wastes also called as effluents contain organic and inorganic compounds. During the dyeing processes, not all dyes that are applied to the fabrics are fixed on them and there is always a percentage of these dyes that remains unsettled to the fabrics and gets eroded out. These unfixed dyes are found to be in high concentrations in textile effluents (Hassan, 2016; Elliot, Hanby & Malcolm, 1954; Hassan & Nemr, 2017; Ananthashankar, 2012).

The usage of cotton has been growing constantly throughout the past century (UNCTAD, 2012). Cotton fibers are mainly dyed using azo dyes which are one of the largest groups of synthetic colorants used in the industry (Mohan, Rao & Karthikeyan, 2002). Azo dyes are difficult to degrade by the current conventional treatment processes. They are characterized by the presence of the nitrogen-nitrogen bond (-N=N-) in the center and hence they are highly electron deficient (Robert, Joseph & Alexander, 2008). These azo dyes are found to be complex in nature and have been found to show carcinogenic evidences on reductive cleavage. These dyes are capable of altering the physical and chemical properties of soil, deteriorating water bodies and causing harm to the flora and fauna in the environment. It was observed that the toxic nature of dyes causes death to the soil microorganisms which in turn affect the agricultural productivity (Savin & Butnaru, 2008).

1,4-diamino benezene is an aromatic amine whose parent azo dyes can cause skin irritation, contact dermatitis, chemosis, lacrimation, exopthamlmose, permanent blindness, rhabdomyolysis, acute tubular necrosis supervene, vomiting gastritis, hypertension, vertigo and, upon ingestion, oedema of the face, neck, pharynx, tongue and larynx along with respiratory distress (Sekar, 1999). Aromatic amines can be mobilised by water or sweat, which encourage their absorption through the skin and other exposed areas, such as the mouth. Absorption by ingestion is faster and so potentially more dangerous, as more dye can be absorbed in a smaller time frame (Puvaneswari, Muthukrishnan & Gunasekaran, 2006). Water soluble Azo dyes become dangerous when metabolized by liver enzymes.

Human toxicity of textile dyes can be considered in terms of acute toxicity and chronic or genotoxicity. Acute Toxicity of Textile Dyes Acute toxicity involves oral ingestion and inhalation; the main problems of acute toxicity with textile dyes are skin irritation and skin sensitization, caused mainly by reactive dyes for cotton and viscose, few acid dyes for polyamide fibers and disperse dyes for polyester, polyamide and acetate rayon (anonymous, 2002).

Hazards of Water Pollution

Mills discharge millions of gallons of this effluent as hazardous toxic waste, full of color and organic chemicals from dyeing and finishing salts. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the effluent highly toxic. (Kant, 2012) Other harmful chemicals present in the water may be formaldehyde based dye fixing agents, hydro carbon based softeners and non bio degradable dyeing chemicals. The mill effluent is also often of a high temperature and pH, both of which are extremely damaging.

The waste water that flows in the drains corrodes and incrustates the sewerage pipes. If allowed to flow in drains and rivers it effects the quality of drinking water in hand pumps making it unfit for human consumption. It also leads to leakage in drains increasing their maintenance cost. Such polluted water can be a breeding ground for bacteria and viruses (Malik & Grohmann, 2014) Impurities in water affect the textile processing in many ways. In scouring and bleaching they impart a yellow tinge to white fabric. In dyeing stage metallic ions present in water sometimes combine with the dyes causing dullness in shades

Textile effluent is a cause of significant amount of environmental degradation and human illnesses. About 40 percent of globally used colorants contain organically bound chlorine a known carcinogen. All the organic materials present in the wastewater from a textile industry are of great concern in water treatment because they react with many disinfectants especially chlorine (Gita, Hussan & Choudhury, 2017) Chemicals evaporate into the air we breathe or are absorbed through our skin and show up as allergic reactions and may cause harm to children even before birth.

Effect on Photosynthetic Activity

The colloidal matter present along with colors and oily scum increases the turbidity and gives the water a bad appearance and foul smell. It prevents the penetration of sunlight necessary for the process of photosynthesis (Ananthashankar, 2012). This interferes with the Oxygen transfer mechanism at air water interface. Depletion of dissolved Oxygen in water is the most serious effect of textile waste as dissolved oxygen is very essential for marine life. This also hinders with self purification process of water. In addition when this effluent is allowed to flow in the fields it clogs the pores of the soil resulting in loss of soil productivity. The texture of soil gets hardened and penetration of roots is prevented.

Biodegradability

Biodegradability of dyes are very less they are very resistant for dyes are stable against cessation by many microorganisms and most dyes do not biodegrade under the aerobic biological treatments, in a municipal sewage plant. Many dyes, including the azo dyes, degrade under anaerobic conditions and the aromatic amines thus formed have been found to degrade further aerobically. Therefore, the aerobic conditions of rivers and lakes should degrade the amines formed from the biodegradation of azo dyes if they accumulate in the river sediments. Due to this recalcitrant nature of dyestuffs under aerobic processes, concern arose as to the toxicity of these compounds towards the microorganisms (Sriram, Reetha & Saranraj, 2013; Carson & Mumford, 2002).

Heavy Metal Emission

Exposure to metal by dyes can be by two reasons that metals are used as catalyst as well as they may be present as impurities. Another option is that they may ac as chelating agent forming metal chelates with dye molecule. The limits of discharge for heavy metals are stringent as they can be toxic to creatures and aquatic life. Metal complex dyes contain chelated chromium, copper, cobalt and nickel. Some cationic dyes contain zinc and trace concentrations of Hg, cadmium and arsenic can be present as impurities from intermediates (Bolzan, 2014)

Auxiliaries Contained in Dye Formulations

Depending on the dye class and the application method employed (e.g. batch or continuous dyeing) different additives such as salts, dispersants, powder binding agents, anti-foaming agents, thickeners, anti-freezing agents, buffer systems etc. are present in the dye formulations. Since these substances are not absorbed/ fixed on the fibers, they are completely discharged in the waste water. While these additives are not toxic to aquatic life, they are in general poorly decomposable and not readily bio eliminable. Other not readily eliminable additives are acrylate and CMC-based thickeners and anti-foam agents.

CONCLUSION

Dyes are essential part of our life from ancient time to modern time and more advance time it is being used in so many purposes weather it is coloring fibers, textiles, food, medicines, paints and varnishes to give attractive aesthetic appeal to these artifacts. Dyes obtained from nature are less hazardous as they can be biodegradable can be reusable and recyclable. Synthetic dyes are very harmful to mankind not only to human being but also other creatures also disturbing complete ecosystem. In view of these facts, many more corrective measures need to be take to control the pollution created by these harmful dyes.

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KEY TERMS AND DEFINITIONS

Dyes: Dyes are organic or inorganic substances obtained from plant or animal products without any chemical treatment and which are used to provide beautiful color to the substances.

Mordant: These are the binding agents that are required for the binding of fiber and dye.

Chapter 3

Toxicology of Dyes

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ABSTRACT

Colours play a prominent and dominant role in human life. The dominating feature of any product has been found with its colours elevating the market of colouration in different sectors. Studies have shown that around 10,000 dyes are being circulated in market. Chemistry has been found to lead this industry of colours. Vast production of fabric colours include azo dyes, whereas anthroquinone is also one of the prevailing complexes for cotton and fabric dyeing. The toxic level of the dyes and pigments are not confined till manufacturing but also have after usage effect of the products. It has been found that the chemicals have a carcinogenic effect on human health. During the manufacturing procedure, around 50% of dye stuff gets along with the effluents of the industry leading to release of colourful water. Modification in choice of chemicals is being considered to lessen the toxic effects of existing complexes. This chapter is mainly focused on the toxicology of dyes.

INTRODUCTION

The two major types of colorants or dyestuffs produced today are dyes and pigments. Dyes are coloured organic (i.e., they contain carbon) compounds that are used to impart color to various substrates, including paper, leather, fur, hair, drugs, cosmetics,

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waxes, greases, plastics and textile materials (Sivashankar *et al.* 2014). Pigments which are finely ground solids dispersed in a liquid, such as paint or ink, or blended with other material pigments may be inorganic compounds (i.e., they do not contain carbon) or organic compounds they generally give brighter colours.

Dyes possess colour because they:

1. Absorb light in the visible spectrum (400–700 nm),
2. They posses at least one chromophore (colour-bearing group that can undergo π-π^* and n-π^* transitions)
3. They have a conjugated system, i.e. a structure with alternating double and single bonds
4. They exhibit resonance of electrons, which is a stabilizing force in organic compounds

When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as *auxochromes* (color helpers that cannot undergo π-π^* transitions, but can undergo transition of n electrons), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups (Anna 2014). Auxochrome are not responsible for colour, their presence can shift the colour of a colorant and they are most often used to influence dye solubility

In Indian chemical industry dyes and dye intermediates industry is an important sector that has grown at a very fast pace (Gonawala & Mehta 2014). India is now the second largest producer of dyes and intermediaries in Asia. Today dyes are being used by almost every industry producing household goods, food, textile paints, paper, pulp, printing etc. The release of toxic and hazardous dyes from these industries has created a global concern due to their huge toxicity toward mankind. Many dyes and pigments are toxic and have carcinogenic and mutagenic effects that affect aquatic biota and also humans (Mathur *et al.,* 2014). Color blocks light penetration which delay the photosynthetic activity and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms. The dyes undergoing oxidation and reduction in water which produces toxic and hazardous intermediates/substances which further increase need for their removal from wastewater. The remnants of dyes in water pose serious problem during water purification process (Pirkarami & Olya 2017). The dyes are being designed with combination of complexes which when leach out in water do not get break down and mark their existence for a very long period of time which disturb the water ecosystem. Presence of dyes in water is serious concern as a high concentration of water being affected by these dyes. In addition, food has also become a huge market for dye industries. Food market use dyes in high concentration to make food more attractive and colourful. The chemicals being utilized for dyeing are found to have high toxicity thus causing serious health problems. With emerging world of textiles and growing market of food, the use of dyes is going to elevate. It is a necessity to have check on the chemicals being utilized as dyes. There are several measures which have come into action for checking the toxicity level within the dyes and also to prevent high consumption of dyes. There is a need of designing environment friendly dyes which have the ability to decompose easily and also to not pose health problem if consumed.

CLASSIFICATION OF DYES

Natural Dyes

From ages humans have been attracted to colours and nature have played a prominent role in illuminating the world of colors. Humans have learned to utilize these colours as dyes in textiles medicines and many more. Indigo dye was found to be the first natural dye with dark blue colour which was obtained by fermentation of plant leaves (Chattopadhyay 2011). Natural dyes have been classified as follows.

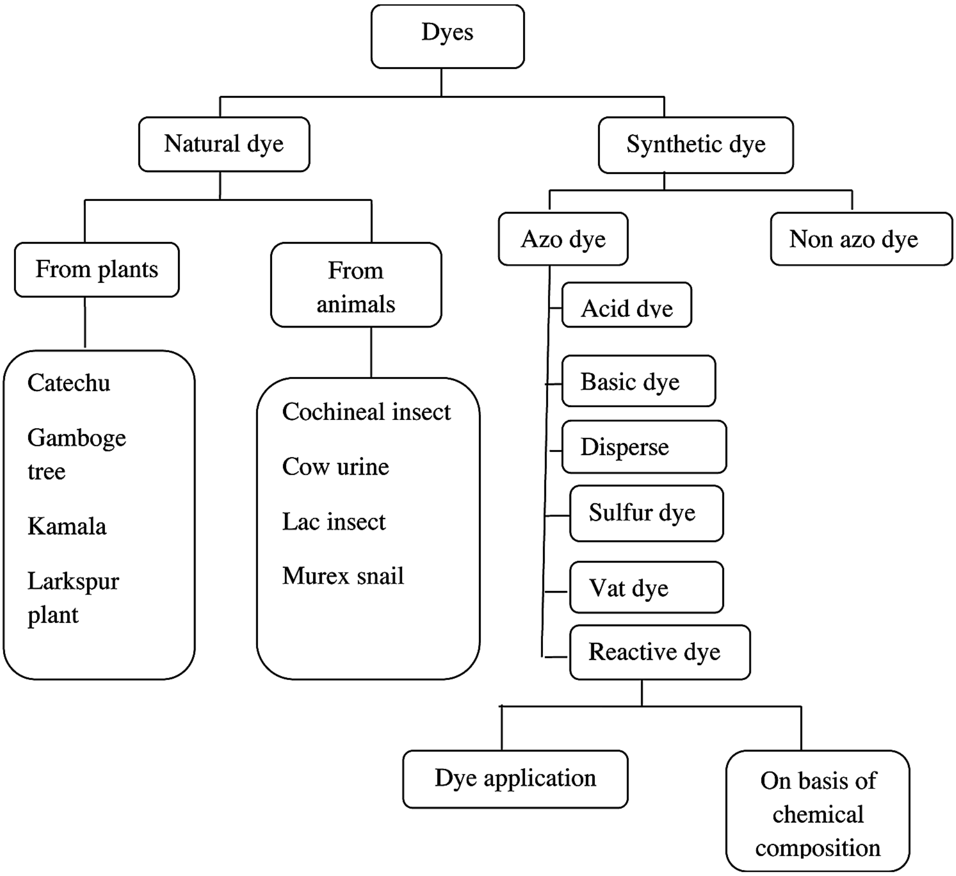
Based on Origin

Natural dyes are obtained from various sources. Some of the dyes such as log wood, madder are obtained through different plant parts such as root, bark, leaves, flowers, skin and fruits (Siva, 2007). Dyes with anthraquinone nucleus such as cochineal, lichen are extracted from insects. Minerals provide inorganic compounds such as cinebor, ultramarine which act as dyes and are insoluble in water.

Based on Their Colours

Natural dyes have been classified on the basis of colours of visible spectrum which may vary due to varied soil quality, extraction from different parts of plant and season of growth. For instance, red colour dye mainly found in root or barks extract. Cochineal dye is found to possess vibrant red colour along with other dyes such as Manjith, Kusumbar and kermiz (Vankar, 2012). Yellow colour is another most widely found dye from plants such as bougainvillea, parijata, teak and many more. Black and blue are also some of the colours found from the sources of plant such as Indigo, Pivet, lac and alder.

Figure 1.



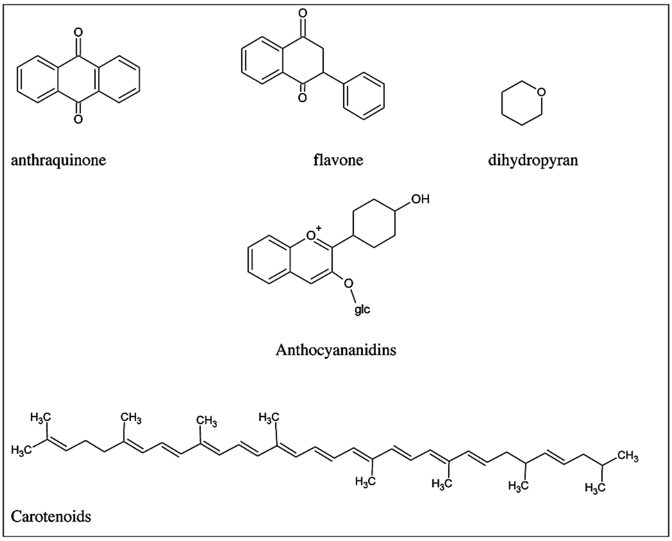
Based on Chemical Structure

Dyes have been classified based on their chemical structure such as indigoid, anthraquinone, alpha-hydroxy-napthoquinones, flavones, dihydropyrans, anthocyananidins, carotenoids.

Synthetic Dyes

Extraction of natural dyes was found to be time consuming. Quantity of product was found low in accordance with the demand which led to the discovery of mauve, a synthetic dye, in 1856 which have catalysed the production of dye (Dweck, 2002). Synthetic dyes prove to be a success in escalating the production of dyes with vast variation in colours. Coal tar has been found to be the pioneer of the synthetic dyes,

Figure 2.



so the synthetic dyes are named ‘Coal tar dyes’ possessing mainly hydrocarbons. Dyes are further classified on the basis of chromophore (Benkhaya *et al.,* 2017) shown in Table 1.

Table 1. Constitution (chemical) classes of dyes recognized in the colour index

Nitroso dyes	Indophenol dyes
Nitro dyes	Azine dyes
Azo Dyes	Oxazine dyes
Azoic dyes	Thiazine dyes
Stilbene dyes	Sulfur dyes
Carotenoid dyes	Lactone dyes
Diphenylmethane dyes	Aminoketone dyes
Triarylmethane dyes	Hydroxyketone dyes
Xanthene dyes	Anthraquinone dyes
Acridine dyes	Indigoid dyes
Quinoline dyes	Phthalocyanine dyes
Methine dyes	Natural organic colouring matters
Thiazole dyes	Oxidation bases
Indamine dyes	Inorganic colouring matters

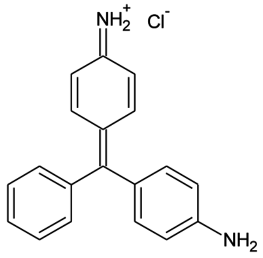
Dyes have been also classified on the basis of applicability.

Acid Dyes

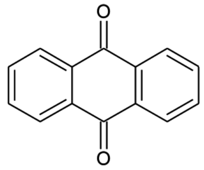
Acid dyes promote ionic interaction between fibre and dye. Acid dye is the salt of sulphonic acid, carboxylic acid or phenolic acid. Acidic dyes are water soluble due to theie ionic interaction with that of the fibre (Kiernan 2019). Acidic dyes are favourable for wool, silk and modified acrylics. Acid dyes have been classified as follows:

- Levelling acid dyes – Dyes with low molecular weight along with high mobility.
- Milling dyes – Dyes have moderate molecular weight which has less mobility in comparison to levelling dyes.
- Metal complex acid dyes – Transition metal combines with different complexes which are more economical and produce relatively dull shades.

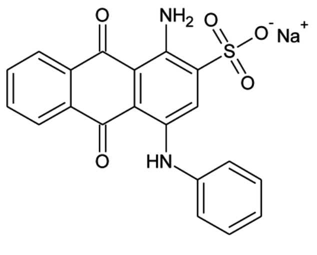
Figure 3.



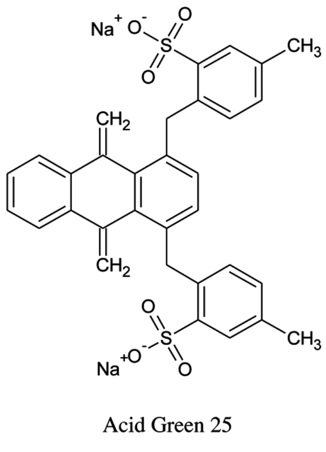
Triarymethane



Anthraquinone



Acid Blue 25



Acid Green 25

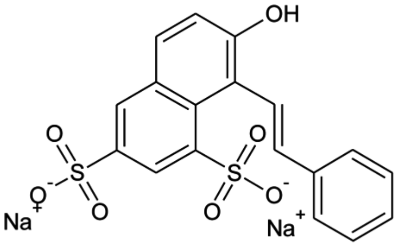
Basic Dyes

Basic dyes combine with anionic entity during dyeing. Basic dyes are cationic dyes composed of positively charged group such as amino in combination with chloride group. Basic dyes impart vibrant shade to fabrics and are water insoluble (Srinivasan & Viraraghavan 2010). Basic dyes are found soluble in alcohol, methylated spirit or glacial acetic acid. These dyes are good for jute, wool and acrylic. They may also be used on cotton after applying mordant.

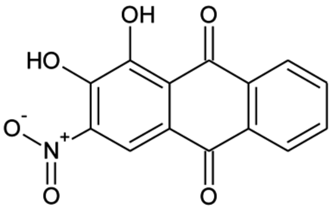
Mordant Dyes

Mordant dyes act as the binding group for the dye and the fibre. Mordant promote the dyeing ability of insoluble dye and are generally dichromates. Mordant dyes improvise the fastness of dyes. Mordant may include acids such as sumac, gall nuts, oleic and stearic acids or it may include metals such as iron, chromium.

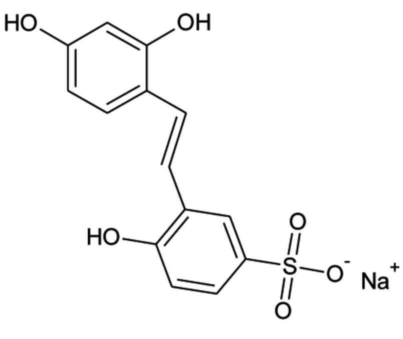
Figure 4.



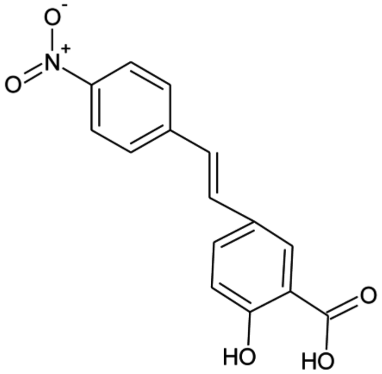
Acid orange 10



Acid mordant orange 14



Mordant red 5

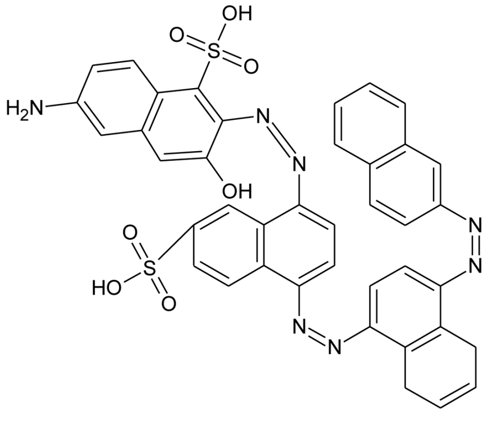


Mordant orange 1

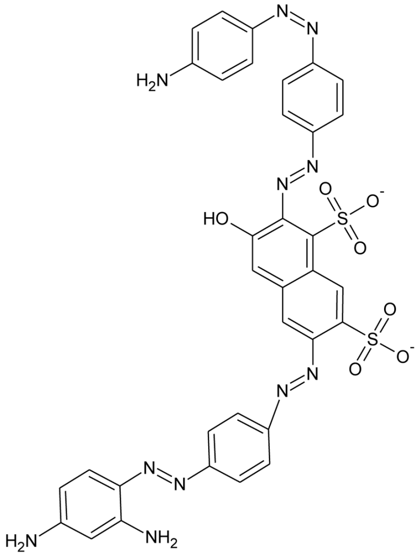
Direct Dyes

Dyes which can be directly applied onto the fabric are direct dyes or substantive dyes. These dyes are water soluble dyes and are composed of salt of sulphonic acid or azo group as chromophore. The process require alkaline medium to disperse the colour of dye onto the fibre.

Figure 5.



Direct Blue 71



Direct Black 19

Vat Dyes

Vat dyes make a different class of dyes which are good for cellulosic fibre as well as cotton fibre. During dyeing, vat dyes are solubilized in in vat through fermentation which is popularly known as vatting. Vat dyeing is performed in alkaline conditions and involves oxidation reactions.

Reactive Dyes

Reactive dyes are covalently linked with the fibres. Reactive dyes get blend with the fibre as they form strong bond with the nucleophilic entity of the polymer chain. Due to this bond the washfastness of the dye have been increased many folds which led to the boost in their usage. These dyes are proved to be highly efficient for wool and nylon.

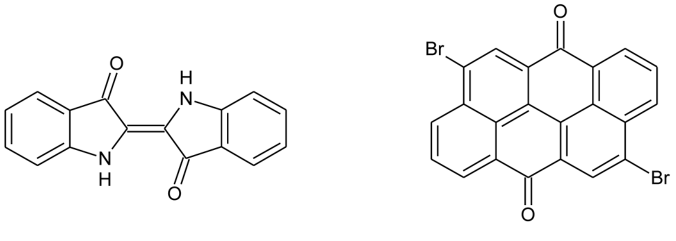
Disperse Dyes

Disperse dyes are designed for synthetic clothing. These dyes are non-ionisable dyes because of which they do not possess water soluble dyes. They are applied mainly on polyester yarn. Generally they are the derivatives of azo, anthroquinone and many more.

Sulphur Dyes

Dyes with sulphur-sulphur bond are placed in different class of dyes. Oxidation reactions are responsible for dying as same as that of vat dyes. These dyes are also applied within alkaline solution. These dyes are water insoluble dye.

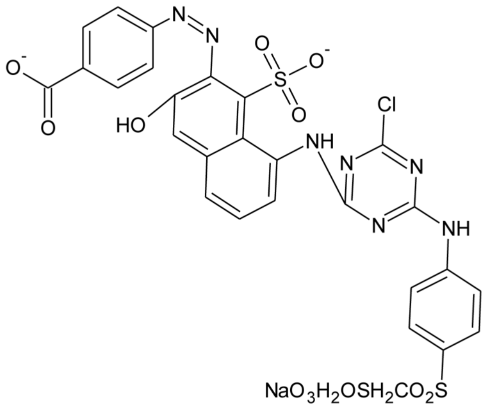
Figure 6.



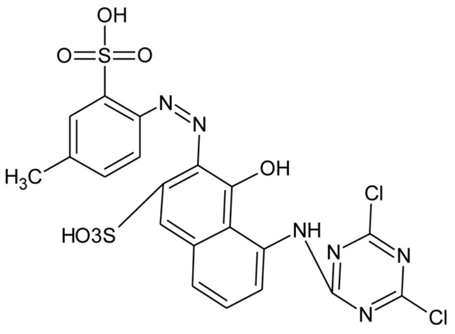
Vat blue 1

Vat Orange 3

Figure 7.

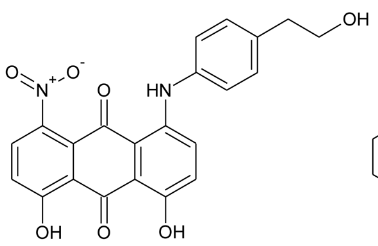


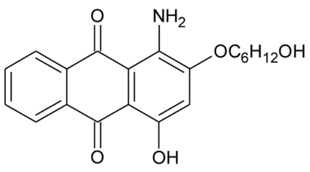
Reactive red 108



Reactive red 8

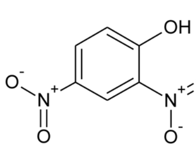
Figure 8.



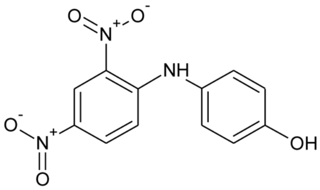


Disperse Blue 27　　　　Disperse Red 91

Figure 9.

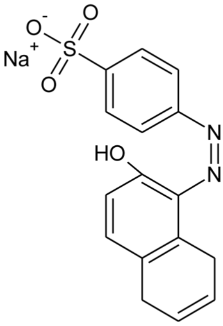


Sulfur Black

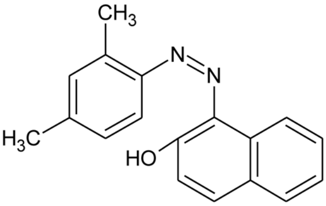


Sulfur Blue Dye

Figure 10.



Acid Orange 7



Solvent Orange 7

Azo Dyes

This class of dyes include nitrogen as azo group. They have been classified further on the basis of their application on different clothes. The aromatic entity of these dyes make them water soluble so that they can have wide range of application such as biological stains, plastics, cosmetics and many more.

TOXICITY OF DYES

Dyes have been in prominent role since years. It has been a medium of imparting colours to the textiles, in understanding biological world in a better way and many more. Later, serious health issues have led to research on dyes effect. Dye industry has been found with hazardous effluents which resulted in water pollution (Rasalingam *et al.,* 2014). In addition, incapability of dyes to bind with the product has posed excess release of organic dyes in water and surroundings. Excess concentration of dyes within nature has been a topic of concern worldwide as it is not only disturbing human life but also whole biosphere. As organic dyes does not oxidise naturally, there is a need to device their proper degradation process.

Aromatic structures in dyes withstand heat and oxidization and are prove to be carcinogenic in nature (Harshad *et al.,* 2015). Since ages, water is being an integral form of life has been in concern for the high rate of increasing pollution. Dyes have played an additional role in water pollution by leaching organic effluents within water bodies (David *et al.,* 2014). These chemicals have been dreadful to the living organism as they are not biodegeradable. Dyes also block light rays from reaching down the water line thus effecting photochemical processing in water. In medical industry, dyes have affected human health adversely.

Azo dye is a diazotised amine. Benzidine is one of the main nucleus of azo dye such as congo red. Reportedly, benzidine entity has carcinogenic effect. Congo red has been banned as it does not support biodegradable as well as photodegedable effort. Congo red cause mutagencity and is also highly stable (Nedra *et al.,* 2018). Decolourized form of the organic entity opens path to high toxicity which causes allergic problems and microbial attack. Dye effected water bodies are difficult to treat due to the structure complexity. Another azo dye which came up with high toxicity is Eriochrome Black T (EBT) having hydroxyl naphthalene entity (Soloman *et al.,* 2009). Due to high complexity within the structure and with conditional stability, it is not possible to degrade the constituents of dye. As Eriochrome Black T is a textile oriented dye, it causes skin irritation and respiratory issues.

Tartrazine when combined with brilliant blue shows off different shades of green colour which has been actively used in food items, medicines and many more. Later, research has unfolded the allergic reactions caused by the use of this combination of dyes. Moreover, it also causes irritation and restlessness in body (Moutinho *et al.,* 2007).

Cationic dyes such as methylene blue, are positive dyes and bind with the fabric through electrostatic interactions. These dyes are being applied on cotton and wool. Dye get strongly adsorb on solids. These dyes are adversely affects the gastrointestinal tract, burning sensation in eyes, methemoglonemia and also convulsive action in case inhaled (Hongmiao *et al.,* 2012).

Nitro dyes, composed off nitro group are mainly derivatives of o-nitrophenols or naphthols. These dyes have high affinity for polyamide, paper, soap and many more. In spite of various applications, dye was found to cause eye irritation, and respiratory problems when in contact to skin. Due to high stability of dye, it stays for long period of time thus stays there to spread toxicity among living beings.

Eradication mediterranean fruit fly (Ihsan *et al.,* 2019) has been a matter of concern with the help of pesticides. Dyes have played a major role in treatment of these flies. Photo activated dyes such as xanthenes, fluoroscein sodium salt and phloxine B have been found as few effective chemicals against Mediterranean fly.

Brilliant blue, a triarymethane (Gupta *et al.,* 2006) is food oriented dye which helps to make food more attractive for consumption. Study revealed that action of brilliant blue on serum creatine, serum urea and glutamate oxaloacetate transaminas led to high adverse effect on the renal and also reduce spermatogenesis (Amin *et al.,* 2010).

Various scientist have studied the effect of hair dyes on human. It has been reported that from past years, the use of hair dyes have increased steeply and so the exposure to chemicals. Hair dyes having ingredients such as aromatic amines have found to be carcinogenic (Peter *et al.,* 2013). The studies have reported that the hair dyes may also result into bladder cancer. It also reported the various health problems including skin irritation and sub chronic toxicity.

Indigo carmine has reportedly come up with their adverse effects. It has acute toxicity and anaemic symptoms towards mice and pigs. Also, it may cause mutagenicity and also may cause eye irritation in living organisms. Indigo carmine is primarily use for denims in textile industry (Filiz *et al.,* 2019). It was found to have carcinogenic effect. In addition, tumour cases have been reported due to the use of this dye. High stability of the dye lead to prolonged presence within the water bodies thus causing harm to the water system.

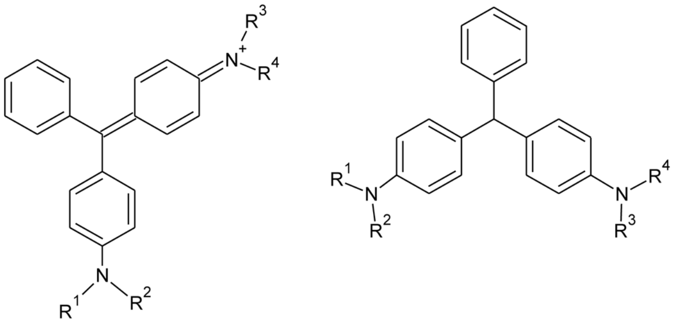
Citrus red 2 is being utilized by the population of florida in order to dye oranges (Sarah & Michael 2012). Recent studies have revealed the inadequacy of the dye in imparting any nutritional value to the food and instead leading to high cancer risk as reported by International Agency for research on cancer.

Fast green is a replacement of light green dye which shows off blue-green colour to during staining of DNA and proteins. Toxicological studies of the dye have revealed high carcinogenicity after applications. Fast green impede the release of neurotransmitter within nervous system and result in sarcomas.

Malachite green, N-methylated diaminotriphenylmethane, have also been marked with cancer causing ability (Culp *et al.,* 2006). Malachite green has the ability to transform cell and cause lipid peroxidation. Cases of tumor have been reported after the use of malachite green as the dye release reactive oxygen species (Wang *et al.,* 2012).

Allura red also known as red 40 is well known dye being utilized for cosmetics and food items (Amold *et al.,* 2012). It has been extracted from plants and animals. According to Food Drug Administration, this has been found to have adverse effect on the reproductive ability of living organisms. People consuming it have been subjected to face tumour of immune system and also lowering the health of new born. It affects the consumer physically which alters their behaviour pattern.

Figure 11.



Malachite green

leucomalachite green

Erythrosine is well known as red 3 and is an organoiodine derivative (Bhat *et al.,* 2017). Red 3 is effectively being used in food items, as ink, as biological stain and many more. These dyes have showed high toxicity by effecting DNA in gastrointestinal area. Research has revealed that this dye is carcinogenic in nature and also it adversely affects the neurotransmitters. Studies have shown that erythrosine is composed of genotoxicity for majorly eukaryotic cells as it had induced reverse mutation and mitotic conversion.

Sunset yellow is a synthetic yellow azo dye having a source from petroleaum based aromatic hydrocarbon (Osman *et al.,* 2004). These dyes have several applications in food products such as ice cream, waffles, starbust and many more. Sunset yellow have been proved to trigger the behavioural changes, sleeping disorders, asthma and also affect respiratory tract of living beings. It has also been found to be one of the reasons for prevailing cancer cases. Besides, it also affects brain and nervous system.

Extra caution should be exercised when using natural dyes especially at home, because even if they are natural, they may not necessarily be safe. Hematin and hematoxlyn, contained in logwood, a naturally occurring dye, is very poisonous and should not be inhaled or absorbed through the skin. Indigo irritates the eyes and the respiratory system. More water is required when using natural dyes.

Evaluation of Toxicity

Evaluation of toxicity is an essential step where the analysis of the dyes is done accurately. Fluorescent technique is one of the essential evaluative parameter which have helped to check the viability of three mammalian cell lines and have found the high toxic effect of propidium iodide, neutral red, alamar blue and 5-carboxyfluoroscein diacetate acetoxymethyl ester. These dyes have been found to have adverse effect on the organisms.

Phytoremediation have emerged as effective technique with cost effective and environmental friendly characteristics (Andreas 2005). This technique utilizes several enzymes during prevention such as tyrosine and laccase. The study was carried out mainly against the harmful effect of reactive blue 160.

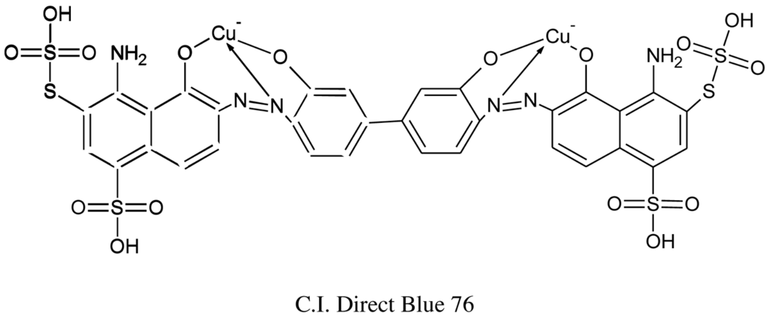
Azo dyes have reached to the alarming level in regard of the toxicity. Soloman *et al.,* (2009) have reported the use of silver nanoparticle which has been designed using leaf extracts of *Azadirachta indica.* Adsorbent with utilization of natural extract has been proved to be environment friendly and also cost effective. Bae & Freeman (2006) reported successful use of Daphnia magna as model for the evaluation of high toxicity of copper complexes direct dyes. Result of the report has given a new method to check the toxicity of dyes in aquatic world.

Mahbub *et al*., (2012) have studied the decolourization ability of some of the micro organisms of *Pseudomonas.* These microbial strains were found to decolourize the azo dyes mainly the chemical entity of 3-chlorobenzoate, phenols and cresols. It was found in the report that azidoreductase enzyme have the ability to break down the complex of dye and mainly the linkage N=N.

For the assessment and treatment use of chemometric methods have been widely used. One of the important method is response surface methodology. It has been reported the efficient ability of consortium to decolourize the methyl orange dye. The study has been carried out with different stains such as Sphingomonas paucimobilis and bacillus cereus. The study have reported elevated concentration of azoreductase, lignin proxidase and laccase which depict their vital role in decolourizing the colour of dye.

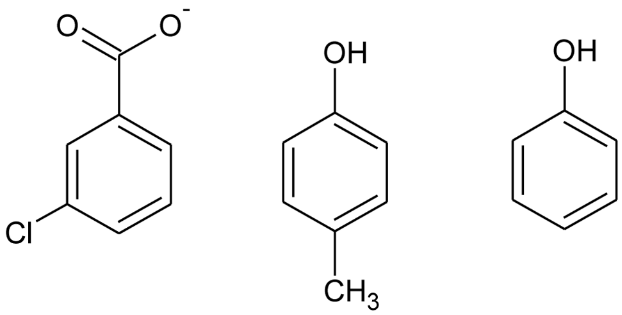
Ayed *et al.,* (2010) studied the toxicity of azo dyes. Halophilic and halotolerant bacteria have been utilized for the decolourization of dye applied on textiles.

Figure 12.



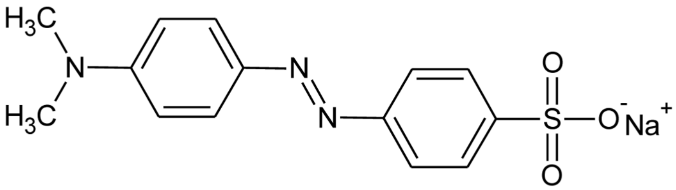
C.I. Direct Blue 76

Figure 13.



3-chlorobenzoate Cresol Phenol

Figure 14.



Methyl Orange

It is necessary to have a check on the toxicity of the dyes and important measures need to be formulated and execute for betterment of the world.

CONCLUSION

Dyes have played a vital role in the world of colours. Prevailing toxicity of these dyes, thus affecting natural resources and living organism, have been a matter of concern. Various parameters have been designed to check the level of toxicity in different dyes. Although several measures have been taken to have a control over pollution of dyes but there is an urge of designing environmentally friendly dyes so that they can be utilized effectively.

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KEY TERMS AND DEFINITIONS

Dyes: A natural or synthetic substance used to add a colour to or change the colour of any substance such as hair and textiles.

Toxicology: The measurement and analysis of potential toxins, intoxicating or banned substances, and prescription medications present in a person's bosdy.

Chapter 4

Impact Assessment of Textile Industries of Rajasthan Using Geo-Spatial Techniques

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ABSTRACT

This chapter highlights water quality parameters of Rajasthan state using satellite remote sensing and GIS technology. Water and soil quality indices have been applied to identify and assess the magnitude of contamination due to textile effluents in the surroundings of textile industries. In the resultant indices, variability caused due to presence of textile effluents is prominently visible and interpreted with geo-statistical representations. Visible change in soil and water quality has been observed in surroundings of textile industries all over the Rajasthan state. Significant variations have been observed in Pali, Sanganer, Bhilwara regions due to presence of textile industries. To conclude, remote sensing and GIS technologies along with natural resource parameters as utilized in the study can be performed for generating assessment reports for extended area at regional as well as national level and providing backgrounds in formulation of government policies for sustainable development and management of textile industries.

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INTRODUCTION

Textile industry is one of the oldest and traditional industry in the world starting from 3000BC. The textile industry is one of the second largest employments and labour intensive Industry. In today's world, fibre or yarns, natural or man-made interlaced material are referred as textile. 'Textile' word is derived from 'Texere' Latin word which means 'to weave'. The fundamental strength of this sector is strong production base. The business of textiles has expanded well beyond just the ordinary needs of the public. Although there still exist pockets where adequate clothing is still not available, it would be fair to say that a high degree of industrialization and the associated economics of scale has made fashion accessible to a large percent of the populace thus giving them greater choice. The textile industry has become one of the pillars of the new consumption driven market economy and encompasses several subsidiary trades which may or may not be directly connected with the production of garments themselves. With today's largely integrated value chains and competition driving down prices, it is highly unlikely that the trend would subside anytime in the near future at least. Textiles have moved up from being a basic necessity into an era of growth where they reflect human aspersion. Development, production, manufacturing and distribution are the major processes involved in converting raw material into final textile industry product. Raw material (wool or cotton) collection, spinning to yarn followed by creation of fabric comes under the accountability of textile industry.

Handloom industry in the form of cottage industry used to exist before the textile industry took roots in India. Many products in the textile were used to prepare at home without using machines but industrial revolution led the production at mass level. Messers Freguson & Company established the first modern textile mill near Kolkata in 1817 and the first spinning mill was established by two Frenchmen in 1830 at Pondicherry. Flying shuttle, spinning jenny, power loom, cotton gin etc. were key inventions which brought the major revolution in industrialization and made it possible to produce mass level fabric. The Indian textile industry from the modern era to present time has created a special place in the world. India poses world's largest Textile Industry. Indian textile industry has improved its production rate with frequent expansion and automation. Textile industry comes under major industries in India because it produces the essential consumer articles. Cotton, Staple Fibre and filament yarn come under the major production in Indian textile industries. The development and growth of this sector has a direct bearing on Indian economy. Around 50 lakhs people are engaged in textile industry in India. Gujarat, Maharashtra, Karnataka, Kerala, Tamil Nadu, West Bengal, Uttar Pradesh, and Madhya Pradesh are the leading textile manufacturing states in India (Chavan, 2001; Govindwar, Telke, Phugare, Jadhav, & Kalyani, 2009).

Rajasthan has deep rooted tradition for textile. In Rajasthan, Krishna Mills Beawar was the first textile mill which was established in 1889. 10 textile mills in the region of Jodhpur, Jaipur, Mewar, Kota and Kishangarh, Ajmer used to be function in Rajasthan before independence. Geographical location, infrastructure, natural resources and government policies are supporting the growth of textile industry in the state. Today, the state consists of Spinning, Weaving, Dyeing, Processing and Printing units in all over the Rajasthan. Majority of the textile industries are indulged in the manufacturing process of synthetic blended yarn. Rajasthan accounts to 40% of the total manufactured yarn in India.

The production and use of textiles include various stages from farming and harvesting (fossil fuel extraction in case of synthetic fibres), knitting and weaving yarns, dyeing, assembly and transport to customer use (which would include laundering inputs) and finally the disposal (which could result in reuse of the product) (Govindwar et al., 2009; Tehrani-Bagha, Mahmoodi, & Menger, 2010; Verma, Dash, & Bhunia, 2012). Chemical processing for the formation of fibre emits hazardous effluents in terms of wastes like liquid, air emission and solid waste. Such wastes harm environment by polluting land, water and air in surrounding area. Azo dyes are used to dye cotton fibres which is one of the major synthetic colorant used in the textile industry (Wang, Yediler, Lienert, Wang, & Kettrup, 2002). Azo dyes have complex nature which indicate carcinogenic evidences on reductive cleavage. Such dyes alter the physical and chemical properties of soil and water. Textile process release about 10-15% of synthetic dyes as liquid effluents. Effluents consist of inorganic and organic compound. Pollutants such as Suspended solid, dyes, acids, detergents, alkalis, heavy metals (Copper, Chromium, Zinc etc.), colours are present in textile effluents. Pollutants should be separated before supplying effluents contained water to domestic, agricultural and industrial use to prevent infectious conditions. There is a need to reduce the quantity of remaining dye in effluents to maintain the quality of water (Paraschiv, Tudor, & Petrariu, 2015)

Textile industries come under the major effluents generators. There are several ways in which the textile industry is contributing to environmental degradation (Chen & Burns, 2006; Hassaan & Nemr, 2017; Insel, Germirli Babuna, Orhon, Eremektar, & Arslan Alaton, 2005; Puvaneswari, Muthukrishnan, & Gunasekaran, 2006). The demand of raw material has adversely affected the environment with the continuous development. Industrial processes and activities, product use, disposal and the use of natural resources pollute land, air and water resources which lead to environmental degradation. The environmental impact of textile sector can no longer be ignored. Effluents not only pollutes the water but also affects the aquatic and terrestrial environment (Banat, Nigam, Singh, & Marchant, 1996; Bruggen, Vreese, & Vandecasteele, 2001; Pelegrini, Peralta-Zamora, De Andrade, Reyes, & Durán, 1999). Rajasthan textile industries are disparaged for polluting environment. Emission of chemical effluents harm the surroundings. Textile sector needs modernization to maintain the standards given by the govt. policies. State government has addressed the concern and given the policies (Singariya & Kumawat, 2017).

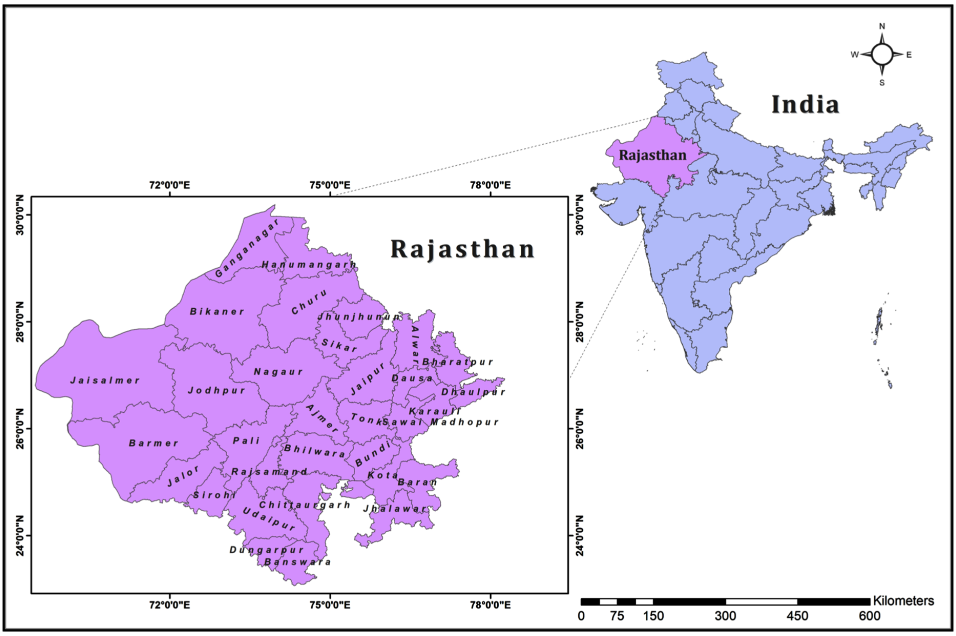
For vast landscape, it is rather difficult to investigate the whole area at once as it consumes lot of time as well as resources. The problem can be solved with the emerging technology such as Remote Sensing & Geographical Information System (GIS). Satellite imageries are being used since 1960's as satellite gives synoptic view of earth. It covers large area in a single imagery which is less expensive than conventional field observation method. Apart from this feature, satellite gives periodical data of the same area in repeat pass (temporal data). Significant number of researches have been through till now using remote sensing technology in various disciplines such as forestry, agriculture, urban, marine, defences, and natural resources. Remote sensing imaging system is widely used to accomplish our requirements in different applications like environmental degradation, ground and surface water quality monitoring, soil quality monitoring, climate change analysis, natural resource management, sustainable development, major pollutant mapping, land cover mapping (Bhavsar, 1984; Chong, Kanniah, Pohl, & Tan, 2017; Joshi et al., 2016; Rowland et al., 2007; Roy, Behera, & Srivastav, 2017). In remote sensing process, energy is transmitted from source to object through atmosphere. Objects on earth surface interact with energy through reflection, absorption, transmission or self-emission. Reflected (visible, NIR range) emitted (Thermal Infra-Red) energy goes back to the sensor. Conversion of this electromagnetic energy to electrical output/ digital image is recorded on board. Later on, the signal is transmitted to ground stations.

STUDY AREA

The Rajasthan State has been taken as study area to know the effect of textile industries on water and soil properties. State comes under West zone of India. Rajasthan is rich in culture, history, geographical features, tourism, economy, minerals, mines and business and in many more sectors. State covers almost 10.4% geographical region of India. Rajasthan shares the boundary with Punjab, Uttar Pradesh, Haryana, Madhya Pradesh, Gujarat neighbouring states and International boundary with Pakistan.

The State comprises of several geographical features including Aravalli Range to The Great Thar Desert along with built-up, agriculture lands, wasteland, wetland, water bodies etc. North-western part of the state is covered by Thar Desert which further extends to the neighbouring country Pakisthan. Jodhpur, Barmer, Jaisalmer, Bikaner and Nagaur comes under the Thar Desert regions and contains scrub forest. The East and South-eastern zone along with Aravalli Range have fertile land with better ground water table conditions. Southern region of State comprises Udaipur,

Figure 1. Study area map



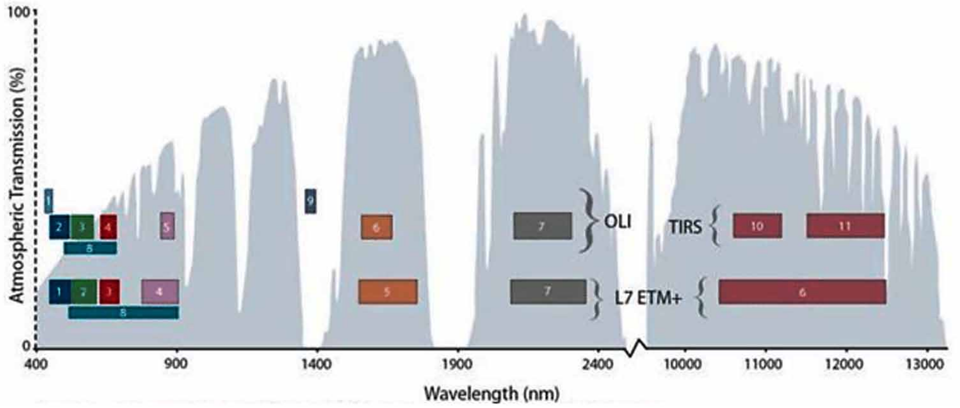
Chittaurgarh, Dungarpur, Banswara dsitricts which are green with tropical dry broadleaf forest. South-eastern zone of the state covers Kota, Bundi, Baran and Jhalawar districts.

Most of the districts in North-east zone are covered by Chambal River. Luni, Ghaggar, Banas, Saraswati, Chambal are the major rivers of the State which cover most of the area. Rajasthan state comes under arid and semi-arid Climatic conditions. State features extreme temperature in summer and winter seasons. Temperature varies between 32ºC to 46ºC during summer season. Temperature ranges from 4ºC to 28ºC in winter season. Rainfall varies from 200-400mm during rainy season. It goes up to 150mm in dry zones of Rajasthan state. Figure 1 shows the study area.

Data Used

Landsat 8 OLI imageries have been used for image processing analysis. Landsat 8 satellite launched on 11th February 2013. NASA and USGS collaborated to develop the Landsat 8 OLI. The satellite payload has two instruments on-board. The Operational Land Imager (OLI) and Thermal Infrared Sensor (TIRS). Satellite gives global coverage with 185km swath and 16 days temporal resolution. OLI sensor has two new spectral bands. One band is used for cirrus clouds and other for

Figure 2. Wavelength description used in Landsat 8 OLI sensor
(USGS, 2013b)

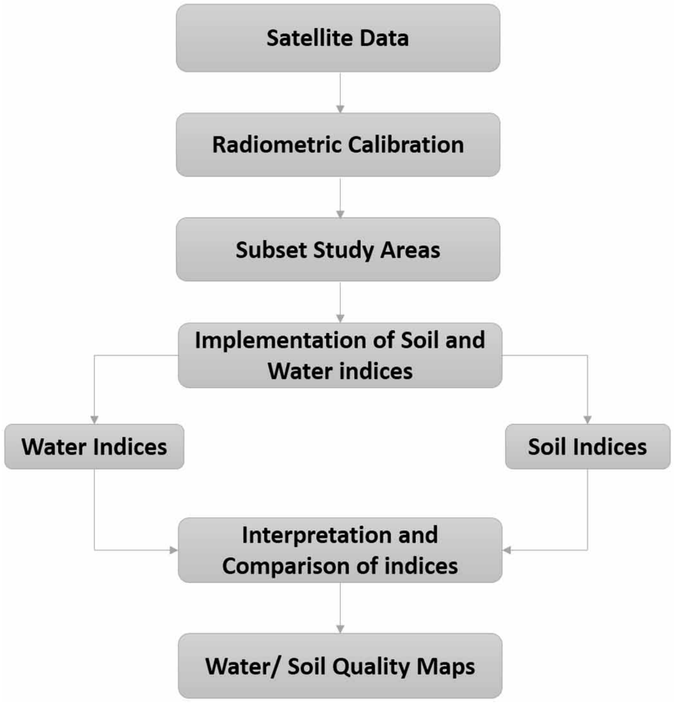


coastal zone observations. In Landsat 8, Visible, Near Infrared (NIR) and Short wave Infrared (SWIR) bands contain 30m, Thermal band contains 100m and panchromatic Band contains 15m spatial resolution (USGS, 2013a). Figure 2 shows wavelength distribution of Landsat OLI sensors.

Methodology

Present study aims to represent impact of textile industries effluent on soil and water quality using geospatial technologies. Landsat 8 satellite datasets for study area have been downloaded from USGS Earth Explorer Website (https://earthexplorer.usgs.gov/). Radiometric corrections have been carried out to get the real ground irradiance. Radiometric corrections enhance the interpretability and quality of the satellite imagery. Soil and water quality based indices have been calculated from the radiance image. Reflectance datasets have been clipped through district boundaries of Rajasthan. Indices give normalised values which range from -1 to +1. Values towards -1 represent poor quality and towards +1 show good quality of the respective parameter. Water quality based Normalized Difference Water Index (NDWI), Modified Normalized Difference Water Index (MNDWI), Water Ration Index (WRI), Normalized Difference Moisture Index (NDMI) and soil quality based Soil Adjusted Vegetation Index (SAVI), and Modified Soil Adjusted Vegetation Index (MSAVI) have been calculated. All resultant indices have been visually interpreted based on soil and water quality. Based on the visual interpretation, comparison of various calculated indices have been carried.

Figure 3. Methodology chart



Result and Discussion

Working with large area takes time especially when field observation is need to be done. Field observation is time consuming as well as costly. Field observation requires more man power. Use of Aerial photographs also increases the cost of the project. Remote sensing technology is more efficient as it captures same area in periodic manner by covering large area in a single image. In passive remote sensing technology, observations are based on electromagnetic radiations from sun or self-emitted radiance. Active remote sensing does not depend on sun's electromagnetic energy or thermal properties of earth surface (Lillesand & Kiefer, 1999). It has its own source of illumination. Electromagnetic energy travels from the source to the earth surface and then reflected/refracted energy goes back to the sensor.

There are significant handloom, cotton and textile industries present in various regions such as Bhilwara, Pali, Sanganer and Bagru of Rajasthan. Present article shows the impact of textile industries on soil and water quality of the surrounding area in Rajasthan, India. Satellite datasets have been downloaded for Bhilwara, Pali, Jodhpur, Ajmer, Jaipur, Bagru and Sanganer. 16th December, 26th December and 28th December 2019 acquired Landsat 8 OLI imageries have been downloaded from USGS Earth Explorer Website. December month has been taken to ensure no change in water extent due to rainfall. Downloaded images have been pre-processed before calculating the Indices. Digital Number (DN) to Reflectance conversion has been performed for each band of downloaded imagery using ERDAS Imagine 2011 version. Atmospheric corrections have been applied on raw imageries to get the land surface properties and to categorise the land surface in various land cover features efficiently. Atmospheric reflectance can be estimated by using the geometric parameters along with the parameters of atmospheric conditions at the instant of image captured (Hadjimitsis et al., 2010; Hadjit, Oukebdane, & Belbachir, 2013; Lisenko, 2018). Errors present in digital number are reduced and corrected with the help of radiometric corrections. Radiometric corrections enhance interpretation of land cover features in image. Energy recorded by satellite sensors can differ from actual radiated energy due to certain counted factors such as azimuth and elevation of sun and atmospheric conditions that can effect and obstruct the energy observed at the onboard sensor. A single pixel records the value of reflected/ emitted radiations of land surface along with scattered/emitted radiations from atmosphere. To get the actual radiations from land surface; radiometric calibrations must be applied before using the image for any other image processing analysis. Energy received at sensor by reflection of earth’s surface is converted to radiance which is further rescaled to represent into digital number with defined range. Values ranges from 0 to 255 for TM and ETM sensors of Landsat satellite. For Landsat OLI sensor, value ranges from 0 to 65536. At reception centre, Satellite data is received in terms of digital number which is further converted to DN into radiance and then radiance to TOA reflectance. DN to reflectance has been converted using LMAX and LMIN method.

$$L_\lambda = \left(\frac{\left(LMAX_\lambda - LMIN_\lambda \right)}{\left(QCALMAX - QCALMIN \right)} \right) * \left(\left(QCAL - QCALMIN \right) + LMIN_\lambda \right)$$

Where L_λ is the cell value as radiance; QCAL = digital number; $LMIN_\lambda$ = spectral radiance scales to QCALMIN; $LMAX_\lambda$ = spectral radiance scales to QCALMAX; QCALMIN = the minimum quantized calibrated pixel value (typically = 1); QCALMAX = the maximum quantized calibrated pixel value (typically = 255)

Reflectance of each pixel is calculated after the estimation of radiance from DN value. To estimate the reflectance values

$$\rho_\lambda = \pi * L_\lambda * \frac{d^2}{ESUN_\lambda} * \cos\theta_s$$

Where: ρ_λ = Unitless planetary reflectance; L_λ = spectral radiance (from earlier step); d = Earth-Sun distance in astronomical units; $ESUN_\lambda$ = mean solar exo-atmospheric irradiances; θ_s = solar zenith angle.

Reflectance image has been used to calculate water and soil based various indices using ERDAS Imagine 2011 image processing software. Soil quality based indices give the soil quality of given area. SAVI and MSVI have been estimated to get the quality of the soil in surrounding area of handloom, cotton and textile industries. NDWI, MNDWI, WRI are Water based indices which quantifies water quality. Subset of all estimated indices have been carried out in order to check the individual area. Subset images have been visually interpreted to check the water and soil based quality in respective indices.

SOIL ADJUSTED VEGETATION INDEX (SAVI)

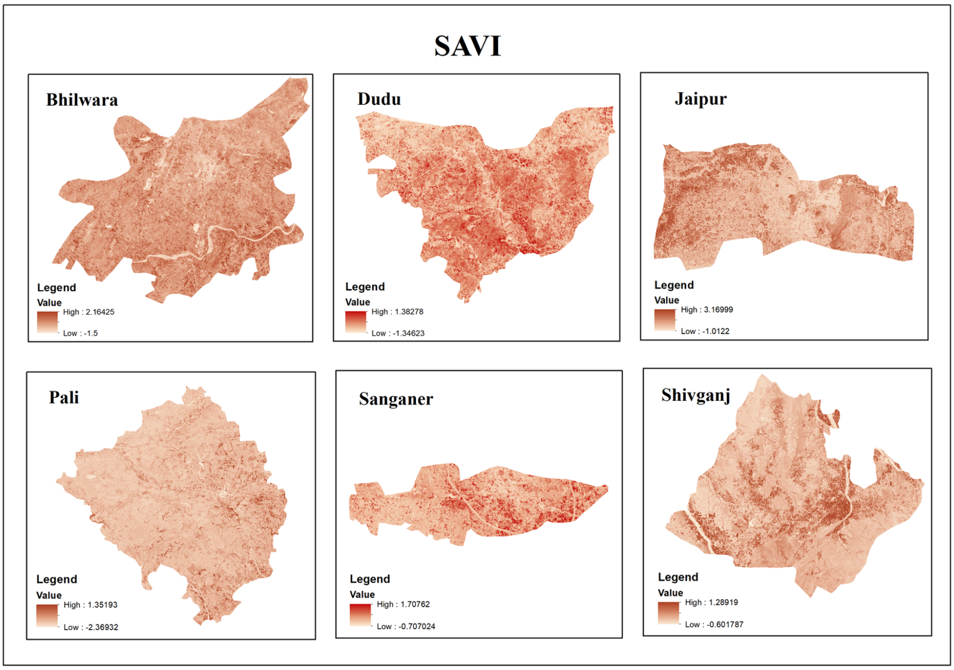
Plenteous methods for quality and quantity of vegetation in form of indices have been emerged as to characterize vegetation parameters such as canopy cover etc. the index use Red and reflected NIR wavelengths of electromagnetic radiation spectrum. Particular index is useful to estimate vegetation parameters including leaf area index, biomass, percent green cover and photosynthetic activity. Atmospheric disturbances influence vegetation parameters. In areas where vegetation cover is comparatively low (less than around 40 percent) resulting in exposed soil surface, the reflected light in Red and NIR region can change the efficacy of vegetation indices (Science, 1988). The Soil Adjusted Vegetation Index is developed as modification of the Normalized Difference Vegetation Index to correct the soil reclamation.

$$\text{Soil Adjusted Vegetation Index (SAVI)} = \left(\frac{\left(NIR - RED\right)}{\left(NIR + RED + L\right)}\right) * \left(1 + L\right)$$

Where L =soil fudge factor; NIR= near infrared Wavelength; RED= Red wavelength

The values of SAVI index depend on the nature of soil. SAVI index represents soil quality of any given area. Bhilwara, Pali, Shivganj, Jaipur, Dudu and Sanganer areas have been taken to calculate all the indices as region owns significant amount of cotton, handloom and textile industries. Resultant SAVI maps of above mentioned area have been shown in figure 4. Maps are showing the variation in soil quality with the colour gradient. Dark colour shows high value of SAVI index which represent greater exposure to the soil surface and less vegetation in the area. Lower values of index represent less exposure to the soil and denser vegetation. Lower values have

Figure 4. Soil adjusted vegetation index map of Bhilwara, Pali, Jaipur, Dudu, Sanganer and Shivganj area



been represented with the lighter shade of the colour gradient. Visual interpretation of index in different area has given the lower values in residential area, industrial area while higher values in crop and fellow land. Significant changes in shade of colour shows the variation in soil in all the regions.

MODIFIED SOIL-ADJUSTED VEGETATION INDEX (MSAVI)

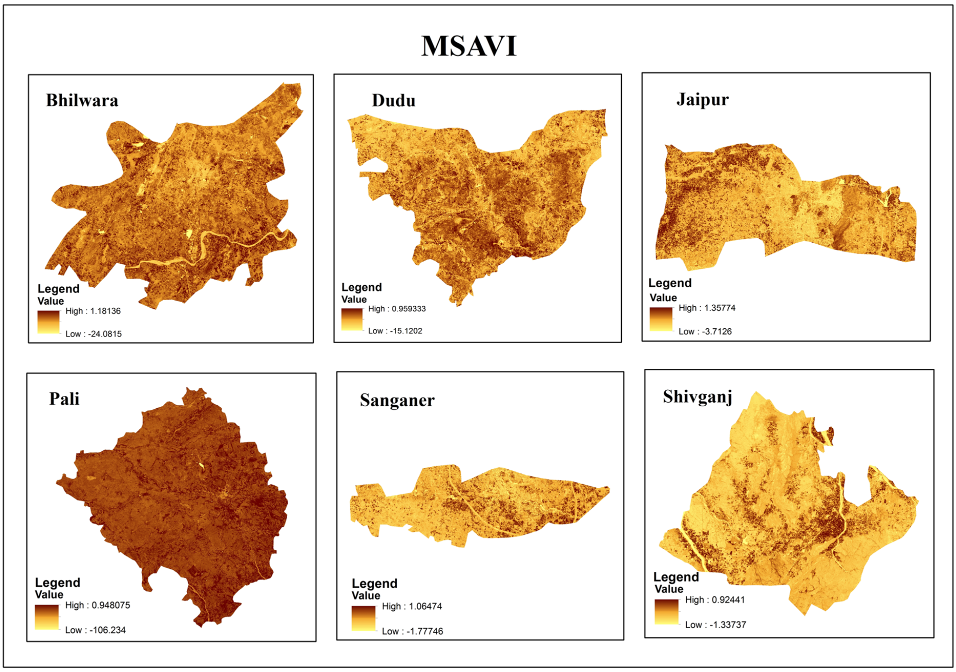
NDVI is used to determine the vegetation cover. Highly exposed soil surface limits NDVI. The modified soil-adjusted vegetation index (MSAVI), MSAVI-2 overcome the limitation of NDVI which is advanced version of SAVI (Qi, Chehbouni, Huete, Kerr, & Sorooshian, 1994). Soil-brightness correction factor, L limits SAVI. MSAVI can expressed as:

$$\text{Modified Soil-Adjusted Vegetation Index (MSAVI)} = \left(\frac{\left(NIR - RED\right) * \left(1 + L\right)}{\left(NIR + RED + L\right)}\right)$$

MSAVI calculates L as: $L = 1 - \left(\frac{(2s * (NIR - RED)(NIR - s * RED))}{(NIR + RED)} \right)$

Where s is the slope of soil line curve from a plot of red versus near infrared brightness values. MSAVI gives better results for soil quality. MSAVI index has been estimated in the similar way for all the area as mentioned above. Values have become precise in MSAVI compared to SAVI index. Resultant MSAVI has been shown in figure 5. Soil quality near the industrial area gives low values as industrial effluents effect the soil quality. Over the time, soil quality degrades due to water logging in surrounding area. Logged water degrades the soil quality over the time. There are enough number of textile industries in Bhilwara near the city area. MSAVI map is showing the change in MSAVI value near RIICO area. Surroundings of industrial area and built-up has come up with lighter shade. Lighter shade shows low quality of soil on that given pixel. In Pali also, textile industry exist in city and its nearby area. Concerned area has shown lower MSAVI values almost near to 0 or negative values that specify lower quality of soil in particular area. A part of the city and

Figure 5. Modified soil adjusted vegetation index map of Bhilwara, Pali, Jaipur, Dudu, Sanganer and Shivganj area



surrounding area has shown almost positive values (high value) of MSAVI. Some parts of Jaipur are famous for block printing. Ample of printing industries exist in Jaipur. Certain areas in Sanganer such as; near the canal has shown significant change in soil due to presence of cloth printing (block printing) industries. Soil quality has been degraded due to these industrial effluents. The degraded soil has been represented in lighter shade of colour which indicate low values (poor quality of soil) of MSAVI and SAVI index respectively.

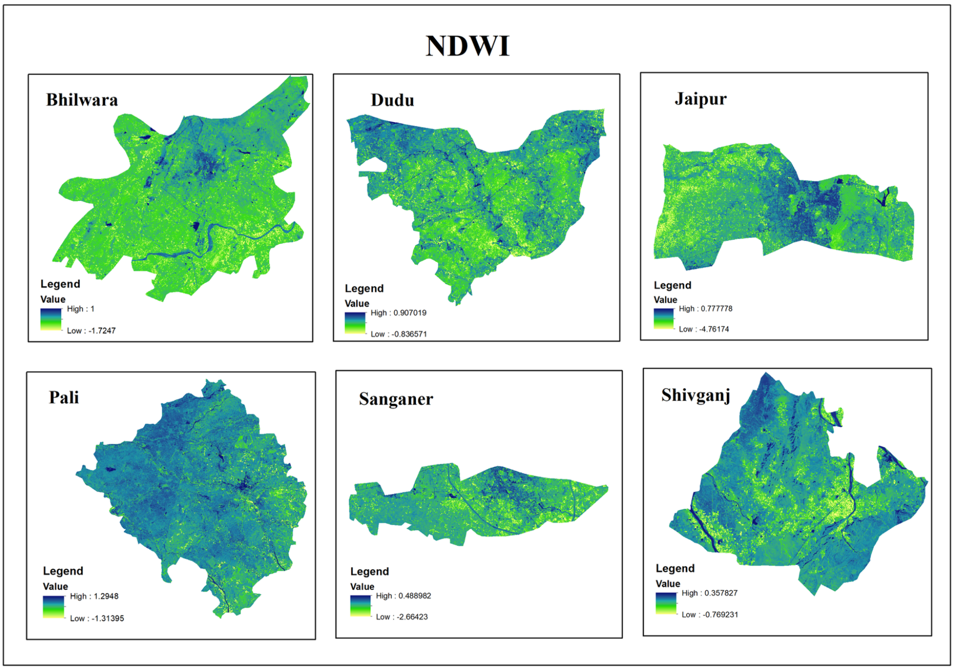
NORMALIZED DIFFERENCE WATER INDEX (NDWI)

NDWI is also known as Infrared Index (II), Normalized Difference Infrared Index (NDII), Normalized Difference Moisture Index (NDMI), Land Surface Water Index (LSWI) and Normalized Burn Ratio (NBR). NDWI is satellite derived index product from Near-Infrared (NIR) and Short-Wave Infrared (SWIR) wavelength of electromagnetic spectrum. Moisture content of leaf is monitored by using reflectance values in NIR and SWIR electromagnetic spectrum channels. SWIR and NIR bands are suitable for extraction of water content (Gu, Brown, Verdin, & Wardlow, 2007; Tucker, 1980). SWIR denotes the change in spongy mesophyll structure and moisture in vegetation and NIR denotes the internal structure of leaf reflectance and dry matter of leaf instead of moisture. The presence of moisture in internal structure of leaf causes SWIR to respond low in reflectance (Ceccato, Flasse, Tarantola, Jacquemoud, & Grégoire, 2001; Gao, 1996). NDWI overestimate water pixels due to mix up with built-up and vegetation pixels.

$$\text{Normalized Difference Water Index (NDWI)} = \frac{\left(NIR - SWIR\right)}{\left(NIR + SWIR\right)}$$

Soil quality of all the major textile industrial regions have been shown with the help of SAVI and MSAVI index. Water quality indices have been estimated for all the regions similar to soil quality indices to check the water quality. Industrial effluents are discharged in nearby water body such as river or its tributaries. These effluents (liquid or solid) degrade the quality of soil as well as water. Water indices are used to extract water bodies present in study area. Water absorbs infrared energy completely. Resultant NDWI index has shown water bodies present in the satellite image. NDWI for Bhilwara, Pali, Jaipur, Dudu, Sanganer and Shivganj regions have been shown in figure 6. Water pixels have been represented by blue colour in the NDWI map. Depth of water body has been shown with the shades of blue colour. Deep water bodies have been represented by dark blue colour (values near to +1)

Figure 6. Normalized difference water index (NDWI) index map of Bhilwara, Pali, Jaipur, Dudu, Sanganer and Shivganj area



while lighter shade of blue have shown the shallow water body. Non-water pixels have been shown with shades of green colour (values near to -1). More emphasis have been given to the water bodies present near the urban and industrial locations. Soil, vegetation and built-up pixels have been mixed up with water pixels in resultant NDWI. NDWI image of Bhilwara, Jaipur and Sanganer areas have overestimated water pixels due to mix up with built-up pixels and Dudu, Pali and Shivganj have overestimated water pixels due to mix up with soil and vegetation pixels. To know the exact water extent of the given area, NDWI results have been modified by using advanced NDWI. The overestimated water pixels have been corrected by estimating MNDWI index for all the region. Advanced NDWI has given better results for water pixels.

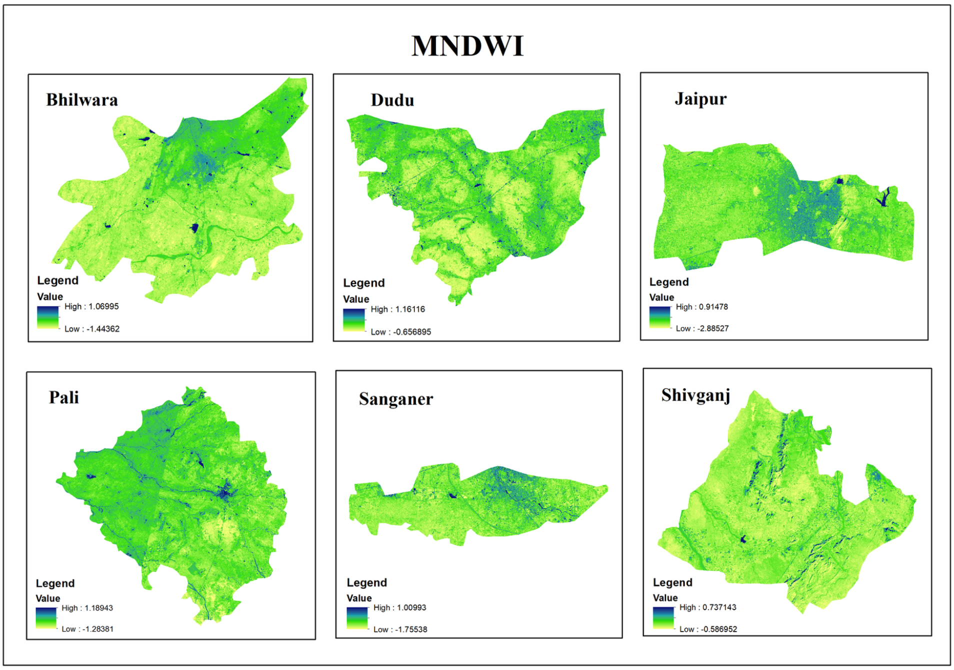
MODIFIED NORMALIZED DIFFERENCE WATER INDEX (MNDWI)

NDWI overestimates water pixels by mixing Soil, vegetation and built-up with water pixels. MNDWI is widely used to supress such mixed pixels. MNDWI gives comparatively positive pixels for water content as Middle Infrared (MIR) have more absorption than to near infrared (NIR) wavelength. Built-up, vegetation and soil pixels have negative values. MNDWI efficiently estimates the open water features as well as water content in built-up dominated regions (Memon, Muhammad, Rahman, & Haq, 2015).

$$\text{Modified Normalized Difference Water Index (MNDWI)} = \frac{(GREEN - MIR)}{(GREEN + MIR)}$$

The use of MNDWI has improved the overestimated water pixels by separating built-up, soil and vegetation pixels from water pixels. True water extent have been achieved with MNDWI results. MNDWI has been estimated for all the regions and shown in Figure 7. Resultant MNDWI has shown better results for water pixels. Water pixels have been shown in shades of blue colour while Non water pixel with the shades of green colour. Crystal clear water give almost zero response in infrared (IR) wavelength as water absorb the energy completely. Impurities present in water (turbid water) give higher response in IR compared to clear water. Industrial liquid

Figure 7. Modified normalized difference water index (NDWI) index map of Bhilwara, Pali, Jaipur, Dudu, Sanganer and Shivganj area



effluents are dumped in nearby area or water body. Impure/turbid (Effluents content) water give different response (high reflectance) than to clear water.

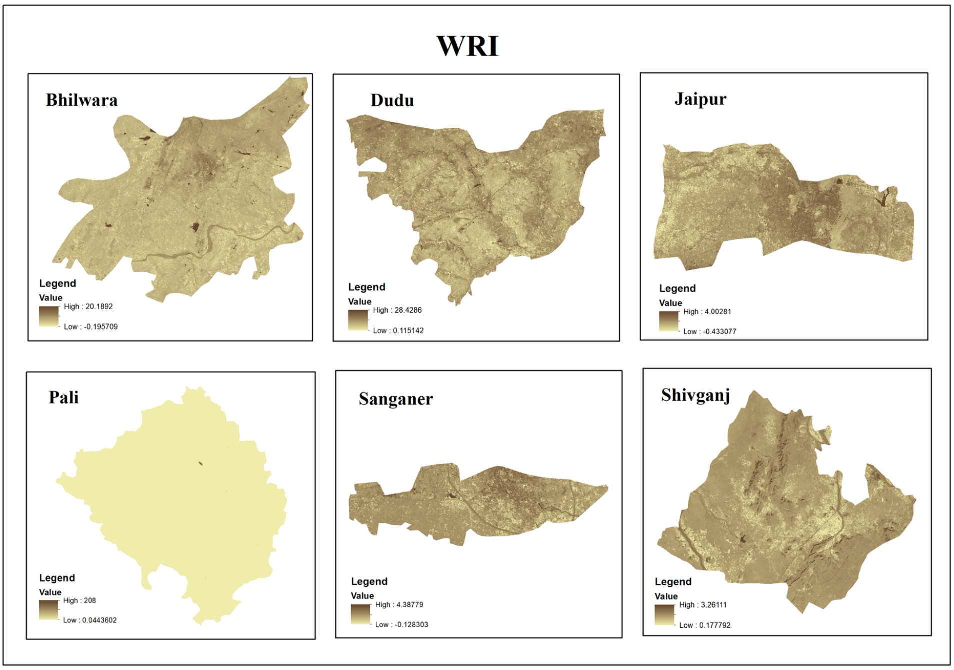
WATER RATIO INDEX (WRI)

WRI is the ratio between the spectral reflectance of RED and GREEN bands to the total of the Near Infrared (NIR) and Middle Infrared (MIR) bands (Shen & Li, n.d.). WRI shows greater than one value due to the dominancy in green and red band (Gautam, Gaurav, Murugan, & Annadurai, 2015).

$$\text{Water Ratio Index (WRI)} = \frac{\left(GREEN + RED\right)}{\left(NIR + MIR\right)}$$

Water ratio index has been calculated for the study area and shown in Figure 8. The resultant index represent substantial results for values greater than 1.9 as it has enhanced water pixels while suppressing the cloud shadows, roads and vegetation in

Figure 8. Water ratio index map of Bhilwara, Pali, Jaipur, Dudu, Sanganer and Shivganj area



the given images. Almost all area has shown convincing results for the WRI index. Higher pixel values have been represented by darker shade of brown colour while the lighter tone of the brown colour shows the absence of water pixels. Water bodies and areas with moisture content pixels have been presented with the dark tone of brown colour while the built-up and other manmade structures have been shown with the lighter tone of the brown colour.

CONCLUSION

The demand of raw material in textile industries have adversely affected the environment with the continuous development over the years. The environmental impact of textile sector can no longer be ignored. Textile industries come under the major effluents generators. Today major water sources such as rivers, oceans are polluted because of the discharge of effluents from the industries. Remote sensing plays an essential role in almost all sectors of today's world. Agriculture, mining, forestry, crime, environmental degradation, environmental pollution, urban planning, forest fire, water resource management etc. are the key sectors in which remote sensing and GIS are being used. Present article have used geo-spatial technology to assess the impact of textile industries effluents on soil, land and water quality of the surrounding area of textile industries. Article highlights water and soil quality parameters of certain parts of Rajasthan State using satellite remote sensing and GIS technology. Landsat 8 OLI's temporal datasets have been downloaded with spatial resolution of 30*30m in optical wavelength from (USGS) Earth Explorer. Pre-processing (radiometric calibration, re-projection and subset) have been performed on the downloaded datasets. Raster based water and soil quality indices have been generated to identify the contamination caused due to textile effluents in the surroundings of textile industries. In the resultant indices variability caused due to presence of such effluents have come up prominently.

Random sites have been selected on satellite datasets on the basis of water and soil related parameters. Further selected samples have been validated using the Google Earth application. Significant variations in soil and water bodies have been observed near and around handloom, cotton, block printing and textile industries in Pali, Sanganer, Bhilwara, Jaipur, Shivgunj and Dudu. Present study can be further enhanced by generating time series results of soil and water indices of the given area. To conclude with, remote sensing and GIS technologies along with natural resource parameters as utilized in above study can be performed for generating assessment reports for extended area at regional as well as national level and providing backgrounds in formulation of government policies for sustainable development and management of textile industries.

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KEY TERMS AND DEFINITIONS

Image Processing: Image processing is a method to perform some operations on an image, in order to get an enhanced image or to extract some useful information from it. Image processing is a type of signal processing in which input is in image form and output can be characteristics/features associated with image. Image processing is one of the emerging technology. Processing steps includes image acquisition tools, analysis/manipulation and the results in the form of image/report.

Landsat 8 OLI: Landsat 8 satellite have two Operational Land Imager (OLI) and Thermal Infrared Sensor (TIRS) instruments onboard. Satellite launched in February of 2013. Landsat 8 satellite collects earth surface images with 16-days temporal resolution. Images have 185km swath with 15m Panchromatic and 30-meter (Visible, NIR and SWIR) Multi-spectral spatial and 100m (Thermal) bands.

Remote Sensing: Remote sensing is an art and science of acquiring information about an object without being in physical contact with that object. Remote Sensing technology is widely used in various allied sectors.

Chapter 5

Effect of Dyes on Water Chemistry, Soil Quality, and Biological Properties of Water

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ABSTRACT

As the textile industries use aqueous method for dyeing processes, the color that is released in the environment is associated with the incomplete absorption of dyes on fibres. So, there is a strong need to reduce the amount of residual dye in textile effluent. Large amounts of liquid wastes are produced from textile industries that contain both organic and inorganic compounds. The degradation of azo dyes is difficult using the conventional processes. These complex azo dyes containing N=N bond have been found to show carcinogenic evidences on reductive cleavage. Azo dyes have capability to alter physical and chemical properties of soil, causing harm to the water bodies. Dyes are toxic in nature, which is lethal for microorganisms present in soil affecting agricultural productivity. The presence of azo dyes in water decreases its water transparency and water gas solubility. This reduces light penetration through water, decreases its photosynthesis activity, causing oxygen deficiency and de-regulating the biological cycles of aquatic system.

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INTRODUCTION

The universal fact for all living or non-living being is; Water is life. But due to enhanced industrialization, this fact has spoiled. The water coming from industries contains lot of contaminants like acids, bases, toxic organic and inorganic dissolved solids, and colors. Among all the waste, most undesirable are colors caused mainly by dyes. The colored water is of no use for domestic or industrial needs. The waste of dyes are predominant complex waste of industrial wastewater. The dye containing waste-water is dark in color and also highly toxic that blocks the sunlight and affect our ecosystem adversely. Of all the dyes present, the contribution of azo dyes for commercial purpose is maximum in textile, plastic, leather, and paper industries as additives. In aquatic environment, the degradation and removal of azo dyes is highly important due to its toxic nature which affects the life of aquatic organisms. Every industry should have an important concern to use clean technology. In this chapter, we will discuss about the processes to decolorise waste water and also the new technologies for textile waste water decolorisation.

EFFECT OF DYES ON WATER CHEMISTRY

Textile wastewater has a major problem due to the presence of colored effluent. Although we can say that all dyes are not as much toxic but they have an adverse aesthetic effect because they are visible pollutants. The colored water reduces the entrance of sunlight into the water bodies affecting the aquatic life. In many cases, if the concentration of dye is present below 1 ppm, that produces an obvious water coloration. The source of major pollution of textile wastewater comes from the dyeing and finishing processes. The major pollutants include highly suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), heat, color, acidity, basicity and other inorganic contaminants. The water insoluble dyes or unreactive dyes like disperse and vat dyes, normally exhibit good exhaustion properties, like these types of dyes have fibre binding properties and can be removed by physical processes such as flocculation. On the other hand, if we have water soluble dyes or reactive dyes as effluents, the removal by conventional methods is not that much useful for color removal. The reactive dyes are colored molecules which are used to dye cellulose fibres generally characterized by N=N azo bonds. The azo bond gives color to azo dyes associated with chromophores. The process includes absorption of azo dyes onto the cellulose and further reaction with fibre. The reaction includes covalent bond formation between the dye molecule and the fibre which is much more resistant to unusual conditions. The reactive parts of the dye react with ionised hydroxyl groups on the cellulose substrate. But in alkaline dyeing condition, the hydroxyl groups are present in the dye bath compete with the hydroxyl groups present on the cellulose fibre that results in the formation of hydrolysed dyes which no longer react with the fibre giving rise to a highly colored effluent. Therefore, it becomes crucial to find an appropriate and effective method of the treatment of wastewater to remove color from textile effluents. Currently, various methods have been used including chemical and physical processes, such as chemical precipitation and separation of pollutants, electrocoagulation, elimination by adsorption on activated carbon etc. But all these methods have a common drawback that they are not destructive instead they transfer the contamination from one phase to another causing a new type of pollution. It becomes necessary to find a new method for further treatment of these effluents (Slokar & Marechal 1998, Galindo et al. 2001, Tunay et al., 1996). Recently, an alternative to conventional methods, is "Advanced Oxidation Processes" (AOPs), which includes the generation of very reactive species such as hydroxyl radicals that has proved very useful for degradation of wide variety of organic pollutants (Kuo & Ho 2001, Legrini et al. 1993). The possible reaction pathways involving the attack of hydroxyl radicals onto organic compounds are: the electrophilic addition of hydroxyl radical to organic compounds (unsaturated or aromatic) that contain a π bond leading to the formation of organic radicals (Equation 1), the hydrogen abstraction by reaction of the hydroxyl radical with a saturated aliphatic compound (Equation 2) and electron transfer with reduction of the hydroxyl radical into a hydroxyl anion by an organic substrate (Bossmann et al., 1998, Tang 2004) (Equation 3).

$$R + {}^{\bullet}OH \rightarrow R^{\bullet}OH \rightarrow \text{Product} \tag{1}$$

$$R + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \tag{2}$$

$$R^{n} + {}^{\bullet}OH \rightarrow R^{n-1} + OH^{-} \tag{3}$$

The hydroxyl radical attack on organic substrates may be influenced by the presence of number of chemical species in water (or originating in the mineralization process), such as carbonate and bicarbonate ions. These ions can react with the hydroxyl radicals (Equations 4 and 5), hence competing with the organic substrates for the hydroxyl radicals.

$${}^{\bullet}OH + HCO_3^{-} \rightarrow CO_3^{\bullet -} + H_2O \tag{4}$$

$$^{\bullet}OH + CO_3^{2-} \rightarrow CO_3^{\bullet -} + OH^- \tag{5}$$

The chemical reactions of the hydroxyl radical in water are of four types-

Addition

$$^{\bullet}OH + C_6H_6 \rightarrow C_6H_6(^{\bullet}OH) \xrightarrow{-H^{\cdot}} C_6H_6OH \tag{6}$$

The hydroxyl radical reacts with an unsaturated compound and forms a free radical intermediate which undergoes further reaction to form final product.

Hydrogen Abstraction

$$^{\bullet}OH + CH_3OH \rightarrow CH_2{}^{\bullet}OH + H_2O \rightarrow CO_2 + H_2O \tag{7}$$

where an organic free radical and water are formed. Organic free radical undergoes further reaction.

Electron Transfer

$$^{\bullet}OH + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^- \tag{8}$$

where ions of a higher valance state are formed or an atom free radical, if negative ion is oxidized.

Radical Interaction

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{9}$$

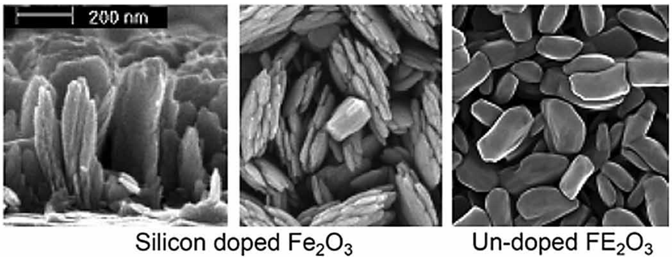
where two hydroxyl radicals react with each other or the hydroxyl radical react with an unlike radical, to combine or to disproportionate to form a stable product. In applying Fenton's reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate. Typical rates of reaction between the hydroxyl radical and organic materials are 10^9 - 10^{10} k (M^{-1} s^{-1}). Advanced oxidation processes

(AOPs) have been successful in treating most of the refractory organic compounds present in polluted water. The reason for the use of AOPs is due to the inability of conventional processes to treat highly contaminated toxic water (Movahedyan et al., 2009). Degs et al. (2000) used activated carbon Filtrasorb 400 (F-400) towards three highly used reactive dyes in the textile industry and investigated the removal efficiency of these dyes. The adsorption capacities for the anionic reactive dyes, namely; Remazol Reactive Yellow, Remazol Reactive Black and Remazol Reactive Red were determined by them. The data of calculated adsorption capacity showed high removal ability for these three reactive dyes and a distinguished ability for R. Yellow. F-400 showed a high adsorption capacity which was attributed to net positive surface charge during the process of adsorption. Surface acidity, surface basicity, H^+ and OH^- adsorption capacities for F-400 were also estimated. Daneshvar et al. (2003) found that a commonly used textile dye Acid Red 14 can be degraded photocatalytically by UV-C lamp (30 W) by using TiO_2 suspensions. It was found that when TiO_2 and UV light were used alone they had a negligible effect. A semi-log plot was drawn between concentration of dye versus time was found to be linear which suggests the reaction to be of first order ($K = 1.41 \times 10-2\ min^{-1}$). The other parameters like pH, TiO_2 amount and the concentration of dye before the experiment were also determined. The addition of hydrogen peroxide enhanced the rate of photodegradation of AR14 and the rate was inhibited by ethanol. Accordingly, it could be stated that the complete removal of color, after selecting optimal operational parameters could be achieved in a relatively short time, about 3.5 h. Daneshvar et al. (2004) also degraded acid red 14 (AR14) photocatalytically by ZnO. By using the technique of advanced oxidation processes (AOPs), zinc oxide was found to be more suitable alternative to TiO_2 for wastewater treatment. In the absence of ZnO, the rate of degradation efficiency was small and negligible in the absence of UV light. A linear semi-log plot of dye concentration versus time was resulted suggesting first order reaction ($K=0.0548\ min^{-1}$). In this also, they examined all the parameters. They found that if hydrogen peroxide is added in proper amount, the rate of dye degradation is enhanced but excess of hydrogen peroxide quenched the formation of hydroxyl radicals ($\cdot OH$).

Degs et al. (2008) investigated the adsorption on activated carbon of various dyes namely, C.I. Reactive Blue 2, C.I. Reactive Red 4, and C.I. Reactive Yellow 2 from aqueous solution onto activated carbon keeping in different experimental conditions. The reactive dyes showed high adsorption capacity on activated carbon. The highest adsorption capacity of C.I. Reactive Blue 2, C.I. Reactive Yellow 2 and C.I. Reactive Red 4 dyes at pH 7.0 and 298 K, was found to be 0.27, 0.24, and 0.11 mmol/g, respectively. Giles and Smith classification indicated an L2-type isotherm and also the data showed good correlation with the Langmuir and Ferundlich isotherm models. The adsorption capacity was higher for acidic as compared to basic solutions and also with the increase in ionic solution the removal of dye was increased. The thermodynamic study was done which indicated that the adsorption of dyes was an endothermic process. Ip et al. (2009) studied the adsorption of Reactive Black 5 dye, in a two stage activation process onto two bamboo based active carbons by using phosphoric acid and three conventional adsorbents, carbon F400, bone char and peat. Langmuir isotherm was used to determine the monolayer saturation adsorption capacities for this dye and was found to be: 176, 157, 7, 447 and 545 mg dye/g adsorbent for active carbon F400, bone char, peat, bamboo carbon (2123 m^2/g) and bamboo carbon (1400 m^2/g), respectively. A sodium phosphate salt was added to study its effect on the adsorption capacities which was found to increase for both bamboo carbons to over 900 mg/g. Habibi et al. (2005) investigated the photocatalytic degradation using TiO_2 in aqueous solution for these textile dyes namely C.I. Direct 80, 3BL, C.I. Direct Blue 160, RL and C.I. Reactive Yellow 2, and X6G. Optimized results were obtained by studying different parameters like oxygen effect, temperature, catalyst loading, UV-light irradiation time, solution pH and inorganic ions such as SO_4^{2-}, Cl^- and NO_3^-. The results of above investigation showed that by use of an efficient photocatalyst and using appropriate parameters leads to complete decolorization and decresase in chemical oxygen demand (COD) of dye solutions. Tang et al. (1995) also studied photocatalytic oxidation using TiO_2/UV slurry reactor for five dyes, namely Acid Blue 40, Basic Yellow 15, Direct Blue 87, Direct Blue 160, and Reactive Red 120. It was found that at all pH values Direct Blue 160 and Reactive Red 120 follows the Langmuir-Hinshelwood kinetic model, on the other hand, Acid Blue 40 fits the model at pH 3, Basic Yellow at pH 3, 5, and 11, and Direct Blue 87 at pH 7 and 9 only. When the dye solutions were studied at neutral pH 7, the rate of oxidation follow the order: Direct Blue 87 > Reactive Red 120 > Basic Yellow 15 > Acid Blue 40 > Direct Blue 160. They also studied the effect of Fe^{2+} and H_2O_2 on the reaction kinetics. Bi et al. (2011) in recent years reported that Ag_3PO_4 has an excellent photooxidative capability for dye degradation and O_2 evolution from water by using UV-visible light. They developed an easy route for fabrication of single-crystalline Ag_3PO_4 rhombic dodecahedrons with only {110} facets exposed and cubes bounded entirely by {100} facets in high-yield. When their photocatalytic study was done it was concluded that rhombic dodecahedrons exhibit much higher activities than cubes for the degradation of organic contaminants, the reason may be due to their higher surface energy of {110} facets (1.31 J/m^2) than of {100} facets (1.12 J/m^2).

Bokare et al. (2007) used Fe−Ni bimetallic nanoparticles for the degradation of Orange G, a monoazo dye. A nanocatalyst loading of 3 g/L showed complete dye degradation (150 mg/L) after 10 min of reaction time. In the degradated products HPLC-MS analysis showed that the synthesized nanoparticles reductively cleaved the azo linkage to produce aniline as the major degradation product. When the study was done for 1-year-stored nanoparticles, an oxidative degradation of Orange G was observed. Surface chemistry plays an important role in directing the mode of degradation. The reductive dye degradation was proceeded by hydride transfer from nickel, whereas formation of a Fe^{2+}–Ni(0) galvanic cell in stored nanoparticles generated hydroxyl radicals from water in a non-Fenton type reaction. The latter were responsible for the generation of radical centers on the dye molecule, which led to a coupling-mediated oxidative degradation of Orange G. The generation of hydroxyl radicals is further substantiated with radical quenching experiments using ascorbic acid indicating that stored nanoparticles degrade Orange G through a predominantly oxidative mechanism. Zhang et al. (2013) studied the phtocatalytic degradation of organic dyes using Graphene oxide/ZnO composites under UV radiations. They prepared composites of reduced graphene oxide/ZnO (RGO/ZnO) with different particles size of ZnO by solvothermal reaction of graphene oxide (GO) and ZnO in an ethanol-water solvent. It was observed that as compare to bare ZnO-S1 sample, the RGO/ZnO-S1 composite with ZnO particle size of 20–100 nm exhibits the enhanced photoactivity toward degradation of organic dyes and reduction of heavy metal ions Cr (VI) in water. However, when the particle size of ZnO is 50-500 nm in the composite RGO/ZnO-S2, it showed decreased photoactivity as compared to bare ZnO-S2. BY studying various characterization techniques, it was concluded that RGO/ZnO-S1 exhibits smaller particle size as compared to RGO/ZnO-S2 which leads to a more interfacial contact and a chemical bonding between RGO and ZnO-S1, and hence it increases the photoactivity. The hybridization of RGO with ZnO in an appropriate manner is able to significantly inhibit the well-known photocorrosion of semiconductor ZnO. This work can found applications of RGO/semiconductor photocatalysts in environment purification. Cesar et al. (2006) deposited thin, silicon-doped nanocrystalline α-Fe_2O_3 films on F-doped SnO_2 substrates by ultrasonic spray pyrolysis and chemical vapor deposition at atmospheric pressure (Figure 1). At pH 13.6 the photocatalytic activity of these films were measred with regard to photoelectrochemical water oxidation. It was observed that silicon doping influences the morphology of the α-Fe_2O_3 which in turn decreases the feature size

Figure 1. SEM images of silicon doped and undoped Fe_2O_3



of the mesoscopic film. The silicon-doped α-Fe_2O_3 nano-leaflets show a preferred orientation with the (001) basal plane normal to the substrate. The best performing photoanode would yield a solar-to-chemical conversion efficiency of 2.1% in a tandem device using two dye-sensitized solar cells in series.

Dong et al. (2007) investigated the use of inorganic salts for photocatalytic decoloration of three azo dyes, namely Mordant Black PV, Reactive Blue MS and Direct Sky Blue 5B, the salts used were sodium chloride, sodium sulphate, sodium nitrate and potassium chloride in water based on Fe(III)–oxalate complexes/H_2O_2 system in a specially designed photoreactor by UV–vis spectrum and TOC measurements. It was found that the degradation is limited in the presence of salts. As the concentration of inorganic salts increases in water it gives reduced decoloration efficiency and kinetic reaction constants of the dyes. The photocatalytic decoloration and degradation was inhibited by Sodium chloride and potassium chloride than sodium sulphate and sodium nitrate under the same reaction condition. Oladoja et al. (2008) investigated the importance of castor seed shell (CSS) for water remediation contaminated with Methylene Blue (MB). The castor seeds were thoroughly washed to remove any water extractable constituents, then re-grounded, sieved and used in series of agitated batch adsorption experiments. Freundlich and Langmuir isotherm models were used to study the equilibrium sorption. They observed that the sorption process of MB was done on heterogeneous surface of the CSS which comes out to be 158 mg/g obeying the pseudo-second-order kinetic model more than the pseudo-first order. This observation made them for further analysis using this kinetic model. The role of chemisorptions in the mechanism of sorption was established by an empirical relationship between the pseudo-second-order rate constant, K, and the initial MB concentration. The results of this relationship showed that pseudo-second-order chemisorptions are important in the sorption process. Namasivayam and Kavitha (2002) studied the adsorption of Congo Red by coir pith carbon using various parameters such as agitation time, dye concentration, adsorbent dose, pH and temperature. Both Langmuir and Freundlich isotherms were followed by equilibrium adsorption data following second-order rate kinetics. The adsorption capacity was found to be 6.7 mg dye per gram of the adsorbent. It was also observed that a range of acidic pH favoured the adsorption of Congo Red. According to the desorption studies done, it was found that chemisorption might be the major mode of adsorption. Chakraborty et al. (2011) studied the equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto NaOH-modified rice husk (NMRH). All the parameters were used like contact time, pH (2–10), adsorbent dose (0.5–5 g) and temperature (293, 303 and 313 K). It was found that the adsorption was favoured at higher pHs and lower temperatures and the data were well described by the Freundlich model that follows pseudo-second order kinetic model. The study of thermodynamic parameters suggests that the adsorption is a typical chemical process, spontaneous and exothermic in nature.

Sun et al. (2011) prepared a magnetite/reduced graphene oxide (MRGO) nanocomposites using a simple one step solvothermal strategy by the use of cost effective and non-toxic precursors for the removal of dye pollutants. Graphene and magnetic nanoparticles when combined together have an advantageous efficiency in the treatment of wastewater. It was found that the efficiency of MRGO composites depends strongly on Fe_3O_4 loading and pH value. They had also used these nanocomposites in the treatment of industrial waste water and lake water. The results give a gist that the MRGO composites are effective adsorbents for removal of dye pollutants and thus could provide a new platform for dye decontamination. Expanding the application of high-strength hydrogels has attracted tremendous attention in the fields of biomedical engineering, agriculture and wastewater treatment owing to their versatility and outstanding deformation resistance. Cui et al. (2015) constructed a new class of graphene oxide (GO)/hydrophobically associated polyacrylamide composite hydrogels (GHA gels) by using one-pot method. Without using any cross linker, the GHA gels gets cross-linked by GO sheets and hydrophobically associated domains giving high mechanical strength, high toughness and have self healing ability and fatigue resistance. With the addition of GO sheets, this gel has improved adsorption capacity for removing dye from waste water. When heated with ethanol, the dyes removed from GHA gels rapidly and get dissolved in ethanol that can be used in next water purification cycle. Graphene oxide (GO) sheets possess highest adsorption capacity for removing organic dye contaminants from water bodies. Taking this as advantage, Guo et al. (2015) prepared GO/polyethylenimine (PEI) hydrogels as efficient dye adsorbents by facile method. The hydrogels were obtained by hydrogen bonding and electrostatic interactions between amine-rich PEI and GO sheets. The removal rates for dyes methylene blue and rhodamine B exhibit within about 4 h following the pseudo-second-order model. The adsorption of dye is mainly because of GO sheets whereas the PEI was added to improve the gelation process of GO sheets. The most important thing is that the dye-adsorbed hydrogels can be easily separated from an aqueous environment which suggests large-scale applications of the GO-based hydrogels for organic dye removal and wastewater treatment.

EFFECT OF DYES ON SOIL CHEMISTRY

The polluted waste water from industrial effluents adversely affects soil fertility and growth of plants. The substances dissolved in industrial effluents changes the physical, chemical and biological properties of water affecting their growth, productivity, making them susceptible to various pathogen and destroy the food chain quality. Among all the polluted sources, the textile wastewater is said to be the most polluted source in both quantity and composition. This wastewater has been found to be toxic to several crop plants.

Ahmad et al. (2012) studied the industrial effluent that was used directly for irrigation at Bhairavgarh area, Ujjain city. The samples were collected from both contaminated and uncontaminated areas at 0-25cm depth for analysis. From ten different locations three sites were selected for collection of soil samples. For selected parameters, the wastewater was analyzed before irrigation which showed that the water was alkaline in nature. The results of soil samples indicated its neutral to slight alkaline nature. The concentration of cation and anion, organic carbon and organic matter were also shows a wide variation in contaminated soil samples as compared to uncontaminated samples. The investigation showed that continue use of waste water deteriorate soil quality in the area. Hardie et al. (2011) studied the effect of soil moisture on preferential flow in a texture-contrast soil by applying 25 mm Brilliant Blue dye tracer to soil profiles at high and low antecedent soil moisture. In the wet treatment, the dye tracer infiltrated to depths between 0.24 and 0.40 m, at an average rate of 120 mm h1 . Whilst in the dry treatment, the same volume of dye tracer infiltrated to between 0.85 and 1.19 m depth at an average rate of 1160 mm h1. As a result of water repellency, in dry antecedent conditions, finger flow developed in the A1 horizon. In the wet treatment, the wetting front developed permutations but did not break into fingers. The flow rate in A2 was slower than A1 despite of similar particle size distributions due to the absence of macropores. In the dry treatment, the dye tracer ponded on the upper surface of the B21 horizon, which then spilled down the sides of the large clay columns as rivulets, at rates of between 2000 and 3000 mm h1 . The dye tracer accumulated at the base of the columns resulting in backfilling of the inter column shrinkage cracks, at an estimated rate of 750 mm h1. In the subsoil, water movement occurred via shrinkage cracks which resulted in flow by-passing 99% of the soil matrix in the B21 horizon and 94% of the soil matrix in the B22 horizon. This knowledge could be used to: (i) improve irrigation and fertilizer efficiency (ii) explain variations in crop yield (iii) reduce salinity through improved leaching practices, (iv) reduce the risk of agrochemicals contaminating shallow groundwater. Heins and Flury (2000) studied that brilliant Blue FCF can be used as a dye tracer to stain flow pathways in porous media. In the solid phase the dye interacts in somewhat complicated manner as it is an ionic organic molecule. They investigated the suitability of Brilliant Blue FCF as a dye tracer in vadose zone hydrology. The main aim was to test the chemistry of aqueous solution on dye absorption spectra and also to analyse the effect of ionic strength and type of cations on dye sorption to soils. Langmuir model was confirmed by sorption isotherms. The soil sample having lowest pH and highest clay content found to have substantial sorption. As the ionic strength increases it leads to sorption of Brilliant Blue FCF. The absorption spectrum of the dye is not sensitive to pH nor ionic strength. Flury et al. (1994) also studied that flow pathways of water and solutes in soils form distinct patterns, which are not a priori predictable. The primary cause is a macropore structure, but other factors like initial or boundary conditions can also influence a soil by producing bypassing of infiltrating water. The study was done to assess the flow pathways of water in different soils and to investigate the effect of initial water content on the flow pattern. They carried dye-tracing experiments in 14 different field sites which represent good portion of soils used for agricultural crop production in Switzerland. The site consisted of two 1.4 by 1.4 m plots, out of which for 2 months before the experiment, one was covered with a plastic roof to achieve different initial water contents. Then the Brilliant Blue FCF (C.I. Food Blue 2) dye was applied within 8 hours onto the plots with a sprinkling apparatus. The plots were excavated one day after irrigation and then the pattern of stained was examined on a vertical 1 by l m soil profile. It was found that the flow pattern showed spatial structure with remarkable differences. Like in most of soils, water was bypassed in the soil matrix. While in some soils, dye penetrated beyond l m depth whereas in others it remained in the top 50 cm. The bypass flow was more prone in structured soils, deep dye penetration and pulse splitting than nonstructured soils. Initially, the water content had less pronounced effect in some soils and no effect in others.

As it is clearly understood that water coming out from industries is major source of water pollution that generates a maximum quantity of chemicals including dyes. Direct discharge of this wastewater causes undesirable changes in the environment. The protection of environment is a major concern so researchers are trying to find out a novel method that can slow down the damage caused to the environment. Verma et al. (2012) investigated some novel pre-hydrolysed coagulants that helps in decolourisation of textile wastewater such as Polyaluminium chloride (PACl), Polyaluminium ferric chloride (PAFCl), Polyferrous sulphate (PFS) and Polyferric chloride (PFCl). Kasteel et al. (2002) studied that the food dye Brilliant Blue FCF is generally used as dye tracer in field studies to observe the flow pathways of water in soils. The other researchers found out that non-linear sorption is important for Brilliant Blue especially at small concentrations. Also, the rate of retardation increases with decreasing concentrations as well as with increasing ionic strength of solutions. They compared the movement of Brilliant Blue with that of bromide in field soil. It was assumed that Brilliant Blue does not follow the same flow paths as bromide. Valentine et al. (2006) screened single strains of nine white-rot fungal species for their ability to degrade polycyclic aromatic hydrocarbons (PAHs) in forest and salt marsh soils. Out of all, *Bjerkandera adusta*, *Irpex lacteus* and *Lentinus tigrinus* were proved to be excellent PAH degraders in both saline and non-saline conditions. The three strains were tested to find out the salinity level and PAH concentration having negative effects on the ligninolytic activity of the fungi as measured by the anthraquinone dye Poly R-487. It was also observed that salinity characteristic of sea water have minimum effect on ligninolytic activity of *I. lacteus* and *L. tigrinus* as compared to *B. adusta* by salinity levels of 32%. The statistical analyses confirmed that the decolorization rate varied with salinity and PAH concentration, and between fungi. Topac et al. (2009) studied that the involvement of organic dyes in soil via wastewater and sludge has been of increasing concern in developing or under-developed countries where the methods to remove this contaminants are very rare. Hence, they did an incubation study to investigate the sulfonated azo dye impact, Reactive Black 5 and sulfanilic acid, a typical representative of aromatic sulfonated amines, on soil nitrogen transformation processes. The result of this study indicated that nitrogen related processes in soil can be used as bioindicators of anthropogenic stress caused by organic dyes. It was found that urease activity, arginine ammonification rate, nitrification potential and ammonium oxidising bacteria numbers decreased in the presence of these dyes. It was concluded that the organic dye pollution restrict the nitrogen-use-efficiency of plants, thus further reducing the productivity of terrestrial ecosystems. Kolekar et al. (2008) isolated dye degrading bacterial strain identified as *Bacillus fusiformis* KMK 5 from the textile dyes contaminated soil of Ichalkaranji, Maharashtra, India based on the biochemical and morphological characterization as well as 16S rDNA sequencing. It was observed that KMK 5 tolerate and degrade azo dyes, Disperse Blue 79 (DB79) and Acid Orange 10 (AO10) under anoxic conditions. The complete mineralization of DB79 and AO10 was observed within 48 h. The degradation potential increases the applicability of this microorganism for dye removal. Licudine et al. (1997) investigated the use of extraction of xanthene dyes, phloxine B and uranine from soil by the use of supercritical fluid (SF) carbon dioxide (CO2) modified by organic solvents and inorganic salts or chelating reagents Methanol (MeOH), n-butylamine (n-BA), and a chelating agent, ethylenediaminetetraacetic acid tetrasodium salt (Na4EDTA), were found to be the most effective modifiers of SF CO_2 for quantitative recoveries of phloxine B and uranine in soils. At these supercritical fluid extraction (SFE) conditions, recoveries of related xanthene dyes (i.e., 2‘,7‘-dichlorofluorescein, 4,5,6,7-tetrachlorofluorescein, eosin Y lactone, erythrosin B, and rose bengal) fortified at 25 μg/g in Hawaiian soils ranged from 65 to 93%. These mixture of dyes were separated by HPLC. A mixture of MeOH, n-BA, and sodium hexametaphosphate $[(NaPO_3)_6]$ was effective for conventional solvent extraction of phloxine B and uranine from fortified soils. However, SFE was more selective and gave cleaner extracts. Recoveries were comparable to those by solvent extraction.

EFFECT OF DYES WASTE ON BIOLOGICAL PROPERTIES OF WATER

In textile waste water, days are considered as important pollutants. Globally, environmental problems associated with the textile industry are those associated with water pollution caused by the direct discharge of untreated effluent and release of toxic chemicals in to the aquatic environment. It drastically decreases oxygen concentration in water body due to the presence of hydrosulfides and blocks the passage of light through water body which is detrimental to the water ecosystem. About 40% of globally used colorants contain organically bound chlorine which is a carcinogen. Heavy metals, present in textile industry effluent, are not biodegradable, hence, they accumulate in primary organs in the body and over time begin to fester, leading to various symptoms of diseases. Untreated or incompletely treated textile effluent can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects (2017). Textile dyes have xenobiotic nature having aromatic structure and are non-biodegradable. These dyes are poisonous to flora and fauna because they reduce the penetration of light and create a obstacle in the process of photosynthesis. The textile industry uses mostly synthetic dyes derived mainly from intermediates of coal tar and petroleum. The dyes are available commercially in the form of powders, granules, pastes or liquid dispersions which are developed regularly for fulfilling the demands of latest technology, new fabrics, detergents, new dyeing machineries causing serious environmental concerns posed by some existing dyes. The dyes used by industry must be risen up to meet all these new and specific technical requirements and hence the consumption of these dyes is increasing through rapid changes. Having attached to toxic effects, these dyes can cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. Hence, a focus should be made to bring specific techniques for the removal of these dyes from different kinds of wastewater streams.

Daneshvara et al. (2007) investigated the potential of *Cosmarium* species that belongs to green algae as a feasible biomaterial for treatment of triphenylmethane dye and Malachite Green (MG). The results of this study revealed the ability of this algal species in dye removal. The effect of other parameters like temperature, pH, dye concentration and algal concentration were also examined on decolorization process. The algal efficiency and stability was also examined in long term repetitive examinations. The correlation between decolorization rate and the dye concentration was also described using Michaelis–Menten kinetics. Hong et al. (2011) conducted a study on global pollution problem caused by textile industries creating impact on quality of water resources. As estimated by World Bank 17 to 20% of water pollution from industries comes from textile dyeing and treatment. Now a days, metal oxide semiconductors have been used in advanced oxidation process (AOP) for the treatment of dye wastewater as it possess good degradation efficiency, low toxicity and physical and chemical properties. Hong et al. in their study discussed metal oxide semiconductors in which the semiconductors are generally divided into three categories: (i) titanium dioxide; (ii) zinc oxide; and (iii) other metal oxides (such as vanadium oxide, tungsten oxide, molybdenum oxide, indium oxide and cerium oxide). The synthetic wastewater treatment containing azo dyes was carried out by anaerobic biological method and chemical oxidation. Turgaya et al. (2011) conducted a study whose main target was to compare different treatment methods and to evaluate the effect of different parameters on effectiveness of treatment. Firstly in the microbial process, the results showed that with the increase in residence time, the yeast extraction amount and microorganisms addition that were growing originally on forest residues had positive effects on the dye removal. Secondly, in the catalytically wet peroxide oxidation process, CWPO, the condition of reaction were optimized at 0.5 g/L activated carbon loading with 2 mL H_2O_2/300 mL solution at pH = 3. It was found that at optimum conditions approx. 93% of dye was removed. This CWPO process was originally tested with textile wastewater at these optimized conditions. The percentage of dye removal with this wastewater was 50%. An investigation on adsorption effect of the activated carbon was also done. The removal efficiency was found to be 15% at pH = 7 by just adsorption. At pH=3 i.e. in acidic conditions and at higher temperature the adsorption effect of activated carbon increased. The adsorption and oxidation efficiency were found to be compatible at 80 °C and at lower temperature, adsorption was found to be more effective than the oxidation. The study concluded that, the decolorization was found to be 60% by adsorption and 40% by oxidation.

Janosa et al. (2009) used spruce wood shavings from *Picea abies* for an adsorptive removal of both basic as well as acid dyes from waters. The properties of sorption were changed by modifying the sorbents with HCl, Na_2CO_3 and Na_2HPO_4. The sorption ability was increased for the wood sorbents treated with alkaline carbonate solution as well as with phosphate solution for the basic Methylene Blue dye whereas when treated with mineral acid sorption ability was decreased for Methylene Blue to some extent. The opposite is observed for the sorption of the acid dye – Egacid Orange. At low pH it was observed that the sorption of basic dye was decreased in accordance to ion-exchange mechanism of the sorption. On the other hand, on increasing pH, the sorption rate of acid dye increases. Only minor effects were seen in the presence of inorganic salts as well as surfactants. Deniz (2013) investigated the capability of *Prunus amygdalus L.* (almond) shell for removal of dye methyl orange from aqueous solutions. The effects of pH, ionic strength, adsorbent concentration and mesh size, dye concentration, contact time, and temperature were evaluated for the removal of dye. It followed pseudo-second-order kinetic model. The thermodynamic analysis favoured the reaction to be spontaneous, favorable, and exothermic. Form the study, a conclusion was made that almond shell is a low-cost adsorbent for removal of methyl orange from aqueous media. Yang et al. (2010) synthesized a novel dumbbell-shaped ZnO photocatalyst by microwave heating. The synthesized photocatalyst was analysed by using different techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV–Vis absorption spectrum (UV–Vis) which indicated the photocatalyst to possess united dumbbell shape with 2 μm diameter and 5 μm length. Methylene blue dye was used to evaluate the degradation capability of this catalyst showing approx. 99.6% of decolorization at optimum condition. Also, the results showed that the degradation follows pseudo-first-order kinetics and the Langmuir–Hinshelwood model. Gupta et al. (2011) developed a mesoporous carbon from waste of rubber tyre for the removal and recovery of of toxic azo dye, Acid Blue 113. They also determined the surface area, porosity, and density. At different parameters like pH, adsorbate concentration, sieve size, adsorbent dosage, contact time and temperature conditions, the adsorption of the dye over the prepared adsorbent and a commercial activated carbon was achieved. Thermodynamic parameters were calculated by applying Langmuir and Freundlich adsorption isotherm models. The kinetic studies followed first order kinetics for adsorption process and recovery of dye was done by eluting 0.1 M NaOH through the column.

Wang and Zhu (2005) investigated that NaOH modified fly ash samples were tested against methylene blue basic dye for adsorption in aqueous solution. The results indicated that the adsorption capacilty was increased on sonochemical treatment of fly ash that depends on concentration of NaOH and treatment time. The adsorption tests showed that pH of solution and temperature of adsorption influence the adsorption behaviour. Salehia et al. (2010) prepared and characterize a novel biocompatible composite (Chitosan–zinc oxide nanoparticle) (CS/n-ZnO). They immobilized zinc oxide nanoparticles onto Chitosan. The textile dyes, Direct Blue 78 (DB78) and Acid Black 26 (AB26) were used as model compounds. They also studied the isotherm and kinetics of dye adsorption that followed pseudo-second order kinetics. It was concluded that the CS/n-ZnO is a biocompatible, eco-friendly and low-cost adsorbent and it might be a suitable alternative for dye removal from colored aqueous solutions. Bradder et al. (2011) prepared Graphite oxide (GO) by a modified Hummers−Offeman method and was tested as an adsorbent for the removal of dyes in aqueous solution. The GO structure was characterized by N_2 adsorption, X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. The GO structure does not showed any significant changes in surface area, on the other hand the layered graphene structure was expanded, and several surface oxygen functional groups were formed palying a significant role in adsorption. It was found that the dye amount adsorped on GO was much higher than that on graphite. The mechanism of adsorption was proposed as electrostatic attraction. Mittal et al. (2008) used bottom Ash and De-Oiled Soya as adsorbents for the removal of a hazardous azo dye—Metanil Yellow from its aqueous solutions. By using Batch adsorption, kinetic studies and column operations extraction of lethal dye from wastewaters can be enabled. The data of adsorption equilibrium confirms both Langmuir and Freundlich isotherm models and also a monolayer coverage of dye over adsorbents. The saturation factors were found to be 99.15 and 99.38% for Bottom Ash and De-Oiled Soya columns, respectively. They also made attempts to regenerate the dye from the exhausted columns using aqueous sodium hydroxide as eluent. Kasgoz and Durmus (2008) prepared Acrylamide (AAm)-2-acrylamide-2-methylpropanesulfonic acid sodium salt (AMPSNa) hydrogel and AAm-AMPSNa/clay hydrogel nanocomposite having 10 w% clay by in situ copolymerization in aqueous solution in the presence of a crosslinking agent (N,N′-methylenebisacrylamide (NMBA)). Safranine-T (ST) and Brilliant Cresyl Blue (BCB) dyes were used to study the swelling properties and kinetics of the hydrogel. They also calculated the swelling and diffusion parameters in water and dye solutions. The study showed that the AAm-AMPSNa/clay hydrogel nanocomposite possess improved swelling capacity as compared to the AAm-AMPSNa hydrogel. It was also found that the diffusion mechanisms show non-Fickian character. Incorporating Clay into the hydrogel structure not only increases the adsorption capacity but also the adsorption rate. It was found that the adsorption of dyes by the hydrogel nanocomposite completed in 10 min while the AAm-AMPSNa hydrogel adsorbed dyes approximately in 90 min. It was found that the adsorption kinetics of hydrogel nanocomposite followed a pseudo-second-order model also the Langmuir model fits the adsorption data better than the Freundlich model.

Das et al. (2010) investigated bioaccumulation of synthetic dyes viz. Acid Blue 93, Direct Red 28 and Basic Violet 3 by growing cells of yeast, *Pichia fermentans* MTCC 189 in growth media prepared from sugarcane bagasse extract. At pH 5.0 they found maximum dye bioaccumulation. They used two kinetic models viz. Noncompetitive and Uncompetitive models for the determination of toxic effects of dyes on the growth rate of *P. fermentans* MTCC 189. Basic Violet 3 was found to be more toxic than the other two dyes. The optimum conditions predicted that *P. fermentans* MTCC 189 have the capability of bioaccumulating Basic Violet 3 dye upto 69.8%. Gamra and Ahmed (2015) presented a simple and successful route to synthesize titania nanoparticles by controlled sol-gel progress. To increase the surface area chitosan as bio-template was involved in the progress of preparation and manipulated the defined particle and pore structure. XRD and TEM were used to study the crystalline behavior and the nanostructure nanoparticles. The crystalline results indicated the existence of anatase phase revealing the role of chitosan in stabilizing titania nanoparticles and stop the growth of these particles into rutile phase. It is obvious to notice that a change in sample crystallography from anatase to completely amorphous nanoparticles upon adsorption of malachite green dye indicates a strong adsorption of this dye that destroys the crystalline feature of titania sample. The enthalpy change (ΔH°) value for malachite green dye indicated the removal process to be endothermic and follows pseudo-second order rate equation and the negative values of standard free energy (ΔG°) suggest that the adsorption process to be spontaneous.

REMEDIATION OF TEXTILE DYES WITH BIOLOGICAL AGENTS

Faraco et al. (2009) evaluated the effect of *Phanerochaete chrysosporium* and *Pleurotus ostreatus* whole cells and their ligninolytic enzymes on models of colored industrial wastewaters. They defined the models of acid, direct and reactive dye wastewaters from textile industry. It was found that *Phanerochaete chrysosporium* has provided an effective decolorization of about 45% in one day of treatment and within 7 days the decolorization rate was reached upto 90%. On the other hand *P. ostreatus* decolorizes and detoxified acid dye wastewater model upto 40% in only 1 day and 60% in 7 days. Alvarez et al. (2013) proposed a novel remediation strategy that consists of sequential biological and physical process for the removal of textile polluted effluent. They proved the decolorization ability of *Anoxybacillus flavithermus* in an aqueous effluent containing Reactive Black 5 and Acid Black 48. In less than 12 h, the decolorization efficiency was reached almost 60% which points out the suitability of the selected microorganism.

Azo dyes are considered as major chemical in textile industrial wastewater and its remediation before it reached to agricultural land is important for the safety of surrounding environment. Darwesh et al. (2014) focused on the isolation, screening and azo dye removal by bacteria which was isolated from dumping site of textile wastewater. They teste total 14 isolates in their study. Out of 14, one was most efficient in decolourization of RB dye which was identified by 16s DNA sequences to *Pseudomonas aeruginosa* strain. Mullan et al (2001) also investigated the bioremediation to degrade textile dyes by using microorganisms such as white-rot fungi and anaerobic bacterial consortia. Wafaa and Rahim (2006) worked on the removal of direct and reactive dyes using biotic and abiotic agents. They investigated the removal of dyes using sugarcane bagasse, sawdust, rice straw, charcoal and fungal biomass as dye removing agents. They used seven fungal strains for the removal of textile dyes. It was found that after 2h of incubation *Penicillium commune*, *P. freii,* and *P. allii* removed 96, 64 and 65%, respectively, of direct violet dye. Rice straw was also found to be more efficient in dye removal, than was bagasse or sawdust. Rice straw was effective in removing 72% of direct violet dye within 24 hours.

CONCLUSION

The water from textile industries which is discharging directly into the natural water bodies is a serious threat not only to the environment but also to the human life for the people who may use this wastewater for drinking purpose. This wastewater also leaves a negative impact on the people who are directly and indirectly associated with this profession. The study by far has proved that the chemicals present in wastewater containing dyes causes appreciable changes in the physical and chemical properties of water. Hence, it is a matter of great concern that the industrial effluents should not be discharged directly into the water bodies without proper treatment.

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KEY TERMS AND DEFINITIONS

Advanced Oxidation Process (AOPs): Advanced oxidation processes (AOPs) are a set of chemical treatment procedures designed to remove organic or sometimes inorganic materials in water and wastewater by oxidation through reactions with hydroxyl radicals (OH).

Azo Dyes: Azo dyes are organic compounds, which contain the colouring azo function (N=N) which is often bound to an aromatic ring.

Biological Oxygen Demand (BOD): Biological Oxygen Demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time period.

Chemical Oxygen Demand (COD): Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals.

Chapter 6

Dyeing Processing Technology:

Waste Effluent Generated From Dyeing and Textile Industries and Its Impact on Sustainable Environment

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ABSTRACT

Among the different substances containing organic compounds, dyes are considered the most important class, and they are now an essential requirement in the modern world, mostly in the textile industries. In addition to the textile colouring, they are used in automobile, leather, paints, paper industries, etc., but their importance in the textile industries is maximum. Because of huge demand of dye, the production of a variety of dyes with advanced properties has drastically increased. Since dyes are complex aromatic organic compounds containing conjugated double bonds, they are highly toxic to the biological community of the world. In this chapter, more emphasis is given for synthesis technologies of various kinds of dyes, different kinds of hazardous pollutants generated from the dyeing industries, and their environmental impact along with the implementation of the technology developed to reduce the pollutant and its effect to our sustainable environment. Hence, more focus has to be given for manufacturing and application of dyes from renewable natural resources.

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INTRODUCTION

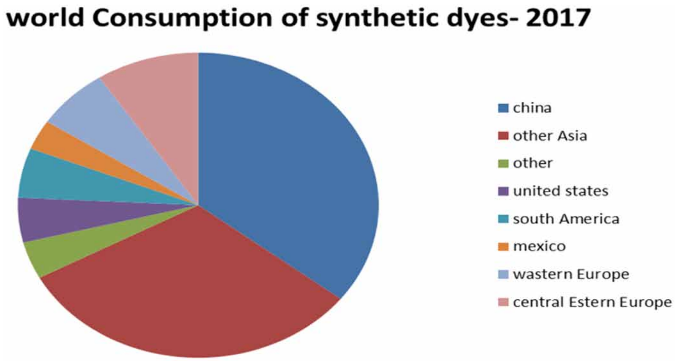
The chemical substances or the materials which are fastness to water, light, heat, moisture, dilute acids, alkalis and used for imparting colour in the materials like paper, textiles, lather etc.is known as dye. The dyes may be natural or synthetic which mostly dispersed in the liquid phase and produces paints, inks or it may be blended with other materials and enhances the colour and beauty of the manufactured products. Dyes are mainly organic aromatic complex compounds, whereas the pigments are organic or inorganic compounds, but both are given bright colour when imparted on any materials or textiles simultaneously. Dyes and colours both are different in natures. The colour is not resistant to acids, alkalis sunlight, water and all other environmental factors and is directly related to the structure of the molecules of the dye. The colour imparted by dyes is due to the following reasons.

- Due to absorption of visible light in the range of 400-700 nm
- It contains chromophore groups within its molecules, which are the colour imparting groups.
- Contains alternate single and double bond with the conjugated system in its molecular structure
- The stabilization of the dye is due to resonance within the aromatic ring of the molecule of the dye i.e. the migration of conjugated electrons will occur within the alternating single and double bond. If any of the features among these is not found, then the dye losses its property of imparting colour. Most of the dyes contain chromophores along with another group known as auxochrome, which has the property of enhancing the efficiency of auxochrome.(L.A. Thi et. al. 2018)

Examples: The groups like carboxylic, sulphonic, hydroxyl etc. are not responsible for imparting colour but if it is present in the molecule of the dye it can influence imparted colour i.e. shifting of the colour of the colorant present in the dye.

The organic aromatic conjugated systems of dyes contain chromospheres; the azo groups present in it are mostly responsible for yellow to orange colour due to bathochromic shift, which explains the extent of conjugation with the aromatic ring structure. Now-a-days people of the world are facing a great problem of rapid environmental degradation and the time may come in which the whole biological world will be destroyed. The major processing technology in textile industries is the fibre processing and dyeing and it requires large amounts of water for this purpose. During dyeing more than 50% of water along with the unused dye are generated in the form of effluent discharge. The coloured waste water discharged from the textile industries are of varying composition and the toxicity effect is also different and depends upon the nature of the dye. Since dyes have the colour imparting capacity, therefore it is used popularly in common industrial sectors, mainly textile, cosmetics, plastic processing, photography and paper industries. Some dyes are also being used in pharmaceutical and food processing units, but this use is the cause of greater hazard to human health. (Bafana et.al.2011, Carneiro et.al. 2007) The dyes when applied on the surface of a substance, it may chemically adsorb on the surface by making a chemical bond with the formation of complex molecules, salts or it may be physically adsorbed on the surface by the process of mechanical retention. The classification of the dyes depends upon its structure, nature of the chromophore and auxochome group present and its application in various sectors. The chromophore group contains different diversified functional groups, mainly anthraquinone, azo groups, methane, arilmethane, carbonyl, nitro groups etc. the auxochrome group present in the dye enhances or intensifies the colour and the efficiency of imparting colour in the chromophore increases. The common auxochrome groups are mainly carboxyl, hydroxyl, amine, sulfonate group etc. (Christie et.al 2001, Dos Santos et.al. 2007, and Arun Prasad et.al. 2010). In an estimated data it was found that more than 10,000 different types of dyes and pigments are generally used all over the world in different industrial purposes and the global annual production of dyes is around $7x10^5$ tons. (Robinson et.al.2001, Ogugbue et.al.2011) The different kind of processes used in the textile industries for dyeing are mainly continuous process, batch process and semi-continuous process which mainly depends upon the type of fibbers, fabric materials or garments to be manufactured. Among all these processes the batch process is most popularly used method in the textile industries (Jin X et.al.2007). It was estimated that annually about 280 thousand tons of dyes are lost in the dyeing process in textile industry globally and these dyes on mixing with water ejected in the form of waste effluents and contributes a major part of surface water pollution. Although the effluent ejected from different industries are subjected to the treatment process before mixed with water sources, but dyes are commonly escape out from the treatment process and persist within the environment for a longer time period. According to the legislation Act the dyeing industries should have to be removing the toxic materials and chemicals along with colour from the effluents before addition into different water bodies. (Forgacs et.al. 2004, Przystaś et.al.2012) Since the effluent of textile industries contains huge quantities of dyes which are non-biodegradable in nature, therefore the COD value of these effluents is exclusively high and on the basis of COD value the effluent may be classified into three categories such as low, medium and high COD content effluents. The textile industry consumes plenty of water for its different operations such as manufacturing, dyeing and finishing and the effluents ejected from it are considered as the most polluting and toxic effluent among the industrial pollutants. Due to increase in the demand of textile worldwide the effluents generated containing toxic substances and chemicals increases and it gradually becomes a major source of surface water pollution and the water quality is degraded due to change in BOD, COD, DO, salinity, pH, colour etc.. The composition of the liquid effluents ejected depends upon the organic compounds and chemicals present in the dyes and the processing technologies (both dry and wet processes). In addition to the toxic chemicals some amount of dyes usually less than 2mg/L and some colorants are also present in the waste water effluents which destroy the aquatic biological kingdom and cause of neurological diseases and deceases the water transparency. Many dyes are mutagenic, carcinogenic and highly toxic in nature and responsible for pollution of surface water due to deficiency of oxygen, decrease in light penetrating power and photosynthetic activity in plants. Among all the group of colorants azo dye are produced in the large scale in worldwide in different dyeing industries and most popularly used in textile, cosmetics and pharmaceutical industries because of its special characteristic properties like properties of fastness to light and damping, dilute acids and alkalies, high structural diversity, maximum value of molar extinction coefficient and cost effective in comparison to other synthetic and naturally occurring dyes it is more popular and useful. The azo dyes may directly impacts toxicity or they generate derivate of aryl amine during the process of reductive biotransformation. The azo dyes can metabolize to aromatic amines by the process of azoreductases of the intestinal microorganisms. If the dye contains nitro groups, then it can be metabolized by the bacteria nitroreductase and produces the microorganism of the same categories. The enzymes of mammalian liver and some other organism can able to catalyse the reductive cleavage of the bonds presents in the azo dyes (azo bonds) and the nitro group present in it undergoes nitro reduction. In both these cases N-hydroxylamines are generally formed which is capable of damaging DNA and RNA of our body. The colour present in the dyes and pigments are non-biodegradable in nature and is very difficult to remove during the treatment process. (Kalyani et.al. 2009) The

Figure 1. This pie chart shows world consumption of synthetic dyes in 2017



productivity, washing efficiency increases with reduction of cost, energy by use of ultrasonic wave as energy source which is one of the effective environmental friendly processes for production of textile dyes. The objectives of this chapter are to suggest different eco-friendly green method for manufacturing of textile dyes because the dying process is considered as one of the most environmentally unfavourable process of the industrial sector.

DYEING TECHNOLOGY

In textile industry not only the fabrication of textile products but also the dyeing process is equally important because consumers are always wants the textile products of proper design, comfort, beautifulness and magnificent colours with high stability to washing and sunlight. Hence dyeing technology is an important factor in textile industry for manufacturing of consumer demand textile products. (Hassan et.al.2009) The dyeing process is said to be good if it exhibits uniform colour, resistance to colour fading, easy to processing and economically feasible. Now we are adopting some modern technology for dyeing which is divided into different steps depending upon the nature of the fabrics used, compactable with the dyeing material, cost factor, availability of the material used etc. In dying process water is used in many steps such as cleaning dyes, application of chemicals to the fabrics, washing of the fibres and fabrics etc. The dyeing technology is divided into broadly three step i.e. preparation of dye, dyeing process and finishing. The first step of the preparation is removal of unwanted substances which is done by cleaning the fabrics in aqueous alkaline substances or by using detergents or may be applying some specific enzymes. Then after that the bleaching agents like H_2O_2 or chlorinated compounds has to be added to remove the natural colour already present in the fabrics and to increase the brightness .The optical brightness agents has to be added during the preparation for imparting extra brightness. Hence it comes to a conclusion that we cannot found any dye which can dyes all the fibres or there is no fibre is found which can be dyed by all the dyes. The second step is the dying process in which different chemicals mainly acids, surfactants, alkalis, electrolytes, levelling agents, chelating agents, promotion agents, oil used for emulsification, softening agents etc. are added for proper dying. This process consists of diffusion of the dyes inside the liquid medium which is followed by adsorption at the outer surface of the fibre used and finally both diffusion and adsorption processes are working at the inner to the fibre. In the third step i.e. in finishing step different kinds of dyes and additives are used to get the required property of dye in fabrics and imparting multiple colours. (Gong et.al.2008, Hammed et.al.2008) In the finishing process the different chemical compounds are added to improve the quality of the fibres. Permanent press, water proofing, protection of antistatic, resistance to oil, release of stain, and protection of microbial action are the different processes are applied in the treatment process during the finishing step. The dying process mainly divided into two categories.

- Batch process
- Continuous process

The process used depends upon types of fibres, fabrics and garments to be prepared, but the batch process is most commonly and more popularly used process for dying of fibres and fabrics in textile industries. In continuous process steaming and heat are used in a long roll of fabric materials through a long series of some concentrated chemicals. At every time the fabric material is passed through a chemical solution and equivalent amount of water in the weight of fabric is used and finally ejected as waste water effluent. The batch technology may be called as exhaust dyeing because the dye used is continuously transferred from batch to the fabric and dyed for a prolonged time period.

Batch Process

This processing technology is a transaction in a batch and during operation once the processing is continued there is no require of user interaction. The disadvantages of batch processing technology are the transaction processing and it involves processing transaction once at a time and usually requires interaction of the user. In the middle of the 20th century many entrepreneurs adopting this technology popularly with organization, completion of the data and generation of the report by introducing in the computer programming but in early stage the batch processing technology involves feeding a stack of punch card to computer with command and direction. These batch processing technologies are adopted regularly or in some time intervals whenever need. The benefits of batch processing are cost effectiveness but the handling of large amount of data at a time is the major difficulty of the batch processing. We have to input correct data otherwise whole result will be wrong and more time and money has to be spending.

Continuous Process

This process is also called as continuous production process because of continuous flow of materials of either in the dry bulk form or in the fluid state and during processing the material is continuously rotating. This processing technology involves chemical reactions, heat treatment and mechanical treatment which is a streamlined process and continued at the end of the service. This process requires seven days in a week with 24 hours per day.

The different dyeing technologies are described below.

The Fabric Dyeing Technology of Rubber Bands with Shibori Tie-Dye

There are many processes are adopted for dyeing fabric materials and these processes are unpredictable and shows beautiful results. The shibori Tie -dyeing process is mainly accompanied by the folding of the used materials in an open pattern and also binding with a rubber band or string, after that the dye obtained may be applied partly to the used material but not in the hidden part of the material. A large range of processing technologies is offered by Shibori.

The Fabric Dyeing Technology of Stitch Resist with Shibori Tie-Dye

By using this technology, the thread prepared from fabrics and dyed may designed to any thickness and applied from simple lines to more complex pattern designed as on the basis of need. This technology is mostly applied in the thread used to create a desired pattern. In this process applied dye resist to penetrate inside the material, therefore the dyeing process is not uniform and is localized. The different steps of this dyeing technology are fabric stitching, the fabric dyeing and finally thread removal with rinsing.

The Dyeing Technology of Shibori Pole

Shibori word is a Japanese word and is used for shaping the cloth and to secure these before it dyeing. This word is meaning to squeeze, wring and press. This is used for dyeing of a particular group of fabric materials. In this process the cloth is treated to form a two dimensional surface with Shibori and produces a three dimensional form by crumpling, folding, stitching, plucking or plaiting and twisting. In this method the shaped textile materials are secured in a verity of ways such as knotting and binding. It is a Japanese technology and more advanced technology recognised worldwide and accepted by international textile vocabulary. We can be experimented it by warping the pole in a variety of ways by using dyes of different colours.

The Dyeing Technology of Shibori Folding

In the technology of Shibori folding a definite geometrical pattern is created like triangle, hexagonal, square, pentagonal etc. by folding the fabric material in different ways and the products of the material can also be flat clamped in both the sides of used fabric products before it dyeing. The various steps involved in this process are as follows.

Step- 1: Folding the fabric materials

The fabric materials are folded in one directional only and crisp fold are obtained then it can have ironed but it is not necessary. The larger the folds, the pattern of the dyeing will be more.

Step -2: Dyeing the fabric materials

The work space is filled with the plastic materials or some other composite materials in order to prevent the staining and soaking used fabric materials from warm water. In this technology heat or enough hot water is covered in the used fabric materials. We can either immerse or dipped the whole material in the edges.

Step -3: Rinsing the fabric materials

Then finally the dyed material is rinsed with slight warm water until the water runs clear. This type of dyeing pattern can be adopted by folding the material in various ways using clamps with dyes of multicolour.

The Dyeing Technology of Ombre Dip

The word Ombre means colour bleeding with dip dyeing or gradated dyeing and the effectiveness of this technology increases by hand dipping the fabric materials in dying process and in this process the material gradually transformed from light colour to dark colour or sometimes the change from one colour to some totally other different colour is achieved but actually the true Ombre is hand dipped in a laboratory with indirect gradations from bottom to top. This technology can be adopted for dyeing various products such as different clothes and pillow cover. (Karim et.al. 2006)

No-Wax Batik Technology

Now-a-days the Batik fabric technology is traditionally and commercially used; in this technology the wax present in it covers the surface of the fabrics materials and resists the dye penetrating inside the fabric, hence dyeing process become uniform over the surface. The similar technique can also be made more easily using glue or gelatine instead of molten wax. Batik is a better technology of wax-resist dyeing technology process which is applied to the total whole textile materials or cloth materials that are fabricated by adopting this technology. This technology is first of all adopted in Indonesia and the product is manufactured either by drawing the dots or lines of the resist with spouted tools termed as tjanting. The wax applied generally resist the dye and allows the crafts worker to select the colour and the cloth may dye in one colour, the wax can be removed by using boiling water, if the multiple colour is required, this process is repeated again and again. In this process instead of wax glue and gelatine may be preferred. (Komarudin Kudiya. et.al. 2016)

The Fabric Dyeing Technology of Low Water Immersion

This is a low water immersion dyeing technology and also termed as crumple dyeing or crackles dyeing or scrunches dyeing process. The advantages of this technology are that we can uses small amount of water as far as possible for crunching the fabric materials. In this dyeing technology process less stirring effect is observed and to get a significant result we have to use a big container with sufficient quantity of water. The efficiency of dyeing varied by using dyes of multiple colours. (Karim et.al. 2006)

The Fabric with Dye – Water Colour Technology of Painting

Every paint or dyes can be manufactured by the combination of the dry pigments with suitable appropriate medium. For water colour dyes and paints the medium used is water, therefore it is important to keep the water clean otherwise some other different colour is marked in the textile material after dyeing the product. A beautiful colour can be imparted in the fabric material on combination of this method with other dyeing technology methods. (Suteu D et.al.2009)

The Dyeing Process of Liposome-Based Technology

This dyeing technology is mainly based upon liposomes which is defined as structure consisting of bilayers of lipid vesicle and effectively encapsulate hydrophilic or hydrophobic substances in the bilayer of lipid or in the aqueous medium respectively.

This structure can be formulated by phosphatidylcholine, which is the hydrophilic part and usually contains phosphate and choline groups and the hydrophobic part consist of two different hydrocarbon chains of different length. The liposomes are always classified and distinguished on the basis of the number of the lamellae units and size of the hydrocarbon chain. The different forms of vesicles are large unilamella or large multilamellar or multivesicular and small unilamellar. Since the scientist and researchers are trying to develop the environmental friendly green technology, therefore the naturally found materials like phospholipids is now becoming important. The phospholipids are one of the naturally occurring surfactant and when it is mixed with water, it is aligned in such a way that it reduces the unwanted interaction between the aqueous phase and the hydrophobic tails, the hydrophobic head groups when exposed to the aqueous medium it forms vesicles. The phospholipid vesicles and liposomes separate clearly the hydrophobic and hydrophilic regions. It was observed that when water is added with phospholipid a spherical shape is immediately formed because one of its ends is water soluble and other end is water insoluble. The liposome has a zwitter ion structure and amphoteric in nature with one end acquires fractional positive charge and other end acquires fractional negative charge. (Upendra Bulbake et. al. 2017, F. Yu. Telegin et. al.2013)

Effect of Ultrasonic Energy on the Dyeing Process

The technology of using ultrasound energy in the process of dyeing was first of all studied by Sokolov and Tumansky. The basic principle and technology involved in this process are the ultrasound energy which increases the mass transfer by decreasing stationary core present in the yarns. This process can be improved by attributing it to the cavitation phenomenon and some other physical effects such as dispersion of the dye, degassing, agitation of the liquid used in this process. (Wafa Haddar et. al. 2015)

HISTORY OF DYEING

In the ancient world the people of Egypt produces coloured linened cloth and later on Indian and Chinese people can able to made coloured cloth by using some natural dyes. The different dyes are also named on the basis of their country and some natural things. The dye alizarin named from the country Arab whereas the blue dye named from indigo or woad. The fast vast dye comes to the picture at the end of 19th century and after that the more popular naphthol dyes are investigated in the beginning of 20th century. In the meantime, many natural dyes are identified and used in the colouring of the textile material but now-a-days the use of natural dyes are limited and more advanced synthetic dyes are prepared and used in textile industries. (Horrocks et.al.2000) Although it is cheap and more durable but the toxicity is very high and now the scientists are searching for modification of natural dyes which can replace the advance synthetic dyes. (Hana Křížová et. al. 2015)

Principle

The aim of the dyeing is to impart uniform colour in the fabric textile material to match the required selected colour. The dye should be uniformly distributed throughout the textile material or substrate and there is no change in colour should be observed as a whole. There are so many factors that depend upon the appearance of the final sheading of the textile materials (final shading appearance, substrate texture, substrate manufacturing in both physical and chemical process). The total dyeing process is divided into three steps such as pre-treatment, during treatment, past-treatment. In pre-treatment process the impurities are removed from the substrate (textile material) and during treatment process dye are applied to impact uniform colour to the fabric material either by continuous or padding process or batch process or in the post treatment process the material is finally subjected to finishing process.

Classification of Dyes

The dyes are classified in to the following categories on the basis of chemical composition and applicability.

Direct Dyes

This dyes are more widely and popularly applicable for dyeing cotton materials. The direct dyes are defined as the anionic dye which is applicable to cellulose fibres in aqueous medium having appropriate electrolytic solution. These dyes can be used for dyeing of protein fibres and more commonly available in the market. These dyes are soluble in water and the dyeing is carried out in alkaline medium in the exhaustion of electrolyte. These dyes are most commonly used in comparison to reactive dyes and mostly applied for dyeing of fibres of cellulose and protein. (N.Sekar 2011)

Vat Dyes

Since these dyes are applied by using bucket or vat, therefore it is named as vat dyes. It is not a specific dye but the different dyes like direct dyes, fibre-reactive dyes and acid dyes can be used as vat dyes. The materials like cotton, leather, wool and some other fabric materials can be dyed with the vat dyes. Indio dye is an original vat dye but now-a-days it can be prepared synthetically in the laboratory. These dyes are although insoluble in water but soluble in the process of vatting and specially applied in the cotton fibre for manufacturing of denim jeans. These are natural colouring dyes and the final colour is achieved after the process of oxidation. It shows excellent fastness properties and applied in alkaline medium. (Moustafa A.B.E 2011)

Sulphur Dyes

These dyes are the most commonly and popularly used dyes having excellent fastness to washing and mainly applied in the cotton fibres. These dyes mostly available in the black, pink, brown and dark blue colour but not available in the red colour. This kind of dyes are easily absorbed by the cellulosic fibre in aqueous medium and easily oxidised. These dyes are excellent fastness to colour, light and washing etc. and mainly available in the powder, granules form or in the liquid state. These dyes are not environmental friendly because of the presence of sodium sulphide and sodium or potassium dichromate.(Priyadarshi Jaruhar et. al. 2018)

Azo Dyes

These dyes contain organic compounds having the functional groups $R{-}N{=}N{-}R'$ where R and R' are aryl groups. These dyes contain the linkage C-N=N-C and mainly used in textiles, leather products and also some food materials. These are insoluble in water and some other solvents. During dyeing process, the functional group (N=N-) bonded with the aromatic ring are broken down and converted into aromatic amines and aryl amines by the process of chemical cleavage or enzymatic cleavage. It is carcinogenic in nature and mostly used for dyeing of textile fibres mainly silk, cotton, wool and some other synthetic fibres. More than 300 different categories of azo dyes are available in the common market and most of these are water soluble in nature.(King-Thom Chung 2016)

Reactive Dyes

In this dyes the atoms or groups present in the chromophores reacts with the substrate (textile material) and impart colour for which it is known as reactive dyes. It mostly used for the dyeing of cotton and flax and sometimes wool and nylon can be dyed by using this dyeing. This is the only class of dye which forms covalent bond with the fibre material during the process of dyeing and most popularly used all over the world in the dyeing technology of natural fibres and cotton. Some of these dyes are water soluble and some are water insoluble.

Acid Dyes

This is a special kind of dye which is used in the dying process of the textile material even at lower pH. It mainly applied in the dyeing of wool fabrics and cannot be applied for cotton. Sometimes it is used as food additives for colouring of some food products. These dyes are highly soluble in water and fastness to sunlight as compare to basic dyes. It mainly used for dyeing of wool, silk and nylon. After solution with water it becomes acidic due to negative group (-NH_2)which later protonated and forms -NH_3^+. In the dyeing process there is a columbic interaction occurs between positive and negative end with the formation of hydrogen bond, dipolar bond and Van-der-Waals interaction. These dyes are anionic in nature. (Mansour, H. B et.al 2007)

Disperse Dyes

These dyes are purely water insoluble containing small molecules among all the dyes. These are widely used in the aqueous suspension form for dyeing of manufactured fabric materials. These dyes are applied for colouring the substances containing no ionizing groups and hydrophobic in nature with low water solubility. These are non-ionic dyes and free from ionizing group having very low water solubility. These dyes are organic colouring substances and mostly suitable for hydrophobic fibre dyeing. It requires dispersing agents for dyeing and is fastness to light and washing. The disperse dyes are mainly the derivatives of anthroquinone, nitro, azo and quinine derivatives. During dyeing process, it undergoes chemical change. (Martínez-Huitle, C. A et.al. 2009)

Basic Dyes

This class of dyes are cationic in nature and can be applied to the material containing negative charges and synthetic dyes. The aniline dye is the most important basic dyes. This dye is not soluble in water, therefore the colour is imparted when the base is converted into its corresponding salts. The fibres made by jute and its products are mostly dyed by these dyes. During dyeing the salt ionises into cationic and anionic part and the cationic part is mainly responsible for imparting colour. These dyes are insoluble in aqueous medium whereas soluble in alcoholic or methylated sprit medium. These are synthetic class of dyes and are hydrochlorides or salt of organic compounds and mostly applied in acidic medium. Although it is better applicable for dyeing of jute fibres but wool and acrylic fibres are also be dyed by using these dyes. (Mathur, N. et.al.2012)

Effluent Generated from the Dyeing Industries

The effluents generated from the textile industries contain higher values of colouring substances and toxic organic chemicals along with high value of COD, BOD, TDS and TSS. It was observed that by using highly substantive dyes during the process of dyeing, printing and finishing in the textile industries, huge amount of effluents is generated. These generated effluents are highly toxic in nature and it should be treated before adding in to the other water sources. The textile industry requires huge amount of water in various steps for manufacturing of textile materials. (Kamal et.al. 2016)

Nature of the Effluents Generated from Textile Industries

Mostly the water based solvent effluents are produced from textile industries but in some cases if the dyes are not soluble in water then the effluent contains some other organic solvents. This generated waste water mainly contains colouring substances and chemicals with some fine solid particles or thread like substances which are used for the dyeing, printing and finally finishing steps. The effluents generated in all the steps during dyeing are highly polluted, toxic and the water parameters are much beyond than the permissible limit. (Jo H. J et.al. 2008)

Consumption of Water in Textile Industry

The textile production requires many steps like spinning of the fibres, weaving of the fabric materials, chemical processing and finally manufacturing of the garments. More than 70% of the waste effluents are generated during chemical processing and colouring of the textile products. Huge amount of water was necessary for dyeing processing and finishing the textile products, some water is also required for washing and cleaning of machinery parts during and after the different operations of dying technology. (Khataee et.al.2010)

Processes of Effluent Treatment for Dyeing Industries

For dyeing and finishing of textile materials large amounts of water is required which can be fulfilled from the source of ground water and river water and is one of the cause of depletion of ground water level and scarcity of surface water. The waste water effluents generated is commonly known as dye bath which contains solid particles of pollutants in the range of 4 to 5% whereas the waste water effluent generated after washing textile materials is called as wash water which contains 0.5 to 1% of solid particles. By using proper advanced technology of processing we can

Figure 2. Percentage of water used in different steps of wet processing of textile materials

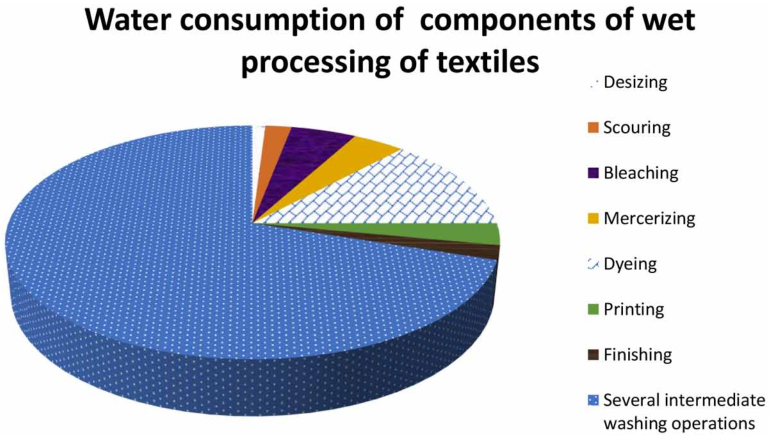


Table 1. Textile industry waste water characteristics

Parameters of Effluents	Standard Parameters of Effluents (in ppm)	Waste Effluents of Cotton (in ppm)	Waste Effluents of Synthetic (in ppm)	Waste Effluents of Wool (in ppm)
pH	5.5-9.0	8-12	7-9	3-10
BOD	30-350	150-750	150-200	5000-8000
COD	100-250	200-2400	400-650	10000-20000
TDS	1500-2100	2100-7700	1060-1120	10000-15000

able to separate hazardous toxic materials from the generated waste water and it can be reused by the industry for dyeing again and again. The salt used for the process of dyeing can also be reused or after purification it can be sold in the market. Hence the advance effluent processing technology not only solves our water problem but also the cause of profit of the industries. (Khadija Siddique et. al. 2017)

METHOD OF TREATMENT OF DYING AND TEXTILE WASTE WATER EFFLUENTS

The Wastewater effluents of dyeing and textile industries are treated mainly by three processes such as physical, chemical and biological processes and an advanced photolytic degraded process. The different processes are described briefly as follows

Table 2.

Sl. No.	Effluents Parameters	Units	Values	Standard Values of Discharge of Waste Effluents
1	pH	-	8-10	6-9
2	Appearances	-	Colloidal	-
3	Colour	-	Intensively coloured	-
4	Solids in suspended form	mg/l	200-300	150
5	Heavy metals	mg/l	10-15	-
6	TDS	mg/l	5000-6000	150
7	BOD	mg/l	500-600	50
8	COD	mg/l	1500-1700	200
9	Surfactants	mg/l	10-40	-
10	Oils and grease	mg/l	40-60	10
11	Sulphides	mg/l	50-60	1

Chemical Methods

Flocculation and Coagulation

In these processes different types of coagulants such as Aluminium Sulphate, some Ferric salts, Ferric Sulphate are popularly used for coagulation of colloidal form of toxic solid particles and heavy metals present in the dye. Then after filtration it is removed from the effluent.

Oxidative Processes

In this process the commonly used oxidising agent is hydrogen peroxide and by using this agent in UV irradiation with chemical decolouration technique the toxic aromatic ring compounds present in the molecules of the dyes is broken down reducing the toxicity effect of the dyes.

By Using Fenton's Reagent

This reagent is commonly used in the chemical treatment method for the effluents containing the pollutants which are resistance to biological oxidation. But if the production of sludge by using coagulant is treated by using this chemical, it is one of the major disadvantages.

Ozonation Process

O_3 is a popular and widely used oxidizing agent and quite unstable in nature. The use of ozone can able to break down the toxic chemicals such as pesticides, phenols, chlorinated hydrocarbons and aromatic hydrocarbons present in the waste water effluents of both dying and textile industries. The breakdown capacity of O_3 increases in alkaline environment. Since its half-life period is very short, it is the major disadvantage of oxidation.

Photochemical Degradation Process

In this process by using UV radiation in the presence of hydrogen peroxide the toxic chemical substances undergoes oxidation and broken down into carbon dioxide and water. The major advantages of this process is no sludge is produced and the disagreeable odour due to dye is reduced.

By Using NaOCl (Sodium Hypochloride)

This technology mainly applied for azo dyes and is not suitable for dispersed dyes. It usually detached the amino groups present in the dyes and eliminates chlorine and its derivatives from the dyes.

By Using the Polymer Cucurbituril

It is a cyclic polymer containing formaldehyde and glycoluril and is a supra-molecular composite material containing aromatic rings and can facilities the process of adsorption especially reactive dyes. It also causes the interaction of hydrophobic end with the formation of insoluble cucurbiturildye-cation compound which is settle down and can be separated easily. (Verma AK et.al. 2012, Kim et.al. 2004)

Electrochemical Destruction

This technique is generally an environmental friendly process used for treatment of waste effluents of dyeing and textile industries and the major advantages of this process is almost no formation of the sludge and the dye molecules are eliminated by using the electrochemical process (cathodic or anodic reaction). The degraded products can easily remove from the treated effluents. (Suteu D et.al. 2009)

Physical Methods

Process of Adsorption

Clay

This technique uses various kinds of inorganic clay materials such as MMT, kaolin etc. as adsorbent materials and effectively eliminates the contaminants present in the waste water effluents of dyeing ad textile industries. The clay materials are commonly used as adsorbent because of its larger surface area, greater ion exchange capacity, higher sorption capacity and plenty availability throughout the world with low cost. MMT has maximum ion exchange capacity among the clays. (Khan et.al. 2009)

Zeolites

It is a compound of three dimensional structure of aluminosilicates containing large number of porous and voids with negatively charged particles in its lattices, therefore used as greater adsorbent of the solid particles and colloidal materials from the effluents.

Alumina

Bauxite is an ore of Al containing crystalline form of alumina with a large number of porous and voids in it. It is also used as adsorbent for removal of many metallic contaminants and chemicals from the waste water effluents. (Ngah et.al. 2008)

Activated Carbon

Activated carbon is basically effective for adsorbing cations from the dye, acidic dyes and moderants used in dyes. The activated carbon mainly prepared from natural low cost materials such as lignite, coconut shells, wood products and other different waste materials of agricultural products and farm waste.

Membrane Filtration Processes

The different membrane filtration processes are ultrafiltration, reverse osmosis, Nano filtration and microfiltration. Its use depends upon the nature of the waste effluents and type of pollutants present in it.

Reverse Osmosis

It is a green process which removes partly the colour and ionic impurities present in the waste water effluents of dyeing and textile industries. A suitable membrane is used to separate the colour and other ionic contaminates. The different kinds of reverse osmosis process are as follows: -

Nanofiltration

In this technique mainly the colour is removed from the effluents of dyeing and textile industries by using a membrane containing porous of Nano size. The Nano filtration blend on combination with adsorption gives better result. The particles separated by using the membrane of nanofiltration depends upon the size of the particle and charge effect which is because of steric effect and columbic forces of attraction on the basis of domain interaction. The particles of high molecular weight can be removed by using sieving mechanism where as that of low molecular weight and the ionic species are removed either by charge effect or mechanism of solution diffusion (R Mulyanti et. al.2018)

Ultrafiltration

In this process partially the pollutants are removed from the effluents of dyeing and textile industries. Hence this process is absolutely applied as pre-treatment process before the process of reverse osmosis or can be applied simultaneously in the biological reactor. The pour size of membrane used for ultra-filtration can remove the particles of size 0.001 – 0.1 µm from liquid effluents. Although virus cannot be completely in microfiltration process but in this process all virus are also be separated

Microfiltration

This process is also applied in the pre-treatment process of nanofiltration and reverse osmosis. It is a biological process for removal of colour and suitable for the dye bath containing pigment particles. The membrane having pour size 0.1 – 10 µm is used for microfiltration. In this filtration process all bacteria and a part of the virus are removed from waste water effluents. Although the size of the virus is smaller than pour size but it can attached with the bacteria and easily filtered. (Khemakhem S. et. al.2011)

Biological Methods

The colour and other toxic colloidal form of particles are removed by using bacteria or different kind of bacteria. The bacterial community are able to broken down the azo bonds present in the azo dyes either by aerobic or anaerobic process. (Kapdan et.al.2005) The different biological methods adopted for suitable treatment of effluents of dyeing and textile industries are as follows

Aerobic Method

In this treatment method one kind of bacteria or a community of bacteria is used to remove colour and breaking down the bonds of azo dyes, tannery and other textile dye in the presence of air or oxygen (O_2).

Anaerobic Method

In this method although the azo bonds present in the azo dyes are easily broken by using anaerobic bacteria but the major disadvantages is the formation of hazardous amine compounds and aromatic amines. These compounds are stable to biotransformation causing different metabolic activity in our body.

Anoxic Method

In this method we are using both aerobic and anaerobic bacteria simultaneously and the decolourisation process from the effluents becomes more rapid and easy. Many bacteria and microorganism are able to survive and functions effectively but the decolourisation process is more effective in anoxic treatment method.

Sequential Method of Degradation

This method is adopted after anaerobic degradation of azo dyes, after the formation of aromatic amine compounds. The degraded products of azo dyes are again further degraded by aerobic bacteria. The degraded product of amine compounds is completely mineralized by the added bacterial community. A number of dyes are degraded completely in microaerophilic method under aerobic condition and facultative bacteria are suitable for this process.

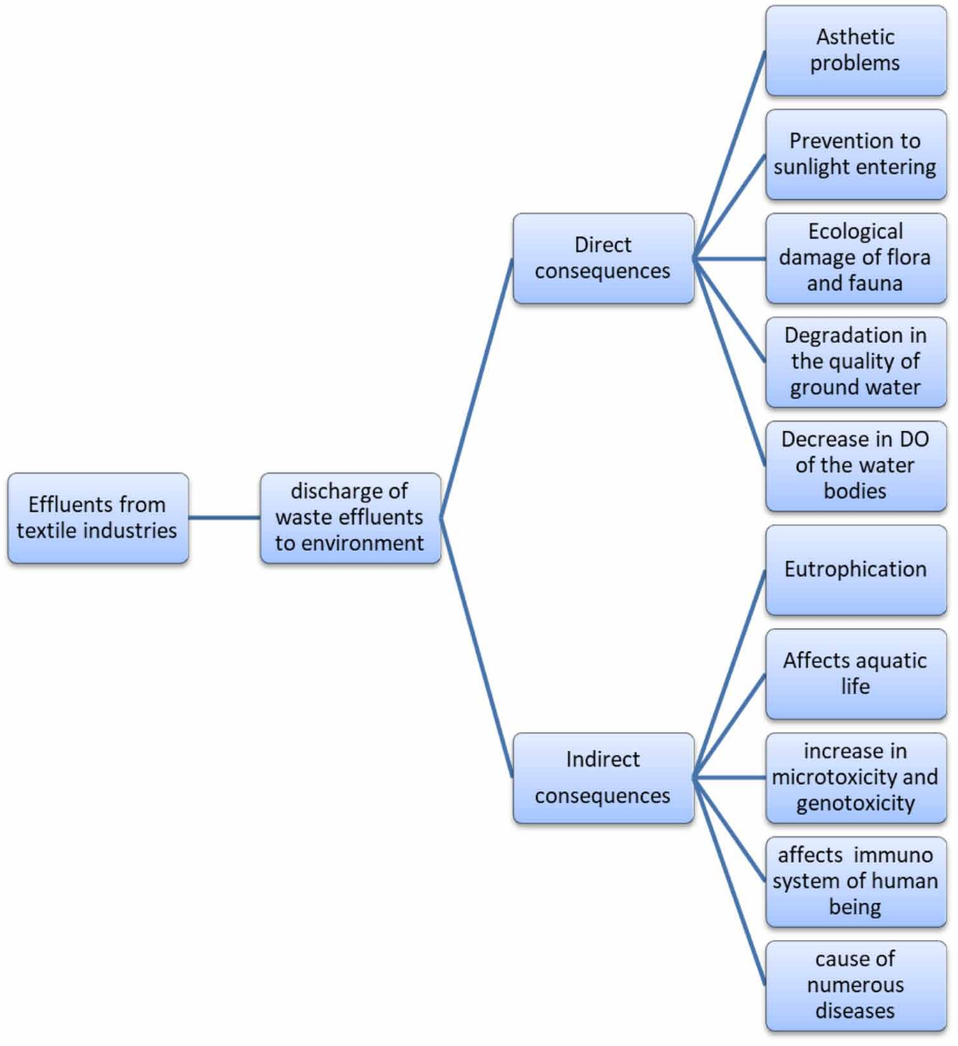
Photocatalytic Method of Degradation

This method is more popular and widely accepted because it is eco-friendly, greater applicability, high oxidation capacity towards the effluents, cost effective and more effectiveness. In the traditional methods of treatment such as ozonisation, reverse osmosis, ultrafiltration, nanofiltration etc. are limited for removal of some specific pollutants but where as in this technique a number of toxic pollutants with colour and pigment materials are removed in an eco-friendly manner. Semiconductor photocatalysis in the modern age is a better effective technique applied by dyeing and textile industries. In this method the effluents can be easily decolorized and dye molecules are broken down into simple inorganic substances mainly carbon dioxide and water. The major disadvantages of this process are the dangerous effect of by-products and generated sludge. (Mamba, G et.al. 2015)

ENVIRONMENTAL IMPACT

For manufacturing and processing of textile materials huge amount of chemicals are ejected with the generated waste effluents and these chemicals are mostly non-biodegradable in nature and cause of many diseases if mixed with different sources of human consumption of water. After final manufacturing of the textile materials, huge quantities of unused chemicals and solid waste are left with the wash water and bath water. Since these chemicals are toxic, not recyclable and not biodegradable, therefore it is a challenge for proper treatment of the generated effluent because it requires some special and advanced treatment process and these processes required special precaution and costly. If we are ignoring the treatment and waste effluents are directly mixed with the surface water then it causes hazards to the dwellers and cause of degradation of our environment. The organic compounds present in the waste effluents are mostly toxic and non-biodegradable in nature which remains in the environment for longer time period and affect our food chain, food web and ecological balance. Due to bioaccumulation and biomagnification of these toxic organic substances within the environment it is the cause of hazards to animals, human beings and other flora and fauna. The heavy metals like zinc, copper, nickel, cobalt, lead, manganese and chromium are present in the waste effluents because these are present in the dyes and finally mixed with the nearest sources of surface water and partly with the soil causing health effect problem and damage to our environment. The contaminate of inorganic materials present in the waste effluents are mainly acidic and basic salts of metals. These salts are cause of diverse biochemical interaction with the compounds present in the received surface water bodies and causes huge degradation of the water quality. In the effluents of textile industries, colour is treated as the first pollutant because very small amount of it is the cause of aesthetic problem, transparency, solubility of the gaseous components, absorption and decrease in reflection of light and photosynthetic activity. (Lukanova, V et.al. 2005, Nachiyar, C. V et.al.2003, Madhu, A et.al 2017)

Figure 3. Effect of effluents ejected from textile industries towards the environment



Various Issues of the Environment

The scarcity of water is the most important sustainable issue of every textile industry because the huge amount of water is required for different stages of manufacturing of textile materials.

- The environmental risk is another issue and function to the exposer to the environment due to toxicity and hazardous properties. Hence the reduction of contaminates from the effluents is a pathway of reducing environmental risk. (Lukanova, V et.al.2005)

- The dye bath water is the cause of high rate of environmental pollution if it is not properly treated.
- The effluent containing azo dyes is the cause of serious problem to the environment and also different process of chemical and physical method are adopted for treatment of effluent water.
- The waste effluents ejected contains different chemicals like naphthol, nitrates, sulphur, acetic acid, vat dyes, compounds of chromium, soaps, detergents and the heavy metals like cadmium, arsenic, mercury, copper, nickel, lead, cobalt and collectively is the cause of high toxicity of the received surface water.
- The ejected effluents are acidic in nature with elevated temperature with non-biodegradable organic and inorganic compounds, heavy metals and colours. Hence it prevents the penetration of sunlight inside the water bodies and cause of damaging aquatic ecosystem. In addition to that when it flows over the surface, the porous of the soil is clogged by it and is the cause of decreasing soil fertility and productivity. The soil texture becomes hard and the root of the plant cannot be easily penetrated inside the soil.
- When it flows through the waste water pipelines it causes corrosion in the pipe lines because of decrease in pH values. Otherwise these waste effluents when added to the river water or other surface water bodies it is the cause of degradation of the water quality and water becomes unfit for human consumption.
- The other issues towards environment besides the waste effluents are emission of pollutants to the atmosphere or air, presence of VOCs, colour, odour and safety precaution.
- During the high temperature curing process hydrocarbons, HCHO, acids, softeners, and many other chemicals are used which imparts badly to our environment.(Mohamed A. et. al. 2017)

Health Related Issues

- Many textile industries discharges waste water effluents directly to different rivers without proper treatment, which causes increase in pollution level of the water and directly affects to the ecological community nearby that area and if the concentration of toxic materials in it is very high then it is the cause of chronic diseases to both human beings and animals.
- The added pollutants from textile industries are the cause of depletion of DO and retard the self-purification capacity of water.

- The dyes used in different textile industries are the cause of many hazards in aerobic condition and cause of carcinogenic effect to human body. It was found that most of the dyes are generally toxic to mammalian animals and fishes; it also reduces the growth and reproduction of different micro-organisms and affects the flora and fauna causing danger to the aquatic life.
- The organic pollutant present in the dyes are cause of intestine cancer, abnormalities found in fetus, allergies, damage of skin, allergies in eye, damage to the respiratory system and affects our membrane.
- Since the reactive dyes can bind the cellulosic material, wool, nylons with–NH_2 and the–SH groups present in the protein molecule of every living being by covalently bonds therefore it affects our biological system.
- The presences of these organic compounds sometimes cause of eutrophication and decrease the DO level of the water causing microtoxicity and genotoxicity.
- Azo dyes are the cause of gastrointestinal diseases, skin damage, lungs cancer, inhabits blood formation due to formation of complex adduct of haemoglobin. It also damages both DNA and RNA system causing genetic disorder.
- Many textile industries use some portable water sources besides the river water and cause of scarcity of the drinking water.
- Many dyes and pigments contains large amount of toxic chemicals can affect directly to the workers of the textile industries or indirectly to the persons wearing these materials especially at summer season and affects the life cycle. This is because the toxic substances are absorbed by the skin easily.
- The heavy metals present in the waste water effluents are bio- accumulated in the different parts of human bodies such as kidney, heart, brain, liver and bone and cause of significant health hazard effect. If the accumulation level goes beyond the permissible limit it may causes danger to human life.
- The heavy metal present in the waste water of dyeing industries significantly affects the growth of the children and cause of many diseases. (Nigam, P et.al. 2000)

CONCLUSION

The synthetic dye usually contains highly toxic non-biodegradable organic aromatic compounds and creates an unfavourable alternation to the environment and also cause of risk to human health. However now-a-days no appropriate and suitable methods are investigated for effective removal of both colour and toxic materials with heavy metallic contaminates present in the dyes, hence scientists and researchers are always trying to investigate an effective method for separation of both colour and other toxic chemicals in an eco-friendly and cost effective way. Each step of dyeing and textile industries are unfavourable processes which produces different kinds of toxic materials and colour in the form of waste water effluents and finally added to the soil and other fresh water bodies affecting the ecological community including flora and fauna. The generated waste water effluent has high value of BOD content along with hazardous toxic chemicals and heavy metals with organic solvents and cause of environmental degradation. In this chapter we are describing different technology for dye manufacturing, treatment methods of waste effluents generated and the environmental impact of textile dyes. Since no method is suitable for complete treatment of generated effluents of dyeing and textile industries, government should formulate and adopt a suitable guideline for reduction of colour and toxic substances and use of portable water sources for different textile and dyeing industries. More research has to be done to investigate proper treatment technology of textile and dyeing effluents in an environmental friendly and cost effective manner for benefit of our society.

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KEY TERMS AND DEFINITIONS

Aerobic: The treatment of water or waste water effluents by using aerobic bacteria in the presence of oxygen or air is termed as aerobic treatment process.

Anaerobic: The process of treatment of water by using anaerobic bacteria in the absence of oxygen or air and converting the COD or organic matters in to simple biogas is known as anaerobic treatment.

Anoxic: It is the process which is mainly used for removal of nitrogen from the waste water effluents by the process of denitrification in which the nitrogenous compounds present in the effluents converted into nitrate which is again converted into free nitrogen gas and nitrous oxide.

Biological Oxygen Demand (BOD): The amount of dissolve oxygen required during a specified period of incubation (5 days) for complete biochemical oxidation of organic matter present inside the water bodies at a temperature of 25°C is known as biological oxygen demand.

Chemical Oxygen Demand (COD): The amount of dissolve oxygen necessary for complete biodegradation of chemically oxidizable substances present inside the water bodies is known as chemical oxygen demand.

Degassing: The emission of gases from a planet either directly during volcanism or May indirectly during weathering of ignited rocks on a plane surface is known as degassing.

Hydrophilic: It literally means water loving (i.e., it is the property of more favourable interaction with water and forms hydrogen bonding with the molecules interact with water).

Hydrophobic: It literally means water hating (i.e., the property of molecules not interacting with water).

Chapter 7

Impact of Synthetic Dyes on Human Health and Environment

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ABSTRACT

Colour is the most important part to make any fabric attractive, but its use for dying has become a major environmental hazard. Colloidal particles present with color increases the turbidity, gives bad appearance, foul odour, and obstructs the penetration of sunlight into water bodies required for the photosynthesis process, which interferes with the oxygen flow mechanism and hence marine life. So, it is essential to remove such pollutants from the waste water before its final disposal into water bodies. Photocatalysis is one of the advance oxidation processes, mainly carried out in the presence of light and suitable photocatalytic materials for the degradation of dyes. This chapter outlines the background of dye chemistry, the application areas, and the impact of dyeing effluents in the environment and on living beings.

INTRODUCTION

Dyes have been very popularly used as coloring agents, additives in textile, food, papermaking leather, printing, ink, drugs, cosmetic and pharmaceutical industries.

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Since many years, synthetic dye especially azo dyes is interestingly used in large amount as compared to natural dye due to its high color fastness and sustainable life, and cost effectiveness. It was proclaimed that nearly more than 10^3 tons of dyes are produced every year (Forgacs et al. 2004). Therefore people are very much concerned about the treatment of such waste water. The considerable concern which arises is due to the release of wastewater containing large concentration of dyes that is highly toxic and colored and poses a threat to the environment. The released waste water is colored and it affects the visibility of water in the littoral zone and prevents the penetration of sunlight in the stream (Namasivayam et al. 1997). Different kinds of chemicals present in synthetic dyes can cause carcinogenic and mutagenic effects to human beings and fauna and ultimately affects the environment . In the textile industries large amounts of dye effluents and aqueous wastes are discharged from the dyeing process, which last long with a high biological oxygen demand (BOD), both of which are environmentally and aesthetically undesirable (Wang et al. 2007).

Nearly 2×10^5 tons of these synthetic dyes are released into the water bodies every year during the dyeing and finishing processes, because of the inefficiency of the dyeing processes (Ogugbueand Sawidis 2011). As a result most of these azo dyes are unable to degrade by classical conventional wastewater treatment processes and remain in the environment for long time, due to its great stability to light, water, temperature, soap, detergents, chemicals, bleaching etc (Couto 2009). Furthermore, anti-microbial agents are antagonistic to the biological degradation are very popularly used in the textile manufacturing, specifically for natural fibers such as cotton (Couto 2009 and O’Neill C 1999). The complex origin and aromatic structures of these azo dyes make them more fractious for biodegradation (Forgacs et al 2004 and Przystaś 2012). However, environmental legislation constrain the different industries to remove the color from their dye-containing effluents, before disposal into water bodies so that the environment of water body doesnot get contaminated (Ogugbue 2011 and O’Neill 1999).

Textile wastewaters are characterized by inconstancy in various parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), salinity, pH and color. The fractional composition of the wastewater will mainly depends on the different chemicals, organic-based compounds, and dyes used in the wet-dry processing steps (Dos et al. 2007 and Talarposhti et al. 2001). The main pollutants in the textile effluents are color, toxicant, surfactant, chlorinated compounds, recalcitrant’s organics and salts (Ben et al. 2012).

Nearly 2-20 percent of these dyes are directly discharged into the water bodies during dying process as aqueous contaminated effluents in different environmental components (Cooper (1995). The discharge of effluents add toxicants to the environment which basically contains colour, dyes released and many breakdown products of dyes, which are carcinogenic to life mainly because of the presence of carcinogens present in it such as benzamine, naphthalene and other aromatic compounds. If these dyes are not treated then it remains in the environment for a long period of time (Forgacs et al. 2004 and Hao 2000). Nowadays, advanced oxidation processes are becoming very popular for the removal of pollutants from waste water. This process is very much economic, ecofriendly and capable to degrade many dyes or organic pollutants present in waste water. These advanced oxidation processes are carried out in the presence of sunlight, visible light and ultraviolet irradiation.

DYES CLASSIFICATION

The discovery of synthetic dyes was done in 1856. The aromatic compounds which are having aromatic rings and contain delocalized electrons with different functional groups are called as dyes (Welham 2000). The major structure element, chromophore group is responsible for light absorption in dye molecules i.e., conjugated double or simple bonds with a delocalized electron system (Gomes 2001). The color of the dye is due to the chromogene-chromophore gives beautiful colors to dyes which ultimately color the fabric, i.e. acceptor of electrons, in the molecule of dye. The presence of auxochrome groups in the dye gives its dying capacity, i.e. donor of electrons. The chromogene is an aromatic structure which basically has naphthalene, benzene or anthracene rings carrying binding chromophores that contain double conjugated links with delocalized electrons forming a closed conjugated systems. The various chromophores groups are the methine group (-CH=), azo group (-N=N-), ethylene group (=C=C=), carbonyl group (=C=O), carbon-sulphur (=C=S; ≡CS-S-C≡), carbonyl group (=C=O), nitro (-NO2; -NO-OH), carbon-nitrogen (=C=NH; -CH=N-), nitrozo (-N=O; =N-OH), carbon-nitrogen (=C=NH; -CH=N-), or chinoid groups.Another group are the ionisable group which is called as the auxochrome groups, which are mainly responsible for the binding capacity of the synthetic dyes molecules onto the material of the textile. There are many common auxochrome groups present such as: -NH2 (amino), -COOH (carboxyl), -OH (hydroxyl) and -SO_3H (sulphonate) (Welham 2000 and Suteu 2011).

FIXATION OF DYES ON TEXTILE FIBRES

Textile fibres get colored by the using these dyes with the help of physical adsorption in which many interactions are involved like hydrogen bonds, vander Waals forces, and hydrophobic reactions between the dye and textile fibres. The nature and chemical constitution of the dye describes the binding potential of dye onto the textile fibres. The color of the dye stick upon different kinds of textile by a process called chemisorption, which associates the formation of a covalent bond together with an additional electrostatic interaction when this synthetic dye ion and fibre carry equally opposite charges. In alkaline conditions between pH 9-12, at temperature 30-70ºC with a salt concentration of 40-100 g/L, a reactive vinyl sulfone (─SO3─CH═CH2) group is formed with a reactive dye, which ultimately forms a connection with the textile fibres. But, the vinyl sulfone group undergoes hydrolysis In the presence of water, the vinyl sulfone group undergoes hydrolysis as a result the products obtained do not have any closeness with the textile fibres thus as a result they do not form a covalent bond with the textile fibres (Daneshvar 2003). Therefore, a huge amount of the synthetic dye is washed away as an effluent in the wastewater thus creating pollution in the ecosystem. The efficiency of fixation of such azo dyes used various with class, and it is about 50% for reactive dyes, 98% for basic dyes (Bertea 2008). Many salts like sodium sulphate, sodium nitrate, and sodium chloride are used in huge amount in the dyebath. For increasing the pH, sodium hydroxide is very commonly used to meet the solution in the alkaline range.

Impacts of Properties of Dyes on Adsorption and Degradation Efficiencies

The main properties of the dyes are basically based on the subsequent factors (Patil et al., 2011)

- Fastness requirements
- Shade (brightness or dullness)
- Economy
- Level dyeing properties
- Ease of application and dusting
- Environmental concerns

A great dye has some basic qualities such as fastness to light, color, fixes itself to fabrics, resistant to the action of water, diluted acids and alkalis (all washing soaps and detergents are alkaline in nature) and different organic solvents used in the dry cleaning process.

Impact of Synthetic Dyes on Environment and Health

Millions of gallons of dye effluent has been discharged from mills, factories as a result a lot of hazardous toxic waste, which is full of color and organic chemicals are evolved from dyeing and finishing salts. The toxic substances like vat dyes, sulphur, naphtha, nitrates, acetic acid, chromium compounds, soaps and heavy metals such as lead, copper, cadmium, arsenic, mercury, cobalt, nickel, and many different chemicals are present in the dye effluent which are highly unacceptable in the environment..Some other harmful chemicals present in the effluent water are formaldehyde based dye fixing agents, many softners which are hydro carbon based and non bio degradable dyeing chemicals which contaminate the water body more efficiently. Due to high temperature and high pH the mill water imposes more damage to the ecosystems. The mill effluent is rich in different color; oil scum etc which makes the water more turbid and thus it obstruct the penetration of sunlight through it. As a result the photosynthesis process is obstructed.The presence of such matter in the water also gives it a foul smell. As a whole the environment gets affected. (Hazardous Substance Research Centers/South and South- west Outreach Program (2005) Environmental hazards of the textile industry. *Environmental Update* #24, *Business Week*).

The soil productivity is lost when this dye effluent is allowed to flow in fields resulting in clogging up of soil pores. The layers of soil get inured and penetration and elongation of roots is prevented. The waste water that flows in drains are normally corrodes by these textiles effluents which ultimately blocked the sewerage pipes. If this effluent is permitted to flow in the rivers and drains it effects the quality of drinking water parameters such as BOD, TDS, pH etc in hand pumps making it not suitable for human and living being consumption. As a result of the damage created by this effluent, there may be many leakages in the water pipes which needs regular repair and maintenance and thus puts cost burden on the person related.

The water body which is polluted by such textile dyes is full of virus and bacteria as this type of water provide nutrient to these microorganism to grow. Water rich in impurities affects the textile processing in many ways. In cleansing and bleaching they transmit a yellow hue to white fabric. Textile dye effluent is the main cause of serious amount of human illnesses and environmental degradation. Approximately 40 percent of world used dyes and pigments contain organic chlorine which is a known carcinogen. All the organic substance present in the effluent water from a textile industry are of great interest in the water treatment because they reat with various disinfectants especially chlorine. Chemicals evaporated from these water bodies get evolved into the air we breathe or are absorbed through our skin and creates many allergies, reactions and may cause harmfull effects on an even unborn child or many adults too.

There are many different kinds of pollutant present in the water bodies which are carcinogenic and mutagenic in combinations cause skin irritation, allergies, or different tissue changes (F.M.D et al. 2011). There is a very high potential health risk by azo dyes which are a aromatic compound.Azo dyes are basically amines and their breakdown product like toxic amines penetrates into the body through the gastrointestinal tract, lungs, skin, and also there is a formation of hemoglobin adducts. With the process of protonation of amino groups the toxicity of waste water can be easily reduced. The various azo dyes for example direct black 38, azo disalecylate and their breakdown derivatives like bezidine, derivatives of benzidine, an enormous number of anilines nitro semis, dimethyl amines etc. are known very commonly to activate cancer in animals and human (Puvaneswari et al. 2006). There are few azo dyes which have been reported to activate bladder cancer in humans, splenic aromas, hepato carcinomas and nuclear anomalies such as chrosomal aberration in mammal cells (Lima et al. 2007). Benzidine is a known carcinogenic aromatic compound which has been reported as the most dangerous dyes for our environment. 1,4-diamino benezene is an aromatic amine whose parent azo dyes can cause chemosis,, skin irritation, contact dermatitis, lacrimation, permanent blindness, exopthamlmose, rhabdomyolysis, vomiting gastritis, acute tubular necrosis supervene, hypertension, vertigo and upon ingestion, oedema of the face, pharynx, neck, tongue and larynx along with respiration related distress (Report by LGC 1999). Azo dyes which are water soluble become very dangerous when gets metabolized by liver enzymes. So it is very necessary to remove this synthetic dye from the wastewater by not just only the removal of dye color but its toxicity should also be removed or reduced from water.

Elimination and Separation Procedures for the Removal of Textile Organic Dyes from Water

The organic azo dyes must be separated out and eliminated from water bodies by effective and feasible water treatments techniques at sewage treatments plants or on site by making an effort to remove, degrade or neutralize the detrimental pollutants so as to neutralize the harmful effects of any industrial effluents which discharge into the water. Such water contains surfactants, detergents, sickly biodegradable substances, suspended solids together with untouched dyes. The textile effluents have many chemicals in it which are very toxic in nature, so it is difficult to treat them with conventional methods. There is a need of much efficient technique to treat them and such technology is called as activated oxidation process (AOP). Chlorination process cannot be used in this type of water purification as it releases mutagenic products even from less harmful azo dyes.

Methods Used for the Removal of Dyes Effluents

There are many technologies which are developed for the removal of synthetic textiles dyes from waters and wastewaters to reduce their environmental impact. These include as:

- **Physical methods** such as membrane-filtration processes or methods (under this comes nanofiltration, reverse osmosis, electrodialysis) and most importantly sorption techniques.
- **Chemical methods** such as flocculation, coagulation combined with flotation and filtration, precipitation, flocculation with Fe(IT)/$Ca(OH)_2$, electrokinetic coagulation, electroflotation, conventional oxidation methods that is with ozone, electrochemical processes or irradiation.
- **Biological methods, such as** aerobic and anaerobic and microbial degradation, and the use of pure enzymes are used to treat water contaminated with synthetic dyes.

All of these techniques have many advantages and disadvantages. As it was mentioned earlier that azo dyes which are synthetic in nature are very much difficult to degrade or reduce their toxicity by the ongoing conventional treatment processes. These azo dyes are characterized by the presence of the nitrogen-nitrogen bond (-N=N-) in the middle and therefore they are have high electron deficiency (Robert 2008). The main environmental concern is the removal of toxic chemicals and harmful color from dyestuff manufacturing and textile wastewater. A great many waste water treatment techniques have been used in different industrial and manufacturing factories such as chemical, biological, food, pharmaceutical, pulp and paper, dye processing etc (Esplugas et al. 2007; Gupta et al. 2012; Moo-Young 2007; Gogate and Pandit 2004).

Synthetic dyes have high recalcitrant nature and the high salinity of wastewater due to which many conventional biological processes are not successful (Johnson and Mehrvar 2008; Rajeshwar et al. 2008; Gupta et al. 2012). Ozonation and Chlorination are very much inefficient in the treatments and also they have a very high operating cost (Rajeshwar et al. 2008; Coleman et al. 2000). The classical physical methods such as ultrafiltration, adsorption on activated carbon, coagulation by chemical agents, reverse osmosis, ion exchange on synthetic adsorbent resins, etc., have been employed for the removal or degradation of textile dye pollutants (Coleman et al. 2000; Esplugas et al. 2007; Gogate and Pandit 2004; Gupta et al. 2012; Johnson and Mehrvar 2008; Moo-Young 2007). These methods are zestful only in transferring organic materials from water to another phase, thus it gives rise to secondary pollution which needs further treatment steps. There is also a regeneration of the adsorbent which makes the processing much costlier. The subsequent important factors must be considered in adopting a technology for the wastewater treatment (Gogate and Pandit 2004; Oller et al. 2011; Serpone et al. 2010):

- Treatment flexibility.
- The final efficiency of wastewater treatment.
- Mineralization of parent and intermediate contaminants.
- Cost-effectiveness and eco-friendliness.
- Recycling capacity and potential use of treated water.

Therefore, adequate attention has been taken on the complete oxidation of organic compounds to harmless products such as H_2O and CO_2 and by the advanced oxidation process (AOP) which appears as one of the most emerging technologies for waste water.

AOPs can be classified into two major groups:

1. **Non-photochemical AOPs:** It include cavitations, wet air oxidation, Fenton and Fenton-like processes, ozonation, ozone/hydrogen peroxide (Fujishima et al. 2000; Malato et al. 2009; Nakata and Fujishima 2012), etc.
2. **Photochemical AOPs and photochemical oxidation processes:** It includes homogeneous (UV/ozone, UV/hydrogen peroxide, UV/ozone/hydrogen peroxide, photo-Fenton, homo and heterogeneous (photocatalysis) processes) (Parida and Parija 2006; Rehman et al. 2009; Gupta et al. 2012). The main function of any AOPs design is to use and produce hydroxyl free radical (OH●) as a strong oxidant to damage compounds that cannot be easily oxidized by the conventional oxidant. The nature of Hydroxyl radicals are non selective and they can react without any other additives with a various contaminants whose rate constants are normally in the order of 106–109 mol/l/S (Rehman et al. 2009). The main and short mechanism of AOPs can be understood as follows:
    a. When the light energy strike on the surface of a catalyst, the valence band electrons are excited and starts moving to the conduction band. Holes are thus created in the valence band of the catalyst. The holes thus formed in the valence band can oxidize donor molecules and it reacts with water molecules and give rise to hydroxyl radicals (These generated hydroxyl radicals have strong oxidizing power which are responsible for the photodegradation of organic pollutants).
    b. These hydroxyl radicals undergo oxidative reaction with organic compounds in the water producing biodegradable intermediates.

c. The biodegradable reactions intermediates with oxidants is called as mineralization (i.e., production of water, carbon dioxide, and inorganic ions).

Advanced oxidation process is more useful as compared to other processes because of its efficiency in removal of organic pollutant, which results in the total mineralization of organic contaminants present in wastewater or effluent (Kdasi et al. 2004). AOPs are considered as a clean technology, which destroys the complex structures of organic contaminations using short lived chemical species with a high oxidation power. The hydroxyl radical (.OH) is the major oxidative power of AOPs (Arslan et al. 1999, and Kestioglu et al. 2005). With the help of electrical, chemical, radiation, or mechanical energies the hydroxyl radicals can be generated. Therefore, Advance oxidation process is considered under chemical, electrical, catalytic, photochemical, photocatalytic and mechanical processes (Chung et al. 1992).

Advance oxidation process is very efficient in the degradation of the organic dye and removal of color. Another reason of its goodness is that it takes less time for degradation of pollutants which are present in the dye effluents. However, there are many circumspections of this method which are directly related to the selection of choice the best fitting catalyst for advocating the generation of these oxidizing species. Photocatalysts that encourage the generation of radicals absorbing radiation in the visible light are the most fascinating for this type of reactions, because of the large percentage emitted in the full solar spectrum (approximately 45%) (Finklea et al. 1998).

Major Advantages of Photocatalysis

The major merits of this photocatalytic technology are as:

1. Conventional treatment methods (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins) is replaced by Photocatalysis process which has the capacity for using renewable and solar energy, a pollution free sorce for energy.
2. The conventional process transfer organic pollutants and toxic compounds from one phase to other phase but photocatalysis gives harmless products, in the environment.
3. Degradation of a number of hazardous and toxic compounds in different synthetic dye effluent or wastewater streams can be done by photocatalysis process.
4. In photocatalyst process less amount of catalyst is required, time for degradation is less and the reaction conditions are very simple.

5. Minimum amount of secondary waste generation.
6. And this process can be used for the hydrogen generation, gaseous phase, and aqueous treatments as well for solid (soil) phase treatments to some degree.

Identification of Products and Mechanisms of Dye Degradation

It was already being discussed that the organic pollutant degradation including azo dyes, alter according to related and dye parameters. From synthetic dyes the identification of products degradation is very much helpful in determining the mechanism pathways involved. Such data are not only important in the observation of the role of organic pollutants, but it is indirectly important in the assessment of the toxicity of the main products and the intermediates. Spectrophotometer is used for determining the absorbance of different textile dyes as these are used as a colorant which absorb maximum wavelength in the visible region of the spectra. Spectrophotometer is the easiest way measuring absorbance. By this recent method, all the molecules present in the test medium or sample are quantified; intermediates and degradation effluent will contribute to the spectra absorbance. There are many conventional and advanced instruments available for chromatography like high performance liquid chromatography (HPLC), gas chromatography (GC), nuclear magnetic resonance spectroscopy (NMR), capillary electrophoresis (CE) and mass spectrometry (Ion-trap, MALDI) to assist in the confinement and characterization of the intermediates present in the sample and products of dye degradation, thus giving a new outlook into the mechanism of degradation of organic pollutants.

CONCLUSION

Where on one side the natural and synthetic dyes fill color in our life on other side make our water bodies polluted. Huge amount of harmful chemical pollutant are discharged by dye manufacturing industries. One of the easiest ways to know the impact of dying industries on water toxicity is by studying the effect on aquatic flora and fauna. Effluent of dying industries must be treated up to certain limit before discharging them into water bodies so that their impact on water resources can be curtailed. Discharge and contamination of water resources by textile industries is an environmental concern. It can be checked and removed by using mechanical, physical, chemical, biological and advanced oxidation process.

FUTURE ASPECTS

It should be taken into account by the manufacturer of synthetic dyes before discharging of dye effluent into the water system that the discharged effluent is free of any contaminant and toxicity. They should keep an eye on the meeting parameters of such colored water. Application of synthetic dyes is utilized in textile industries in making fabric colorful but it should not put an adverse impact on the environment. These colored water or effluents face effective treatment processes, before discharging them into the water bodies. The dyes degradation is very much complex and the existence of an different varieties of structurally different dyes, symbolizes the requirement for more research and further studies. The study and implementation of the new emerging treatments of such waterways shall not only be limited on pollution elimination or reduction, but also in the reuse of water and harnessing the final by-products for many other applications. This will give a better insight to the pollution control bodies.

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KEY TERMS AND DEFINITIONS

Acid Dyes: Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colors fall in this category.

Azoic Dyeing: Azoic dyeing is a technique in which an insoluble Azo dye is produced directly onto or within the fiber. This is achieved by treating a fiber with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components.

Basic Dyes: Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

Photocatalysis: Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron-hole pairs, which generate free radicals (e.g., hydroxyl radicals: OH) able to undergo secondary reactions.

Synthetic Dyes: Synthetic dyes are found in a wide range of products such as clothes, leather accessories, and furniture. These dyes are commonly used every day. However, a side effect of their widespread use is that up to 12% of these dyes are wasted during the dying process and about 20% of this wastage enters the environment (mainly into water supply).

Chapter 8

Impact of Textile Dyes on Human Health and Environment

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ABSTRACT

The textile industry is one of the important industries that generates a large amount of industrial effluents. Color is the main attraction of any fabric. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry. Synthetic dyes have provided a wide range of colorfast, bright hues. However, their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds, and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. These organic materials react with many disinfectants, especially chlorine, and form byproducts (DBPs) that are often carcinogenic and therefore undesirable. This effluent, if allowed to flow in the fields, clogs the pores of the soil resulting in loss of soil productivity. This chapter gives an overview on the health and environmental impact of dyes.

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INTRODUCTION

Dyes may be defined as substances that, when applied to a substrate provides color by a process that alters, at least temporarily, any crystal structure of the colored substances (Othmer, 2004, Bafana et al., 2011). Such substances with considerable coloring capacity are widely employed in the textile, pharmaceutical, food, cosmetics, plastics, photographic and paper industries (Zollinger, 1987, Carneiro et al., 2007).The dye manufacturing industry represents a relatively small part of the overall chemical industries. In the world-wide production of dyes is nearly 800,000 tons per year. About 10-15% of synthetic dyes are lost during different processes of textile industry. Synthetic dyes are valuable in numerous industries such as textile, paper printing, food, pharmaceutical, leather and cosmetics. It is classified into acid, reactive, direct, basic, vat, disperse, metal complex, mordant and sulphur dyes. There are more than 10,000 dyes used in textile Manufacturing alone nearly 70% being azo dyes which is complex in structure and synthetic in nature (Hassaan, 2016, Ananthashankar, 2012). A major source of colour release into the environment is associated with the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has become a major concern in recent years. (Hassaan, 2016, Ananthashankar, 2012).

HEALTH AND ENVIRONMENTAL IMPACT OF DYES

There is no confirmation to propose that the greater part of the dyestuffs at present utilized in material coloring and completing are dangerous to human wellbeing at the dimensions of introduction that laborers by and large face in the industrial facilities. Nonetheless, with long haul or incidental over introduction, there can be likely wellbeing dangers and all colors and synthetic substances should thus be treated with consideration. The most widely recognized peril of responsive colors is respiratory issues because of the inward breath of color particles. Once in a while they can influence an individual's resistant framework and in outrageous cases this can imply that when the individual next breathes in the color their body can respond drastically. This is called respiratory sharpening and side effects incorporate tingling, watery eyes, sniffling and indications of asthma, for example, hacking and wheezing (Hassaan, 2016). Maybe the most dominating medical issues identified with coloring and completing procedures emerge from introduction to synthetic substances going about as aggravations. These may cause skin disturbance, irritated or blocked noses, sniffling and sore eyes. They incorporate formaldehyde-based gums, smelling salts, acidic corrosive, some psychologist oppose synthetic concoctions, some optical whiteners, soft drink cinder, burning soft drink and blanch. Certain responsive, tank and scatter colors are likewise perceived as skin touchy (HSE, 2016). Material enterprises produce a lot of fluid squanders. These material effluents contain natural and inorganic mixes (Elliott, 1954). Amid the coloring forms, not all colors that are connected to the textures are fixed on them and there is dependably a bit of these colors that remaining parts unfixed to the textures and gets washed out. These unfixed colors are observed to be in high fixations in material effluents (Hassaan and Nem, 2017). The measure of water devoured and discharged likewise shifts relying upon the kind of textures created (Ananthashankar, 2012). Practically 0.08 – 0.15 m3 of water is utilized to create 1 kg of textures. It is evaluated that 1,000 – 3,000 m3 of water is let out in the wake of preparing around 12 – 20 tons of materials for each day (Kdasi et al., 2004). These effluents are wealthy in colors and synthetic substances, some of which are non-biodegradable and cancer-causing and represent a noteworthy risk to wellbeing and the earth. A few essential, optional and tertiary treatment forms like flocculation, streaming channels and electrodialysis have been utilized to treat these effluents. Anyway these medicines are not discovered powerful against the evacuation everything being equal and synthetic concoctions utilized (Eswaramoorthi et al., 2008, Hassaan et al., 2016a). The effluents don't just contain high centralization of colors utilized in the business, yet in addition contain the synthetic concoctions utilized in the different preparing stages. Some follow metals, for example, Cr, As, Cu and Zn are available in these effluents and are equipped for causing a few medical issues including drain, ulceration of skin, sickness, serious aggravation of skin and dermatitis. Material effluents are additionally found to contain other natural and microbial polluting influences (Nese et al., 2007, www.fibre2fashion.com (2007)). The use of cotton has been expanding continually all through the previous century (UNCTAD, 2003). Cotton filaments are basically colored utilizing azo colors which are one of the biggest gatherings of manufactured colorants utilized in the business (Mohan et al., 2002). Azo colors are hard to corrupt by the current traditional treatment forms. They are portrayed by the nearness of the nitrogen-nitrogen bond (- N=N-) in the inside and henceforth they are very electron inadequate (Robert et al., 2008). These azo colors are observed to be mind boggling in nature and have been found to demonstrate cancer-causing confirmations on reductive cleavage. These colors are equipped for adjusting the physical and concoction properties of soil, breaking down water bodies and making hurt the widely varied vegetation in nature (Manu, 2003, Hassaan et al., 2016b). It was seen that the harmful idea of colors makes demise the dirt microorganisms which thusly influence the farming profitability (Savin and Butnaru, 2008). The nearness of little measure of Azo colors in water (<1ppm) are exceptionally noticeable (Chung, 1983). This influences stylish legitimacy, straightforwardness and water-gas dissolvability. Diminishing light infiltration through water diminishes photosynthetic action, causing oxygen lack and de-directing the organic cycles of amphibian biota (Apostol et al.,2012).

Numerous Azo colors are additionally exceedingly harmful to the environment and mutagens, which means they can have intense to endless impacts upon life forms, contingent upon introduction time and Azo color focus. 1,4-diamino benezene is a fragrant amine whose parent azo colors can cause skin aggravation, contact dermatitis, chemosis, lacrimation, exopthamlmose, perpetual visual impairment, rhabdomyolysis, intense cylindrical corruption supervene, regurgitating gastritis, hypertension, vertigo and, upon ingestion, oedema of the face, neck, pharynx, tongue and larynx alongside respiratory misery (Report by LGC, 1999). Sweet-smelling amines can be activated by water or sweat, which energize their ingestion through the skin and other uncovered zones, for example, the mouth. Assimilation by ingestion is quicker thus conceivably increasingly perilous, as more color can be invested in a littler time span (Puvaneswari et al., 2006). Water dissolvable Azo colors become risky when processed by liver proteins.

Logical investigation in 1992 at first found out that word related presentation to some sweet-smelling amines, especially benzidine, 2-naphthylamine, and 4-aminobiphenyl, drastically lifts bladder malignant growth hazard (Report by LGC 1999, Chequer et al., 2011, Puvaneswari et al., 2006). In one German color plant, 100% of specialists (15) engaged with refining 2-naphthylamine created bladder malignant growth (OECD, 2005). Sweet-smelling amines are additionally present in tobacco smoke, which may disclose why smoking appears to raise the danger of bladder disease. EU confined fragrant amines have additionally been connected to splenic sarcomas and hepatocarcinomas (Report by LGC 1999). 1,4-diamino benezene is a sweet-smelling amine whose parent azo colors can cause skin aggravation, contact dermatitis, chemosis, lacrimation, exopthamlmose, perpetual visual deficiency, rhabdomyolysis, intense cylindrical corruption supervene, retching gastritis, hypertension, vertigo and, upon ingestion, oedema of the face, neck, pharynx, tongue and larynx alongside respiratory trouble (Puvaneswari et al., 2006). Sweet-smelling amines can be prepared by water or sweat, which helps their ingestion through the skin and other uncovered territories, for example, the mouth. Retention by ingestion is quicker thus conceivably progressively risky, as more color can be invested in a littler time span (Report by LGC 1999). Water dissolvable Azo colors become unsafe when utilized by liver compounds. Azo color discharge in mechanical gushing can likewise affect human wellbeing in specific nations. In 2007, an investigation connected an Azo coloring plant as one of the wellsprings of mutagenic action distinguished in the Cristais River in Brazil, a wellspring of drinking water for 60,000 local people (Lima et al., 2007). Despite the fact that the drinking water was treated in a plant 6km downstream of the release site, testing affirmed the nearness of cancer-causing fragrant amines. At the point when lab rodents devoured modern gushing at 1-10% fixation, an expansion in pre-tumor injuries of the colon was watched (Lima et al.,2007).

ENVIRONMENTAL CONCERNS

Ecological Impact of Azo Dyes

The material business is a substantial polluter of waste gas, solids, water and clamor. Wastewater is the most naturally harming, and the emanating from material plants is named the most dirtying of all the mechanical divisions (Chequer et al., 2013), considering the volume produced just as its organization.

The dyestuff lost through the procedures of the material business represents a noteworthy issue for wastewater the board. An expected 200,000 tons of dyestuff is ousted into the worldwide condition each year (Chequer et al., 2013). The convergence of Azo color in material profluent can achieve 500 sections for every million (ppm).

Through the coloring procedure it has been determined that colorant misfortune to the earth can be as high as half. Shading is the main wastewater contaminant to be perceived, since a little measure of Azo color in water (<1ppm) are exceptionally obvious (Chung, 1983). This influences stylish legitimacy, straightforwardness and water-gas solvency. Diminishing light infiltration through water diminishes photosynthetic movement, producing oxygen lack and de-directing the natural cycles of amphibian biota (Apostol et al., 2012). Numerous Azo colors are additionally profoundly harmful to the biological system and mutagens, which means they can have intense to unending impacts upon creatures, contingent upon introduction time and Azo color focus. For instance, color gushing has been associated with development decrease, neurosensory harm, metabolic pressure and passing in fish, and development and efficiency in plants. Sullying in this manner constrains downstream human water utilize, for example, amusement, drinking, angling and water system (Chung, 1983).

CONCLUSION

Synthetic textile dyes exhibited a great group of organic compounds that could have detrimental impacts on the environment, as well as, some of them can cause hazards to humans. The growing complication and struggles in treating textile wastes has led to a continuous examination for new approaches that are applicable and economically feasible. However, till now, there is no very highly effective technique capable of complete removal of both the color and the toxic properties of the dyes released into the environment. Fabric production, materials and chemicals used for production cause deterioration of ecological balance and human health. Making analysis of the chemicals and other substances in fabrics is very important and more research of this subject is necessary. Apparel products can contain harmful chemicals. We need to raise the awareness between the people, about the potentially harmful fabrics.

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Chapter 9

Chemical and Biological Treatment of Dyes

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ABSTRACT

Life of living or non-living being depends on water; in short, water is life. But these days, with the growing industrialization, it is spoiling a lot. Wastewater contains contaminants like acids, bases, toxic organic and inorganic dissolved solids, and colors. Out of them, the most undesirable are colors caused mainly by dyes. Color and other compounds present in water are always not desirable for domestic or industrial needs. The wastes of dyes are predominant amongst all the complex industrial wastewater. This water is dark in color and highly toxic, blocking the sunlight and affecting the ecosystem. Among all the dyes, azo dyes contribute to commercial dyes used widely in textile, plastic, leather, and paper industries as additives. The removal and degradation of azo dyes in aquatic environment is important because they are highly toxic to aquatic organisms. For every industry, clean technology has become an important concern. In this chapter, the authors discuss about existing processes as well as promising new technologies for textile wastewater decolorisation.

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INTRODUCTION

The consumption of water and chemicals in textile industries is tremendous for the wet processing of textiles. The reagents used varies from inorganic or organic compounds to polymers (Mishra & Tripathy, 1993; Juang *et al.* 1996). The low concentration of dye effluent presence in water is visible and not desirable (Nigam *et al.* 2000). Almost there are more than 100,000 dyes are available commercially and over tons of dye-stuff are produced annually (Meyer, 1981). Dye has complex structure and due to that they are resistant for degradation to light and also to many chemicals (Poots & Mckay, 1976a). The dyes according to structural varieties are classified as acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes. Municipal sewerage systems are not effective in decolouration of textile dye effluent (Willmott *et al.* 1998). There are other varieties of dyes like cationic, nonionic or anionic type. Anionic dyes are the acid, direct as well as reactive dyes. The most problematic are those dyes which are bright in colour, water-soluble, reactive and acid dyes because they are unaffected by the conventional treatment systems. The general aerobic municipal treatment systems are not effective in removal of these dyes (Moran *et al.* 1997). The nonionic dyes are disperse dyes as they do not ionise in an aqueous medium. There is great concern because most of the dyes used in textile industry are highly carcinogenic such as benzidine and other aromatic compounds (Baughman & Perenich, 1988). Azo and nitro-compounds are reduced in sediments (Weber & Wolfe, 1987) and similarly (Chung *et al.* 1978) illustrated their reduction in the intestinal environment, resulting in the formation of toxic amines. Because of fused aromatic ring structure the anthroquinone-based dyes are most resistant to degradation. The ability of some disperse dyes for bioaccumulation has also been demonstrated (Baughman & Perenich, 1988).

CHEMICAL TREATMENT OF DYES

By Fentons's Reagent

Fenton Process

Henry John Horstman Fenton discovered Fenton's reagent which is a solution of hydrogen peroxide and ferrous ions reported in 1894 that this solution in acid medium had high oxidizing power (Fenton, 1894). The use of Fenton's reagent in oxidation processes to destroy toxic organic compounds has been reported (Neyens & Baeyens, 2003). This classic reactive system discovered by Fenton in the last century, now today is underlined by a significant number of investigations devoted to its applications in wastewater treatments. The discovery found out that this reagent has ability to destroy toxic compounds in waste waters such as phenols and herbicides. Production of $^{\bullet}OH$ radicals by Fenton reagent occurs by means of addition of H_2O_2 to Fe^{2+} salts (Haber & Weiss, 1934).

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

This is a very simple way of producing $^{\bullet}OH$ radicals. Neither special reactants nor apparatus is required for this type of reactions. This reactant is an attractive oxidative system for waste water treatment due to the fact that iron is very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. The oxidation using Fenton‘s reagent has proven a promising and attractive treatment method for the effective decolorization and degradation of dyes (Wang *et al.* 2005). The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants (Titus *et al.* 2004). Ferrous ions react with hydroxyl radicals to form ferric ions or react with organics:

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

$${}^{\bullet}OH + \text{organics} \rightarrow \text{products} \quad (3)$$

Hydroxyl radicals can also react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, as shown below (Titus *et al.* 2004)

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (4)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (5)$$

During the reaction, radicals and ferrous ions are produced. The other reactions taking place during the oxidation are as follows (Titus *et al.* 2004):

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \quad (6)$$

$$FeOOH_2+ \rightarrow HO^{2\bullet} + Fe^{2+} \quad (7)$$

$$HO^{2\bullet} + Fe^{2+} \rightarrow HO^{2-} + Fe^{3+} \tag{8}$$

$$HO^{2\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^{+} \tag{9}$$

The degradation of Amido black 10B in aqueous solution by Fenton oxidation process was investigated (Sun *et al.* 2007). They assessed the different parameters like initial pH, the initial hydrogen peroxide concentration, the initial ferrous concentration, the initial Amido black 10B concentration and also the temperature. It was observed that 99.25% degradation efficiency was achieved under optimal conditions. The UV–visible changes were also studied during Fenton treatment process. The azo linkage (–N=N–) group was easy to destruct than the aromatic rings of Amido black 10B by Fenton oxidation. The experimental result of Fenton oxidation was found to be an effective process for the degradation of azo dye Amido black 10B keeping the concentration of H_2O_2 and Fe^{2+} low. The decolorization of commonly used disperse and reactive dyestuffs was also studied by combination of chemical coagulation and Fenton oxidation (Kim *et al.* 2004). Also they compared the performances between Fe^{3+} coagulation and Fenton oxidation of dye solutions and they measured the COD and removal of dye, zeta potential distribution and concentration of suspended solid. On combining with Fe^{3+} coagulation Fenton oxidation was found to be highly effective in removal of COD and dye. At optimum condition about 90% of COD and 99% of dye removals were obtained. When compared to reactive dyes, the disperse dyes have lower solubility, higher suspended solids concentrations and lower SCOD/TCOD ratios. It was observed that the COD and the removal of dye per unit Fe^{3+} coagulant was higher for disperse dye as compared to reactive dye solutions. Therefore, the decolourization of disperse dye solutions are more easily decolorized by chemical coagulation than reactive dye solutions. It was concluded that the solution of reactive dye have high applicability than disperse dye solutions. The removal of Reactive Black 5 was investigated by Fenton's oxidation process from synthetic wastewater (Meric *et. al.* 2004). It was found out that 75 milligram per litre of RB5 caused 25% toxicity on 24-h born daphnids whereas 100 mg L^{-1} of RB5 displayed 100% toxicity on Daphnia magna. At optimum condition 99% color removal was observed. At 200 mg L^{-1} of RB5, 84% COD removal was obtained using 225 mg L^{-1} of FeSO4 and 1000 mg L^{-1} of H_2O_2. Removal of COD significantly affects temperature at high degrees. The toxicity was completely removed at optimum removal conditions.

An effective degradation of various mono- and bifunctional aminochlorotriazine reactive dyes by the heterogenous photocatalytic treatment process using ferrioxalate-photo-Fenton and titanium dioxide was carried out (Arslana *et al.* 2004). These advanced oxidation processes was irradiated by a solar simulating installation in a novel batch photoreactor. It was found that the process of decolorization was three times faster by the ferrioxalate-photo-Fenton oxidation process. After the treatment process partial mineralization and complete decolourization in time period of 1 hour were observed for ferrioxalate-Fenton/UV-A and TiO_2/UV-A processes, respectively with 17–23% total organic carbon (TOC) and 73–86% UV280 nm removals. The emphasis was laid on the effect of dye house effluent strength on decolourization kinetics. It was observed that the more dilute the dye house effluent the faster was the rate of decolourization. The treatability of synthetic azo dye production wastewaters via Photo-Fenton-like process from Acid Blue 193 and Reactive Black 39 production and real Reactive Black 39 production effluent was investigated (Alaton *et al.* 2009). They employed response surface methodology for the assessment of critical process parameters on treatment performance in terms of color, COD and total organic carbon (TOC) removal efficiencies. Under optimum conditions, 98% color, 78% COD and 59% TOC removals were obtained that fitted the model predictions well. This same model also explained the treatment of synthetic Reactive Black 39 production wastewater satisfactorily. (Iurascua *et al.* 2009) synthesized a novel photo-Fenton catalyst by the use of synthetic layered clay laponite (laponite RD). They had synthesized two series of Fe-laponite catalysts with or without thermal treatment of the mixture Fe polycations-laponite in the intercalation procedure. In each series, they calcined the intercalated solids at four different temperatures, 250, 350, 450 and 550 °C. Fenton conversion of phenol was done using this catalyst that analyzes the influence of five operating factors: the wavelength of the light source, the amount of the catalyst, the initial phenol concentration, initial concentration of hydrogen peroxide and the initial pH of the solution keeping the temperature constant in all experiments. It was observed that only after 5 min. of reaction time the conversion of phenol was possible. The catalyst prepared and calcined at 350 °C showed the best catalytic performance. For the process, a kinetic model was proposed which tests the validity and also estimate the rate constants. (Kalal *et al.* 2016) dealed with the degradation of non-biodegradable Evans blue azo dye using heterogeneous photo-Fenton process by the use of copper pyrovanadate ($Cu_2V_2O_7$) and chromium tetravanadate ($Cr_2V_4O_{13}$) as catalysts prepared by wet chemical method. The catalyst was characterized by different techniques. They also studied the effect of various parameters such as initial pH, dye concentration, catalyst amount, H_2O_2 amount and light intensity on the reaction rate. The degradation efficiency was found to be 77.78 for copper pyrovanadate ($Cu_2V_2O_7$) and 79% for chromium tetravanadate ($Cr_2V_4O_{13}$). The observations of this study revealed that the rate of photo-Fenton-like degradation of dye followed pseudo-first-order kinetics. A model for azure-B degradation by photo-Fenton reagent using ultrasound in homogeneous aqueous medium was described (Vaishnav *et al.* 2014). They observed that the rate of decomposition of azure-B increased in the presence of ultrasound which is a cheaper method for wastewater treatment. They also studied the effect of different variables on the reaction rate. The rate of sono-photochemical degradation was monitored spectrophotometrically. They observed that the dye was completely oxidized and degraded into CO_2 and H_2O. A study was also done on the photochemical degradation of phenol-red using photo-Fenton reaction. The reaction rate was monitored spectrophotometrically. They had also observed the effect of various organic additives e.g. resorcinol, hydroquinone and catechol on the rate of photodegradation (Jain et al. 2009).

By Ozonation

There are two pathways of mechanism of reaction of ozone, first one is the direct action of molecular ozone, and the second one is the indirect action in which there is deterioration of ozone to radicals and this decay is supported by alkaline pH in which the response is started by hydroxyl ions. (OH^-) (Hoigne, 1988; Dore, 1990). For decolorization of dyes present in wastewaters, ozone is very effective because of its ability to target conjugated double bonds which are often associated with color (Carrieare *et al.* 1993). An investigation was done on degradation of azoic dyes present in chlorinated wastewater (Sarasa *et al.* 1998). Firstly they carried out the characterization of the spillage water by GC/MS and GC/FID and secondly, ozone and $Ca(OH)_2$was combined to determine its efficiency on waste water. It was found that the aniline derivatives and azo compounds were present in the wastewater majorly. Some organochloride compounds were also identified as a result of chlorination treatment which is being the most important with respect to the legislative control, namely: chloroanilines, chloronitrobenzenes and chlorophenols. The results showed that the concentration of the compounds present in wastewater is reduced to good extent after ozonation. The nitrobenzene derivatives and organic acid compounds were mainly formed as by-products after the treatment. The addition of $Ca(OH)_2$ along with ozone leads to almost total elimination of the remaining compounds after complete treatment process. However, after chemical coagulation aniline and chloroanilines are formed due to the strong basic medium at which the sample in this process is set. COD is reduced 25% after ozonation, while it decreased 50% after the final treatment. In ozonation treatment TOC remained constant, but a 42% reduction was observed after chemical coagulation. During ozonation reaction, color faded gradually and after the treatment the reduction in color was 62%. Thus, the complete process of ozonation and chemical coagulation with $Ca(OH)_2$ is, in general, very effective to treat this kind of wastewaters. For the reduction of recalcitrant present in water, the combination of chemical and biological water treatment processes is a promising technique. The key to the efficiency of such a system is a better understanding of the mechanisms involved during the degradation processes. Ozonation process is very important in many fields for water and wastewater treatment. Ozonation process is highly efficient to enhance biodegradability, destroy phenols, high color removal, and reduce the chemical oxygen demand (COD) for textile mill effluents. In ozonation there is some information about the reaction intermediates and products formed during ozonation. (Koch et al. 2002) studied the degradation of hydrolyzed Reactive Yellow 84 (an azo dye), which is widely used in textile finishing processes. The ozonation of the dye solution was performed in a laboratory scale cylindric batch reactor. The degradation of dye was determined by measuring the optical density of light in the visible range (λ_{max} =400 nm). The result revealed that the ozone concentration was reduced to 18.5 and 9.1 mg/L after 60 and 90 min, respectively. After ozonation, the COD value was decreased to 50% of the initial value and the TOC/TOC0 ratio was about 30%. The BOD to COD ratio was increased from 0.01 to 0.8. After the oxidation and breakdown of the azo group, nitrate group was obtained. The amount of sulfate was also increased due to release of the sulfonic acid groups of aromatic rings. The major oxidation products were formic acid and oxalic acid determined by high performance ion chromatography (HPIC). The concentrations of these major products were monitored after the regular time intervals during ozonation. The ozonation of wastewater containing azo dye in a semi-batch reactor was studied (Wu *et al.* 2001). Results demonstrated that the rate of ozonation was increased with the increase in the initial dye concentration with the applied ozone dosage and temperature. This model empowers the assumption of mass exchange coefficient of ozone from the accompanying parameters: applied ozone dose, temperature, initial dye concentration, and concentration of dissolved ozone in the organic-free water. It has found its application for large size reactors also. The kinetic studies also revealed to be pseudo-first-order. The estimation of apparent rate constant was also increased with the applied ozone dose and temperature. However, the apparent rate constant diminished logarithmically with increasing initial dye concentration. Additionally, ozonation diminished chemical oxygen demand and improved the biodegradability of the wastewater. (Ciardellia & Ranieri *et al.* 2001) reported two oxidation processes, i.e., ozonation and electroflocculation, on a pilot scale to test their effectiveness in expelling contaminating substances from wastewaters of textile industries. Both pilot plants utilized to reproduce a full-scale treatment in order to obtain indications about the plausibility of a transfer on industrial scale. Extremely high color removal (95– 99%) was accomplished by ozone treatment and treated waters were reused in dyeing again with light colors also. This proof in spite of the fact that the COD of treated waters was still in a range (75– 120 mg/L, a reduction up to 60%) that was normally viewed as unreasonably high to reuse purposes, particularly especially for dyeing with light colors. Treating plants working at the previously mentioned conditions should ensure low operating costs. A biological pre-treatment and a sand filtration are significant. The transfer on industrial scale of the treatment is as of now in progress under already financed European project. Electrochemical treatment appeared to be extremely effective in evacuating color (80– 100%) and chemical oxygen demand (70– 90%). Additionally, a reasonable depletion of chloride and sulfate particles were identified. Expulsion of flocculated material (post-treatment) must be perfect so as to build up a right costs-to-benefits ratio and hence, propose a usage of the method on an industrial scale.

Central composite design experiment is utilized to study the impact of ozone treatment for acid dye effluents and to optimize the variables such as salt concentration, pH and time, which impact the efficiency of color and COD removal of dye effluents (Muthukumar *et al.* 2004). Acid Red 88 dye is used in this study and sodium sulphate, the salt additive is varied between 5 and 15 g/L, pH is varied between 3 and 11 and the treatment duration is varied between 30 and 360 s. It is observed from the outcome that the treatment time plays a key role in dye effluent's decolouration and COD removal. As the treatment time increases decolouration efficiency also increases. The efficiency of ozone, in terms of decolouration is low at neutral pH when compared with that at acidic and alkaline pH. The effluent decolourizes faster at lower salt concentration while an increase in the salt concentration interferes with the decolouration efficiency. At lower salt concentration maximum amount of COD removal was obtained with 64% in time duration of 195 s at alkaline pH. The ozonation of raw textile wastewater was carried out in a pilot-scale plant and the efficiency of this treatment was assessed based on the parameters of color removal and soluble organic matter measured as chemical oxygen demand (COD), at values of two pH (9.1 and 3.0) was investigated (Somensi *et al.* 2010). Identification of intermediate and final degradation products of ozone pre-treatment, as well as the evaluation of the final ecotoxicity (Lumistox test) of pre-treated wastewater, was also carried out. After 4 h of ozone treatment with wastewater recirculation (flow rate of 0.45 m3 h^{-1}), the average efficiencies for color removal were 67.5% (pH 9.1) and 40.6% (pH 3.0), while COD reduction was 25.5% (pH 9.1) and 18.7% (pH 3.0) for an ozone production capacity of 20 g h^{-1}. Furthermore, ozonation enhanced the biodegradability of textile wastewater (BOD5/COD ratios) by a factor of up to 6.8 fold. A GC-MS analysis of pre-treated textile wastewater showed that some products were present at the finish of the pre-treatment time. Despite this fact, the bacterial luminescence inhibition test (Lumistox test) showed a noteworthy toxicity reduction on comparing the raw and treated textile wastewater. In conclusion, pre-ozonation of textile wastewater is a critical step for improving wastewater biodegradability, as well as reducing acute ecotoxicity, which should be removed completely through sequential biological treatment. (Tehranii *et al.* 2010) investigated the decolorization and degradation of an anthraquinone dye (C.I. Reactive Blue 19) by ozonation using cylindrical batch reactor. Ion chromatography (IC), UV–Vis, chemical oxygen demand (COD) and total organic carbon (TOC) analyses were determined. The effect of operational parameters such as ozone dosage, pH, dye concentration and the electrolytes on decolorization was observed. It was shown that for decolorization, the ozonation was proved to be effective method for reactive dye . During the ozonation process, there is a rapid decrease of pH which gave the evidence for production of acidic by-products like sulfate, nitrate, formate, and acetate. The COD and TOC values were decreased which showed the partial degradation and mineralization of the dye. Due to the application of ozonation has been increasing in current years, it should be studied much and more. But the ozonation treatment has main drawback related to by-products, which can have poisonous and carcinogenic properties, and therefore should be studied much and more. (Souza *et al.* 2010) reported the combined treatment of ozonation and subsequent biological degradation with a biofilm, to reduce the color and chemical oxygen demand (COD). This experimental study contained two parts. The first part was the ozonation process, the results obtained in this showed that the ozonation of Remazol Black B dye at pH values of 3–11 was effective, partially oxidizing and completely decolorizing the waste matter, even at relatively high concentrations of the dye (500 mg/L). Color removal efficiencies were greater than 96% obtained in all cases. The kinetics of degradation with ozone is of pseudo-first-order reaction with respect to the dye concentration. It was verified that the ozonation process as a pre-treatment increases the dye degradation efficiency. For the biological treatment, there is a reduction in dye concentration with increase in ozonation time for hydrolyzed dye synthetic effluent. The toxicological results of the tests with Daphnia Magna demonstrated that the increase in toxicity after ozonation and a decrease after submitting the ozonized synthetic wastewater to biological treatment with a biofilm. The mineralization of an azo-dye, the congored, in aqueous solutions by ozonation process was investigated (Khadhraoui *et al.* 2009). Phytotoxicity and the inhibitory outcomes on the microbial activity of the raw and the ozonated solutions were also lead to achieve the goal of water reuse and environment protection. Primary parameters like decolorization of the aqueous solutions, chemical oxygen demand (COD), disappearance of the parent compound and total organic carbon (TOC) removal have been monitored in this observation. To control the mineralization of the Congo red, pH of the ozonated solution and heteroatoms released from the mother molecule such NH_4^+, NO_3^- and SO_4^{2-} were analysed. It was concluded that ozone through itself was strongly sufficient to decolorize these aqueous solutions in the early stage of the oxidation process. Nonetheless, efficient mineralization had not been achieved. Significant drops in COD (54%) were registered. The extent of

TOC removal turned into almost 32%. Sulfur heteroatom was totally oxidized to SO_4^{2-} ions while the central –N=N– azo ring was partially converted to NH_4^+ and NO_3^-. Results of the kinetic studies demonstrated that ozonation of the selected molecule was a pseudo-first-order reaction with respect to dye concentration. The obtained results also showed that ozone process decreased the phytotoxicity of the raw solution and enhanced the biodegradability of the treated azo-dyes-wastewater. The treatment of organic dyes in wastewater with ozone showed that it is one of the effective technologies for the discoloration and the detoxification of dyes. To take into consideration of stringent environmental rules imposed through regional, national, and international (e.g., European Union) authorities for better environment, the technologies used for treatment of dye-contaminated effluents should be innovative and environment friendly are needed in color industries. The production of dye effluents from industries were subjected to various treatment pathways to follow an initial qualitative characterization (Vanhulle *et al.* 2008). The parameters such as toxicity, residual color, on human cells, and genotoxicity was undertaken for comparing the effectiveness of ozonation and a treatment using white rot fungi (WRF) and their enzymes. Further a combined ozonation/WRF process was also undertaken for study. The effluent exhibited significant toxicity that was achieved a 10% reduction through ozonation, whereas the fungal treatment decreased up to 35%. A combined treatment (ozone/WRF) induced an abatement of the toxicity by more than 70%. In addition, the initial genotoxicity of the effluent was still present after the ozone remedy, while it was completely removed through the fungal treatment.

(Wang *et al.* 2003) investigated the effect of ozonation (20.5 mg l^{-1}) on the degradation methods of an azo dye, Remazol Black 5 (RB5; CI). Conventional parameters such as pH, chemical oxygen demand (COD), conductivity, total organic carbon (TOC), colour removal, biodegradability (BOD5/28), and toxic potential of the dye and its degradation products were monitored during the process. The results showed that for the removal of color from a corresponding dye solution, ozonation is a highly effective way. However, high COD and TOC residues clearly indicated that a considerable organic load still left. The COD, TOC reductions were about 40% and 25% for 6 h ozonation of 2 g l^{-1} RB5 aqueous solution. The formation of acidic by-products and small fragments and ions during the ozonation process indicates the rapid decrease of pH and the sharp increase of conductivity which were identified by high performance ion chromatography. The BOD28 data revealed that first by-products after partial ozonation (10–150 min) of RB5 were more biodegradable than the parent compound and ozonation can enhance the biodegradability of azo dyes. During the first 150 min of total 360 min of oxidation, The formation of first by-products with high toxic potential took place as it could be confirmed by two acute toxicity-screening tests, the bioluminescence test (Vibrio fischerii) and the neutral red cytotoxicity assay (rat hepatoma cells). A long-term ozonation significantly enhances the microbial biodegradability and it could also be seen in form of decrement in toxic intermediates during ozonation time as indicated in BOD28 biological degradation test results. There is two important process related to textile yarns and fabrics are dyeing and finishing which are necessary for quality as well as for environmental concerns. Disperse dyestuffs in the commercial textile dyes are of more useful in form of environment interest because of their widespread use because of their low removal rate during aerobic waste treatment and their potential for formation of toxic aromatic amines as well as advanced chemical oxidation. Thus, (Arslan, 2001) studied the ozonation, ferrous iron coagulation and ferrous iron-catalyzed ozonation were employed in the range of pH of 3–13 and doses of Fe(II)-ion in the range of 0.09–18 mM for the treatment of a simulated disperse dye-bath (average initial apparent color as absorbance at 566nm=815.4 m^{-1}; COD0=3784 mg l^{-1}; TOC0=670 mg l^{-1}; BOD5,0=58 mg l^{-1}) that more closely resembled an actual dye house effluent than an aqueous disperse dye solution. At pH 11 coagulation with 5000 mg l^{-1} FeSO4·7H2O (18 mM Fe^{2+}) decolorizes 97% color and 54% of COD, whereas oxidation by ozonation alone at dose of 2300 mg l−1was only effective at pH 3, resulting in 77% decolorization and 11% removal of COD takes place. Fe (II)-ion-catalyzed ozonation (3.6 mM Fe^{2+} at pH 3; Fe^{2+}:O_3 molar ratio 1:14) eliminated 95% color and 48% COD and appeared to be the most attractive option among the available methods of chemical treatment for its applicability at the natural acidic pH of the disperse dye-bath effluent and at relatively low Fe^{2+} ion doses as compared to ferrous sulfate coagulation. In the reaction conditions of 14 g l^{-1} O_3 at pH 3 there is reduction in TOC was not observed for ozonation and catalytic ozonation. An average six-fold enhancement in the biodegradability parameter of the synthetic dye wastewater expressed in terms of the BOD5/COD ratio could be achieved by the investigated chemical treatment methods. (Ince & Tezcanli, 2001) studied the degradation of a reactive dye by combined sonolysis (520 kHz) and ozonation using C.I. Reactive Black 5 as a model dye. It was observed that the action of ultrasound followed by ozone induced a synergistic effect on both the decolorization of the dye and the overall degradation process. Inefficiency of ultrasonic irradiation by itself causes significant degradation under the conditions employed, the synergy was attributed mainly to mechanical effects of ultrasound to enhance the mass transfer of ozone in solution. During thermolysis of water and ozone in collapsing cavities radical chain reactions take place. This reaction may contribute chemically to the synergy by providing additional decomposition pathways for ozone, and an excess of electron-deficient chemicals in solution. Effluents from dyeing processes of woolen textile finishing industries are highly polluted with recalcitrant compounds compared to effluents from rinsing and finishing processes. (Baban *et al.* 2003) investigated the oxidation of woolen textile dyeing effluent consisting of wastewater generated from spent dye baths and first and second rinses (remaining composite wastewater). Ozone oxidation (CO_3=18.5 mg/l; input rate) was applied for various time intervals on remaining composite wastewater, before and after the biological treatment. The efficiency of treatment was monitored by decolorization rates and COD removal rates. Additionally, toxicity tests (bioluminescence test) were carried out to determine the effect of oxidation process. The obtained results indicate that 40 min ozonation of biologically treated wastewater yielded nearly colorless effluent with a decolorization efficiency about 98–99% with a related ozone absorption rate of 58.0 mg/l. the overall toxicity reduced about 92% by biological treatment followed by 10 min ozone oxidation. The result of ozonation was found to have slightly effect on COD removal.

By Photochemical Method

The efficiency of heterogeneous photocatalytic processes for degradation of many persistent chemicals has been extensively documented, especially with the use of titanium dioxide (Hoffmann *et al.* 1995; Linsebigler *et al.* 1995). Recently, several papers on photochemical degradation of isolated dyes have been published (Vinodgopal & Kamat, 1994; Vinodgopal et al. 1996). Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants present in water. In the UV/H_2O_2 process the photochemical decolorization of three dyes, Methyl Orange (MO), Acid Orange 8 (AO8) and Acid Blue 74 (AB74) by using a continuous photochemical reactor with a 15 W low pressure mercury lamp was studied (Aleboyeh *et al.* 2003). Decolorization completes in very short time and follows apparent first order kinetics with respect of dye concentration. In visible maximum absorption wavelength region the rate of disappearance of a given dye was monitored spectrophotometrically. It was found that by increasing the initial amount of H_2O_2 up to a “critical” value at which it shows maximum the rate of decolorization rises and beyond which it is inhibited. The pathway of simple reactions describe adequately the process has been studied. Based on this reaction schema, A mathematical relationship is established between the apparent rate constant of the dye removal and applied H_2O_2 dosage which presented by the ratio of its initial mass concentration to that dye. The rate constant values for the three dye solutions are obtained by model in good agreement with the experimental data and the model parameters have been determined. (Muruganandham & Swaminathan, 2004) studied the photooxidation of a chlorotriazine reactive azo dye Reactive Orange 4 in the presence of H_2O_2 using UV-A light. The effects of pH of reaction, UV light power, and applied H_2O_2 amount have been studied. These parameters strongly influence the decolourisation and degradation. Removal rate decreases by increasing the initial dye concentration. The kinetics of degradation and decolourisation follow pseudo-first order. The efficiency of solar– H_2O_2 process is comparable with UV– H_2O_2 and solar– H_2O_2 process is also able to oxidize the dye. The influence of dye assisting chemicals such as NaOH, NaCl and Na_2CO_3 on photodecolourisation has been investigated. Addition of these chemicals inhibits the removal rate. Dye is used in order to colour the products in many industries such as paper, food, cosmetics, and textiles industries. The presence of these dyes in water even at very low concentration is highly visible and undesirable. Colour is the first recognizable contaminant. Colour from wastewater can be removed by photocatalytic technique and adsorption methods. In the present paper these two methods were used for removal of Congo red and both the techniques were found to be very useful and cost effective for a better removal of dye. The results were compared. The operating variables such as adsorbent dose, adsorbate concentration, pH etc were optimized (Jain & Sikarwar, 2006). (Alaton & Balcioglu, 2001) studied that aqueous solutions of hydrolyzed Reactive Black 5 (RB5) dye is a well-known surrogate for non-biodegradable azo dyes and it is photochemically and photocatalytically treated by employing the TiO_2/UV-A and H_2O_2/UV-C advanced oxidation systems. The observed effects of oxidant dose, reaction pH and initial dyestuff concentration were used to explain the $OH^{\cdot}$ induced color disappearance kinetics empirically. Accordingly, the waste dyestuff solutions could be effectively mineralized ($k_{TOC,max}$=0.01 min^{-1}; H_2O_2/UV-C system) and completely decolorized ($k_{d,max}$=0.155 min^{-1}; H_2O_2/UV-C system) with an average overall TOC removal of 78% after 120 min advanced oxidation take place at specified optimized reaction conditions. The bleaching effect of the TiO_2//UV-A process could be successfully fitted to the empirical Langmuir–Hinshelwood (L–H) kinetic model ($k_{L–H}$=4.47 mg l^{-1} min^{-1}; $K_{L–H}$=2.01 l mg^{-1}). (Gupta *et al.* 2012) investigated the photo-catalytic degradation of an azo dye Amaranth (AM) –in TiO_2/UV aqueous suspensions. The obtained results from the experiments during addition of H_2O_2/TiO_2 show that the highest decolorization rate is provided by the combination of (UV + TiO_2 + H_2O_2). The decolorization efficiencies for UV, UV+ H_2O_2, UV + TiO_2 and (UV + TiO_2 + H_2O_2) were 17%, 26%, 38% and 64% in the runs after approximately 100 min illumination periods, respectively. The dye degradation rate follows pseudo-first order kinetics with respect to the substrate concentration under the experimental conditions used. Different experimental conditions, such as pH, temperature and presence of electron acceptor were investigated. The effect of temperature was investigated at the range of 293–313 K and it was observed that decolorization rate increased by increasing the temperature. Dye absorbance and chemical oxygen demand of the photodegraded dye solution substantially decreased. Effect of pH was also investigated and if lower the pH than higher will be the degradation of dye. It was observed that by the Addition of hydrogen peroxide as an electron acceptor enhances the photodegradation rate. The adsorption trends of Amaranth dye at various initial concentrations followed the Langmuir isotherm trend. The role of this work at global level is discussed for advanced oxidation processes in water treatment. (Rosa *et al.* 2015) studied that ten different dyeing were made using reuse water obtained from effluent after treatment by homogeneous photocatalysis. The concentration of sodium chloride (NaCl), the absorbance (Abs) and the amount of total organic carbon (TOC) were monitored before and after the UV/H_2O_2 treatments. The removal of TOC was above 88% and all rates of decolorization were above 92% in all treatments. The total deviation (ΔE^*) between the colors did not exceed compared for the same dyeings made with deionized water was 1.05. Currently the monthly production of 20 dyeing of 100 kg each, 160 m^3 of water is consumed and an equal volume of effluent is generated. The same dyeing made by the process proposed in this study, with an addition of 10 m^3 of water after 20 dyeing, would consume just 60 m^3 of water. (Jain *et al.* 2005) reported photocatalytic and adsorptive treatment of a hazardous xanthene dye, Rohdamine B, in wastewater. The photocatalytic degradation was carried out in the presence of the catalyst TiO_2 and the effects of pH, amount of TiO_2, temperature, concentration of the dye, and electron acceptor H_2O_2 on the degradation process were observed. It was found that removal of Rohdamine B from aqueous solutions by photocatalytic degradation by TiO_2 is an effective, economical and faster mode. The attempts were also made for utilization of activated carbon and rice husk as potential adsorbents to remove Rhodamine B from wastewater. The adsorption studies were carried out at 40, 50 and 60°C, and the effects of pH, temperature, amount of adsorbents and concentration of adsorbate etc., on the adsorption were measured. Langmuir and Freundlich adsorption isotherm models were also confirmed by adsorption data. The adsorption isotherm constants thus obtained were employed to calculate thermodynamic parameters like change in enthalpy, entropy and Gibb's free energy. To observe the quality of wastewater COD measurements were also carried out after and before treatments. A significant decrease in the COD values was observed, which clearly indicates that both photocatalytic and adsorption methods offer good potential to remove Rhodamine B from industrial effluents. (Chang *et al.* 2004) carried out treatment of the lignin-containing wastewater by photochemical UV/ TiO_2 oxidation process for parameters dissolved organic carbon (DOC), color and reducing A254(wavelength 254 nm). The data obtained in this study confirms that the UV/ TiO_2 process is effective in oxidizing the lignin thus reducing DOC and the color of the wastewater treated. The better removal of DOC and color obtained from combined UV/TiO_2 treatment rather than the UV treatment alone. If the pH is maintained at 3.0 by the addition of 1 g l^{-1} TiO_2 than color removal based on

American Dye Manufacture Index (ADMI) measurement is greater than 99%. The oxidation reduction potential (ORP) value is reached to result in an 88% removal of both DOC and color when 10 g l^{-1} TiO_2 is applied. A model was developed to simulate the decoloring process based on the variation of ORP during the photochemical reaction. The proposed model can also use for prediction of color removal efficiency of the UV/TiO_2 process. (Gad-Allah *et al.* 2009) prepared a photocatalyst TiO_2/SiO_2/Fe_3O_4 (TSF) that was used for the treatment of synthetic dyes wastewater. To determine the optimum operating conditions different operating conditions such as catalyst load, pH and dye concentration were investigated. The optimum operating conditions were found to be dose of TiO_2 photocatalyst 2500 ppm and pH 3. More catalyst dose led to increase the opacity inside photoreactor as well as reduction in rate of reaction due to aggregation of photocatalyst. The rate of reaction increases for acidic medium favored adsorption of studied dyes on photocatalyst. Under optimum conditions, complete decolourization and degradation of the organic dyes could be achieved within less than 45 min. Rate of reaction depends on three parameters- dye concentration, photocatalyst load, and transmittance inside photoreactor in kinetic studies. When TSF photocatalyst was used several times efficiency was nearly the same. The reuse of the photocatalyst decreases the final cost of the treatment process. (Rahmani *et al.* 2012) studied ultrasonic irradiation (US), ultraviolet radiation (UV), UV/H_2O_2 and US/H_2O_2 processes for degradation of Basic Violet 16 (BV16) in a laboratory-scale batch photoreactor equipped with a low-pressure mercury vapor lamp and a sonoreactor. The results indicated that in the UV/H_2O_2 and US/H_2O_2 systems a very high concentration of H_2O_2 would inhibit the reaction rate so sufficient concentration of H_2O_2 was enough. The optimum H_2O_2 concentration was achieved in the range of 17 mmol/L at dye concentration of 30 mg/L. A degradation of BV16 was obtained 99% with UV/H_2O_2 within 8 minutes while decolorization efficiency by using UV (23%), US (<6%) and US/H_2O_2 (<15%) processes were negligible for this kind of dye. Pseudo-first order kinetics with respect to dyestuffs concentrations was found to fit all the experimental data. In this work (Goel *et al.* 2010) studied the performance of integrated photocatalytic and biological treatment was studied for the degradation of 4-chlorophenol (MCP) present in wastewaters. For pre-treatment of biological degradation photocatalysis was used. Pollutant removal efficiency was expressed using MCP removal and total organic carbon (TOC) removal. By use of TiO_2 as the photocatalyst both photocatalytic as well as biological treatments were carried out in batch reactors. Effect of TiO_2 concentration on the photocatalytic degradation of MCP was studied along with the effect of the duration of photochemical oxidation and glucose concentrations (0 g/L, 1 g/L and 2 g/L) on the biodegradation of MCP. At higher concentrations (400 mg/L) integrated biological and photochemical degradation was found to be more effective for treating MCP. 96 h required for complete mineralization of initial MCP concentration of 400 mg/L when treated with the process combination, whereas for biodegradation the treatment went on up to 264 h when it was done alone. (Pandey *et al.* 2015) carried out the photocatalytic degradation of methylene blue using naïve titanium dioxide, nano-sized titanium dioxide and H_2O_2 under visible light. The catalysts, naïve and nano-sized titanium dioxide were prepared by the sol–gel method. Characterization of synthesized catalysts has been done by SEM, XRD and UV–Vis. spectroscopy. By measuring absorbance of dye at regular time intervals the rate of degradation of dye was monitored spectrophotometrically. The effect of various parameters such as concentration of dye, pH, dose of catalyst, added amount of H_2O_2 and light intensity on the rate of reaction has been studied. Various parameters like conductance, chemical oxygen demand (COD), TDS, pH, salinity and dissolved oxygen (DO) for the reaction mixture have also been determined. The rate of reaction drastically reduced in the presence of of **.**OH radical and participation was confirmed by using 2-propanol (scavenger). The heterogeneous photo-Fenton process is a green chemical pathway for removal of dye. In photo-Fenton processes does not requirement of removal of ferrous/ferric ions in the form of sludge. By wet chemical method (Kalal *et al.* 2014) prepared copper pyrovanadate or Volborthite ($Cu_3V_2(OH)_2O_7 \bullet 2H_2O$) composite as photocatalyst. The photocatalyst was characterized by numerous spectroscopic techniques. Experiments demonstrated that catalyst could effectively catalyze degradation of neutral red and azure-B in presence of H_2O_2 in visible light. When $Cu_3V_2(OH)_2O_7 \bullet 2H_2O$ used alone as photocatalyst than photo-Fenton-like catalytic activity of $Cu_3V_2(OH)_2O_7 \bullet 2H_2O$ was much higher than CuO and V_2O_5. The effect of variation of different parameters like pH, concentration of dye, amount of photocatalyst, amount of H_2O_2 and light intensity was also investigated. The kinetics of degradation for neutral red and azure-B was well fitted under pseudo-first-order reaction with a rate constant of 2.081×10^{-4} sec^{-1} and 3.876×10^{-4} sec^{-1}, respectively. The high catalytic activity of $Cu_3V_2(OH)_2O_7.2H_2O$ shell not only increases the surface hydroxyl groups, but also enhances the interfacial electron transfer.

BIOLOGICAL TREATMENT

By White Rot Fungi

(Swamy and Ramsay, 1999) investigated that decolorization of dyes Amaranth, Remazol Black B, Remazol Orange, Remazol Brilliant Blue, Reactive Blue, and Tropaeolin O by five species of white rot fungi in agar plates, Bjerkandera sp., Phanerochaete chrysosporium, BOS55, and Trametes versicolor displayed the greatest extent of decoloration. Three cultures of fungal mats which did not decolorize any dye in static aqueous culture. The biomass grew as mycelial pellets when agitated at 200 rpm. Bjerkandera sp. BOS55 pellets decolorized only Amaranth, Remazol Black B, and Remazol Orange. T. versicolor and P. chrysosporium pellets were capable to decolorize most dyes. Decoloration by T. versicolor being several times more rapid than P. chrysosporium. Batch cultures of Bjerkandera sp. BOS55 and P. chrysosporium could not decolorize the repeated dye additions but T. versicolor was able to rapidly decolorize repeated additions of the different dyes and dye mixtures without any visual sorption of any dye to the pellets. The choice of buffer had a profound effect of addition of dye on pH stability and consequently decoloration. For excellent pH control and high decoloration ability 2,2′-dimethylsuccinic acid is used. (Faraco *et al*. 2009) evaluated for models of colored industrial wastewaters the effect of Phanerochaete chrysosporium and Pleurotus ostreatus whole cells and their ligninolytic enzymes. Models of acid, direct and reactive dye wastewaters from textile industry have been defined on the basis of discharged amounts, economic relevance and representativeness of chemical structures of the contained dyes. Phanerochaete chrysosporium provided an effective decolourization of direct dye wastewater model, reaching about 45% decolourization in only 1 day of treatment, and about 90% decolourization within 7 days, whilst P. ostreatus was able to decolorize and detoxify acid dye wastewater model providing 40% decolourization in only 1 day, and 60% in 7 days. For wastewater models decolourization the laccase production (up to 130,000 U/l) is induced by the growth conditions of P. ostreatus. By known composition of laccase isoenzyme a extra-cellular enzyme mixtures were produced. Laccases is the main agents for wastewater decolourization by P. ostreatus. The mixtures of laccase detoxified and decolorized the acid dye wastewater model. The immobilized mixture of laccase was used for investigation and the immobilized enzymes were also effective in batch decolourization, however the additions of dye for a total exposure of about 1 month. (Revankar & Lele, 2007) investigated that an indigenous strain of white rot fungus isolated from bark of dead tree is used for decolorization of recalcitrant dyes and WR-1 identified as Ganoderma sp. A combination of one factor at a time and orthogonal array method is used for optimization of fermentation. Maximum decolorization (96%) of 100 ppm amaranth was achieved in 8 h with medium containing 2% starch and 0.125% yeast extract. Rate of dye decolorization for the indigenous isolate Ganoderma sp. WR-1 was very high compared to the most widely used strains of T. versicolor and P. chrysosporium. By using chemically different dyes the broad-spectrum decolorization efficiency of the isolate was assessed. For decolorization of industrial effluent the isolate was further evaluated. Complete decolorization by Ganoderma sp. was achieved in 12 days. (Selvama *et al*. 2003) investigated that a white rot fungus Thelephora sp. was used for decolourization of azo dyes such as orange G (50 µM), congo red (50 µM), and amido black 10B (25 µM). Decolourization using the fungus was 33.3%, 97.1% and 98.8% for orange G, congo red and amido black 10B, respectively. An enzymatic dye decolourization study showed that a maximum of 19% orange G was removed by laccase at 15 U/ml whereas lignin peroxidase (LiP) and manganese dependent peroxidase (MnP) at the same concentration decolourized 13.5% and 10.8%, orange G, respectively. A maximum decolourization of 12.0% and 15.0% for congo red and amido black 10B, respectively, was recorded by laccase. In batch and continuous modes the dye industry effluent was treated by the fungus. A maximum decolourization of 61% was observed in batch mode on third day and a maximum decolourization of 50% was acheived on seven day in the continuous mode. The obtained results suggest that the batch mode of treatment using Thelephora sp. may be more effective than the continuous mode for decolorization of dye industry effluents. (Kim *et al.* 2004) studied that a membrane bioreactor (MBR) using white-rot fungi was used for the decolorization of dye solutions. Trametes versicolor KCTC 16781 and membrane filtration were combined for decolorization of dye solutions and applicability of this process was investigated by using reactive dye solutions. A study is carried out for the feasibility of MBR using fungal biodegradation with nanofiltration and reverse osmosis (RO) membranes to improve separation efficiencies and permeate flux. The effects of dye types on fungal biodegradation and membrane filtration (permeate flux and rejection) were also investigated. The fungal MBR combined with RO was found effective for decolorization and organic removal of dye from wastewater. Decolourization activity of P. chrysosporium for three synthetic dyes viz., congo red, malachite green and crystal violet was carried out (Pant *et al.* 2008) and impact of additional carbon and nitrogen supply on decolourization capacity of fungus. Urea is used as nitrogen source and glucose as carbon source for addition which significantly enhances decolourizing capacity (up to 87%) of fungus. In all the cases, both colour and COD were reduced more in non-sterilized treatments as compared to sterilized ones. By additional of carbon and nitrogen significant reductions in COD content of dye solutions (79- 84%) were recorded by fungus. (Nilsson *et al.* 2006) described a batch and continuous reactors inoculated with white-rot fungi operated in order to study decolorization of textile dyes. For first part of the study of synthetic wastewater containing either Reactive Blue 4 (a blue anthraquinone dye) or Reactive Red 2 (a red azo dye) was used while in the later part Tanzania was used for real wastewater from a textile industry. When glucose was added as a carbon source then Trametes versicolor decolorize both Reactive Blue 4 and Reactive Red 2. Reactive Blue 4 was also decolorized by growth of fungus on birch wood discs in a continuous biological rotating contactor reactor. The absorbance decreases by 70% during treatment at wavelength of 595 nm at which the dye absorbs maximum. The initial concentration of dye in the medium was 200 mg/l and the hydraulic retention time in the reactor was 3 days as well as no amount of glucose was added in this experiment. Aromatic structures of the dyes were altered when exposed to UV range which indicates changes of the absorbance in this region. *Pleurotus flabellatus* growing on luffa sponge packed was used for real textile wastewater decolorization in a continuous reactor. Hydraulic retention time of the reactor for operating was 25 h. The absorbance decreases from 0.3 in the inlet to approximately 0.1 in the effluent at wavelength of 584 nm at which the wastewater absorbed the most. (Kiran *et al.* 2013) studied a two stage sequential Photo-Fenton's oxidation followed by two white rot fungi *P. ostreatus* IBL-02 (PO) and *P. chrysosporium* IBL-03 (PC) for aerobic biological treatment to check decolorization and enhancement in mineralization of azo dye Reactive Blue 222 (RB222). Decolorization percentage of selected dye for Photo-Fenton's oxidation was ~90% in first stage but when it is subjected to aerobic treatment using two white rot fungi *P. ostreatus* IBL-02 (PO) and *P. chrysosporium* IBL-03 (PC) than it further increases to 96.88% and 95.23% respectively. Mineralization efficiency was accessed by measuring the water quality assurance parameters like COD, TOC, TSS and Phenolics estimation. For two stage sequential processes reduction was observed for COD, TOC, TSS and Phenolics were found to be 95.34%, 90.11%, 90.84% and 92.22%, respectively. By UV–visible and FTIR spectral techniques degradation products were characterized and their toxicity was also measured. Both fungal strains were able to oxidize and mineralize the selected azo dye was confirmed by the evidence of results into non-toxic metabolites. (Yang *et al.* 2009) obtained two microbial cultures exhibiting high decolorization efficiencies of reactive dyes. Dye mineralization rates were obtained about 50–75% and efficiencies of color removal were obtained 70–80%. Additionally the microbial community on the biofilm was monitored during whole running process. The obtained results indicates that fungi as a dominant population in the decolorization system with the ratio of fungi to bacteria from 6.8:1 to 51.8:1 under all the tested influent conditions. Under sterile conditions a variety of white-rot fungi can oxidize textile dyes as well as similar degrees of treatment can be achieved under non-sterile conditions for their use in treating wastewater containing textile dyes studied (Libra *et al.*2003). C.I. Reactive Black 5 (RB5) is a wastewater containing diazo textile dye which is treared by using the fungus Trametes versicolor in non-sterile culture, four strategies were investigated for this. In suspended culture the decolorization activity increases from a given amount of *T. versicolor* inoculums, three strategies with suspended culture were designed and amount of *T. versicolor* inoculums is based on its pH reduction in medium, production of extracellular enzymes, and its ability to produce enzymes independent of growth (nitrogen limitation in medium). The results showed that reduction of the medium pH to 3 did not suppress bacterial growth, while enzyme production by *T. versicolor* ceased. The decoupling of the process of fungal growth from wastewater treatment by use of the extracellular enzymes alone would allow however, under non--sterile conditions the enzyme activity of an enzyme suspension decreased rapidly. Under non-sterile conditions cultivation of fungi is done on organic solids to produce inocula for a decolorization process. Under non-sterile conditions a high degree of decolorization of RB5 was achieved with *T. versicolor* grown on grains as sole substrate. The rate of decolorization was dependent on the amount of fungal inoculum used.

By Anaerobic Bioremediation Methods

The degradation of an azo dye mixture by an aerobic bacterial consortium in a rotating biological reactor was studied (Abraham *et al.* 2003). On gramophone records laterite pebbles of particle size 850 µm to1.44 mm were fixed using an epoxy resin on which the developed consortium was immobilized. Rate of degradation, biomass determination, BOD, enzymes involved, and fish bioassay etc. were studied. For high concentrations of dye (100 µg/mL) RBC has a high efficiency for dye degradation and high flow rate (36 L/h) at alkaline pH and salinity conditions normally encountered in the textile effluents. Bioassays (LD-50) using Thilapia fish in treated effluent showed that the percentage mortality was zero over a period of 96 h, whereas the mortality was 100% in untreated dye water within 26 h. Effluent obtained from RBC can be discharge safely into the environment was confirmed by fish bioassay. (Mohan *et al.* 2012) evaluated the functional behavior of anoxic–aerobic–anoxic microenvironment on azo dye (C.I. Acid black 10B) degradation in a periodic discontinuous batch mode operation for 26 cycles. Until 13th cycle dye removal efficiency and azo-reductase activity (30.50 ± 1 U) increased with each feeding event and further stabilizes. Gradually increment and stabilization of (2.0 ± 0.2 µg/ml) dehydrogenase activity also indicates the stable proton shuttling between metabolic intermediates which provides higher number of reducing equivalents for dye degradation. For dye removal there is consumption of reducing equivalents during stabilized phase showed drop in redox catalytic currents for voltammetric profiles. The observed dye removal and biocatalyst behavior is correlated with change in polarization resistance, Tafel slopes and other bioprocess parameters. Microbial community analysis documented the involvement of specific organism pertaining to aerobic and facultative functions with heterotrophic and autotrophic metabolism. A biological method for decolorizing wastewater from fiber reactive dyeing of cotton by sequential anoxic/aerobic treatment steps using a single biomass was investigated and evaluated for color removal and chemical oxygen demand

(COD) (Smith *et al*. 2007). For a sequential anoxic/aerobic treatment process a viable biomass was developed that effectively removes both color and chemical oxygen demand from wastewater. For treating dyeing wastewater this method is the retrofitted to existing aerobic wastewater treatment systems that are typically used. The upflow of anaerobic sludge blanket (UASB) reactor for its usefulness in reduction in chemical oxygen demand (COD) and decolourization of real textile wastewater (RTW) under different operational conditions were evaluated (Somasiri *et al*. 2008). The efficiency obtained by UASB reactor in reducing COD was 90% as well as colour removal because of biodegradation was achieved 92%. During the treatment of textile wastewater the activities of the anaerobic granules were not affected. In textile wastewater treatment Cocci-shaped bacteria were the dominant group over Methanothrix like bacteria. In textile wastewater treatment volatile fatty acids (VFA) content, alkalinity, and pH present in effluents indicated that the anaerobic process was not inhibited. It is concluded that for the treatment of textile wastewater UASB reactor system can be effective for removal of colour and in the reduction of COD. Inhibitory effect of azo dyes on anaerobic methanogenic wastewater treatment (AMWT) has been studied (Dai *et al*. 2016) which mainly focus on biological toxicity in the batch test with simulated sole co-substrate. Mechanism of azo dyes and detailed information on inhibitory effect during the long-term operation with real complex co-substrate is limited. Moreover, under the complex scenario redox mediator (RM) could remediate the inhibition is still unclear in previous studies. In this study, a lab-scale high-rate anaerobic methanogenic bioreactor was operated for 127 days with the real textile wastewater and alternative concentrations of azo dyes (0-600 mg/L) were used as well as 50 μM anthraquinone-2-sulfonate (AQS) was also added as RM at the last period of operation. An overall (decolorizing and methanogenic) performance of AMWT with concentration of 600 mg/L of azo dyes could cause significant inhibition on AMWT. Acetoclastic methanogens was more susceptible to high concentration azo dyes for specific methanogenic activity than hydrogenotrophic methanogens. In the anaerobic granular sludge (AGS) spatial distribution of extracellular polymeric substance showed the high biological toxicity of azo dyes which was mainly caused to enrichment effect in tightly bound-EPS (TB-EPS). The channels of AGS were clogged by azo dyes, which was evidenced by the hard release of aromatic amines in EPSs as well as decreased porosity of AGS and scanning electron microscope images. Meanwhile, the settling ability, particle size and strength of AGS all deteriorated after azo dyes concentration exceeded 450 mg/L. Overall performance of the bioreactor was remediate by dosing of AQS even if the recovery of acetoclastic methanogens was slow. It suggested that additional attention should be paid to prevent sludge from washout if RM was practically used to remediate the anaerobic reactor inhibited by azo dyes. (Pandey *et al*. 2007) studied that azo compounds constitute the largest and the most diverse group of synthetic dyes and are widely used in a number of industries such as textile, food, cosmetics and paper printing. Azo dyes compund are having xenobiotic nature due to this generally recalcitrant to biodegradation. However under certain environmental conditions microorganisms enzyme systems were developed for the decolorization and mineralization of azo dyes being highly versatile. In the bacterial metabolism of azo dyes initialy reductive cleavage of azo bond take place leading to the formation of aromatic amines in the reaction. Decolorization of azo dyes by several mixed and pure bacterial cultures for anaerobic/anoxic, under these conditions this reaction is non-specific with respect to organisms as well as dyes. For non-specific reductive cleavage various mechanisms was proposed which include enzymatic as well as low molecular weight redox mediators. Azo dyes as growth substrates used by only few aerobic bacterial strains have been isolated. These types of organisms generally have a narrow substrate range. Chemical structure and the conditions play a role for degradation of aromatic amines. It is now known that sulfonated aromatic amines are resistant while simple aromatic amines are not, on the other hand mineralization of sulfonated aromatic amines require specialized aerobic microbial consortia and aromatic amines can be mineralized under methanogenic conditions.

By Enzymes and Bacteria

The implementation of increasingly stringent standards for the discharge of wastes into the environment has necessitated the need for the development of alternative waste treatment processes (Karam & Nicell, 1999). Enzymatic treatment systems were developed for solid, liquid and hazardous wastes. For waste treatment applications a large number of enzymes have been reported from a variety of different plants and microorganisms. Enzymes can remove specific recalcitrant pollutants by action of precipitation or transformation to other products. Enzymes can also change the characteristics of a waste material to render it more amenable to treatment or converting waste material into value added products. In future reaction by-products, the disposal of reaction products and reduction of the cost of enzymatic treatment will be researched. (Ali *et al.* 2009) investigated effluent of a local textile mill that physicochemical and bacteriological status showed considerably high values of temperature, pH, EC, BOD, COD, TSS, TDS, heavy metals ions and color above the prescribed fresh water limits. However, almost all pollution indicators from source to sink indicate signs of natural remediation. Ten bacteria strains isolated from effluent showed comparatively higher resistance (MRL) (mg l^{-1}) (average) for 10 heavy metals than against four structurally different dyes tested on solid media of mineral salt. Overall bacterial resistance was quite high against Cr^{3+} (1203), Fe^{3+}

(2820), Mn^{2+} (804), Zn^{2+}(1122), and Pb^{2+} (435), whereas, it varied amid 300–500 in four dyes. Experiments carried out in liquid broth on solid media for bacterial degradation/decolorization of dyes was confirmed. (Won *et al.* 2004) studied that the removal of Reactive Orange 16 (RO16) by the use of protonated waste biomass of Corynebacterium glutamicum discharged from an industrial lysine fermentation plant. The biomass show maximum sorption capacities as high as 186.6 ± 7.1 and 154.8 ± 2.8 mg g^{-1} at pH 1 and 2, respectively, which can compare with activated carbons and ion-exchange resins type of commercial sorbents. If the solution pH decreases then dye uptake increases and under neutral conditions it was negligible. RO16 cannot be bound to a negatively charged carboxyl and/or phosphonate sites of the biomass because the RO16 molecule has two negatively charged sulfonate groups. Dye binding sites can be positively charged amine-occurring protein molecules. A high concentration of salts do not affect the uptake of RO16, and the biomass can be repeatedly reused up to eight times per sorption/desorption cycle. Toxic chemical waste water generated from textile industry is considered as one of the largest way in India. Dyes released by the textile industries are responsible for environmental safety. Recently, dye decolourization through biological means has gained momentum as these are cheap methods and can be applied to wide range of dyes. (Saranraj, 2013) focused on the bacterial biodegradation of toxic textile dyes. Various biological methods for the biodegradation of textile dyes by microorganisms are given in this study. He indicated that biological decolourization by bacteria has a great potential to be developed further as a decentralized wastewater treatment technology for small textile or dyeing units. However, further research work is required to study the toxicity of the metabolites formed by dye degradation and the possible fate of the utilized biomass in order to ensure the development of an eco-friendly technology. (Khouni *et al.* 2012) investigated the biological decolourisation of a widely used textile reactive dye in Tunisia, the Blue Bezaktiv S-GLD 150 dye, using a sequencing batch reactor (SBR). SBR was inoculated with an acclimated novel microbial consortia 'Bx'. Under aerobic conditions decolourisation efficiency was studied for different volumetric dye at loading rates (3–20 g dye/m^3·d) at room temperature and at pH 7. When volumetric dye loading rates were under 15 g dye/m^3·d than experimental results indicated that under aerobic conditions Bx displayed highest purification capabilities giving COD removal percentages of about 95–98% and maximum decolourisation rates in the range of 88–97%. Rates of decolourisation and COD removal were decreased to 70% and 90% respectively when volumetric dye loading rates were increased to 20 g dye/m3·d. Obtained results indicate that the efficiency of dye removal through a sequencing batch reactor influenced by the volumetric dye loading rate. The removal of coloured textile effluents in the aquatic environment is undesirable as these reduce light penetration, therefore affecting life of aquatic species and limits utilization of the water media. These toxic effluents can be treated by microbial bioremediation, it is an alternative treatment option available other than the commonly employed physicochemical and biological methods. (Leena & Selva, 2008) worked on the decolourization of an actual textile effluent that contained the diazo dye compound Reactive Black-B. In their study they observed the potentials of certain selected bacteria on effluent soil-adapted and non-adapted bacteria. Among all Five effluent-adapted and four non-adapted bacterial isolates were tested. The results confirm that non-adapted species were not better option for decolourizing the effluent than the effluent-adapted strains. Wastewater effluents from the textile and other dye-stuff industries contain significant amounts of synthetic dyes that require treatment to prevent groundwater contamination. In research aimed at biotechnology for treatment of azo dyes. (Khalid *et al.* 2008) studied 288 strains of azo-dye degrading bacteria to identify efficient strains and determine incubation times required for decolorization. Initial enrichment cultures were carried out using a mixture of four structurally different dyes (Acid Red 88, Direct Red 81, Reactive Black 5, and Disperse Orange 3) as the sole source of C and N to isolate the bacteria from activated sludge, soil, and natural asphalt. To decolorize the dyes individually or in mixtures six bacterial strains were selected for further study based on their prolific growth and ability to rapidly decolorize. 4 h are required for complete decolorization of 100 mg l^{-1} of AR-88 and DR-81 dyes under static conditions by the most efficient strain AS96 (Shewanella putrefaciens) and it is the shortest treatment time. 6 and 8 h are required respectively for complete decolorization of RB-5 and DO-3. For azo-dye degradation these bacterial strains are the most efficient bacteria and may have practical application for biological treatment of dye-polluted wastewater streams. The use of microorganisms to clean up contaminated environment is the cheapest alternative method to the conventional treatment methods. But a major challenge arises that is the choice of easily grown, viable and effective natural occurring microorganism to do the cleaning. The application of photosynthetic bacteria in bioremediation were presented and reviewed (Idi *et al.* 2015) due to their minimum nutrients requirement and the possibility of generating valuable products simultaneously cleaning the contaminated environment. The specific photosynthetic bacteria are capable to degrade pollutants such as heavy metals, pesticides, dyes, crude oil and odour. The possible value added products to be generated as well as the mechanism of degradation are also discussed. The use of these bacteria in bioremediation have environmental as well as economic benefits because utilization of CO_2 and the generation of value added products while cleaning up polluted environment are the major advantages of using bacteria. Ligninolytic extracellular enzymes, including lignin peroxidase, have high redox potential and prospective industrial applications. (Falade *et al.* 2017) studied some articulated applications of these enzymes including ethanol production, textile effluent treatment and dye decolourization, coal depolymerization, treatment of hyperpigmentation, and skin-lightening through melanin oxidation.

(Mahmood *et al*. 2016) critically reviewed biological treatment of dye polluted wastewater and the role of bacterial reductive and oxidative enzymes/processes. The complete mineralization of azo dyes normally includes two-step process: first anaerobic treatment for decolorization, and second an oxidative process that results in degradation of the toxic intermediates that are formed during the first step. They did a molecular study revealing first reductive process which can be brought by two classes of enzymes involving flavin-dependent and flavin-free azoreductases under anaerobic or low oxygen conditions. The second step that is carried out by oxidative enzymes that primarily involves broad specificity peroxidases, laccases and tyrosinases. Laccasses are ecofriendly biocatalyst having capacity to transform complex xenobiotics making them useful in enzymatic bioremediation. (Mate & Alcade, 2017) reviewed the most significant recent advances on the use of laccases and their future perspectives in biotechnology. (Meerbergen *et al*. 2018) aimed to study, isolate and characterize bacterial strains that are capable of decolorizing or degrading azo dyes commonly applied in textile production. They followed a prescreening of 125 isolates and out of that five strains were retained for further evaluation of decolorization rate. Out of those five strains, one strain belonging to the genus Acinetobacter and another belonging to Klebsiella out performed the other tested strains. It was found that both strains exhibited strong decolorization ability (>80%) within a wide temperature range (20 °C–40 °C).

CONCLUSION

The dye waste not only cause environmental pollution but also medical and aesthetic problems associated with human health and society. Although the biological treatment is a promising technology for degradation of dyes, the method relies on success of finding out a suitable organism and designing of condition for the process. Also the biological method of degradation alone cannot tackle the problem successfully. Hence, along with biological processes some other pre and post treatment methods are required. Pre-treatment of dyeing effluent by advanced oxidation processes (AOP) catalyzed by a source of ultraviolet (UV) light and a powerful oxidant is a promising alternative for the effective removal of color and refractory organics from the effluent. Some metal oxides like TiO_2 in combination with a agents like UV rays are used for this process. Zinc oxide appeared to be a suitable alternative to TiO_2 for water treatment. An understanding of the use of bacteria and fungi for dye degradation will further enhance the efficiencies of these processes towards its successful application.

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KEY TERMS AND DEFINITIONS

Advanced Oxidation Process (AOPs): Advanced oxidation processes (AOPs) in a broad sense, are a set of chemical treatment procedures designed to remove organic or sometimes inorganic materials in water and wastewater by oxidation through reactions with hydroxyl radicals (OH).

Fenton Process: Fenton process is attractive alternative to conventional oxidation processes in effluent treatment of recalcitrant compounds. The oxidation of organic substrates by iron (II) and hydrogen peroxide is called the "Fenton chemistry" and it was first described by H.J.H. Fenton.

Photo-Catalysis Process: Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate.

Chapter 10

Advanced Oxidation Processes for Dye Removal From Wastewater

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ABSTRACT

Advanced oxidation processes (AOPs), namely the Fenton oxidation, ozonation, electrochemical oxidation, and photocatalysis, are potential alternative techniques for dye removal from textile effluents. Their inherent ability to completely mineralize pollutants including those recalcitrant to biodegradation and to be compatibly integrated in conventional technologies present grounds for consideration of AOPs as alternative wastewater treatment options. Advanced oxidation involves generation and subsequent reaction of various radicals and reacting species with the target compounds. This chapter discusses the fundamentals and chemistry and efficiencies of the Fenton process, ozonation, electrochemical oxidation, and photocatalysis processes for complete dye removal from wastewater. The reaction mechanisms, performance, and factors affecting efficiency are discussed.

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INTRODUCTION

The textile, printing and leather industries are known for the use of chemicals, especially, in the wetting processes where bleaching, dyeing and finishing take place. The large volumes of wastewater from these industries present serious environmental problems due to their high concentration of non-biodegradable dyes responsible for the intense colour of the effluents, variations in pH, temperature, high levels of dissolved solids and COD together with presence of toxic heavy metal content such as As, Cr, Cu among others (Sundrarajan et al., 2007). Removal of dyes from wastewater is therefore a subject of interest for academicians, environmentalists and regulatory authorities.

The most widely used traditional wastewater treatment process for textile effluents is chemical precipitation. However, alum coagulants generate large volumes of sludge that present disposal challenges among other inherent limitations. Furthermore, conventional wastewater treatment strategies are incapable to completely remove dye compounds or reduction to molecular levels considered safe for human and aquatic life and can therefore be reintroduced into receiving surface waters. To circumvent these challenges, advanced oxidation processes (AOPs) are emergent techniques based on reaction of active radicals, generated by different methods, with organic contaminants. Advanced oxidation processes include the use of hydrogen peroxide (H_2O_2), ozone (O_3) and UV radiation singly or combined. Table 1 highlights the oxidation potentials of certain chemical oxidizers (Babuponnusami and Muthukumar, 2011).

Table 1. Standard potential of common oxidants

Oxidant	Oxidation Potential (V)
Fluorine (F_2)	3.03
Hydroxyl radical (HO•)	2.80
Atomic Oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Hypochlorite	1.49
Chlorine (Cl_2)	1.36
Potassium permanganate ($KMnO_4$)	1.67
Chlorine dioxide (ClO_2)	1.5
Hypochlorous acid (HClO)	1.49
Oxygen (O_2)	1.23
Bromine (Br_2)	1.09

This chapter reviews the fundamentals and chemistry of advanced oxidation processes, specifically the Fenton process, ozonation, electrochemical oxidation, and photocatalysis. The factors affecting the efficiency of these techniques are also concisely discussed. Finally, selected studies on the application of the Fenton process, ozonation, electrochemical oxidation, and photocatalysis for dye removal from wastewater and cost analysis of AOPs is presented.

ADVANCED OXIDATION PROCESSES

Advanced oxidation processes are categorized based on the reactive phase (homogeneous and heterogeneous) or means of hydroxyl radical production (chemical, electro-chemical, sono-chemical and photochemical). Table 2 is a summary of the categories of conventional advanced oxidation processes according to the source used for production of hydroxyl radicals. The processes involving synergy of traditional and new advanced oxidation processes like photo-electro-Fenton and sono-electro-Fenton are also highlighted. However, other non-conventional advanced oxidation processes such as ionizing radiation, microwaves and pulsed plasma techniques are not herein discussed (Klavarioti et al., 2009). Noteworthy, solar-irradiated processes are intended to lower the costs related with the dependence on light from non-natural sources though they suffer the inherent limitation of applicability in regions with insufficient solar radiation (Anderson et al., 1991).

The next section discusses the chemistry and mechanisms of the Fenton process.

Table 2. Categories of advanced oxidation processes

Process	Example	References
Photocatalysis	UV/TiO_2, UV/TiO_2/H_2O_2	Tang & An (1995)
Fenton-based	Fe^{2+}/ H_2O_2, Fe^{2+}/US/H_2O_2 Fe^{2+}/UV/ H_2O_2	Bokare & Choi (2014)
Ozone-based	O_3/H_2O_2, O_3/UV, O_3/UV/ H_2O_2	Huang-Yee & Ching-Rong (1995)
Sonolysis	US/H_2O_2, US/O_3, US/UV/TiO_2	Cuiping et al (2011)
Electrochemical oxidation	Electron Fenton	He & Zhou (2017)
Other AOPs	Supercritical water oxidation	Gong & Xi (2008)

The Fenton Process

The Fenton processes, named after the discoverer H.J.H. Fenton in 1894, involve the reactions of peroxides (mostly H_2O_2) with iron ions to form active oxygen moieties that oxidize the target compounds. Fenton discovered that H_2O_2 could be activated by ferrous (Fe^{2+}) ions to oxidize tartaric acid (Fenton, 1894). Literature is replete with data dating back to decades ago on the application of the Fenton process involving $HO^{\bullet}$ reactions with organic and inorganic compounds in aqueous solution (Buxton et al., 1988). The Fenton reaction has been demonstrated to be an efficient technique for abatement of toxic organic contaminants from wastewater treatment.

Sychev and Isak (1995) reported a detailed mechanism and reaction rates for the Fenton process. The step represented by equation 1 encompasses the oxidation of iron Fe^{2+} to Fe^{3+} ions with concomitant decomposition of hydrogen peroxide into hydroxyl radicals and this step is recognized as the fundamental of the Fenton process. Furthermore, other intermediate reactions need to be investigated to comprehensively describe the entire Fenton process:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{-}OH + HO^{\bullet} k_{2.1} = 40\text{-}80 \text{ L mol}^{-1} \text{ s}^{-1} \tag{1}$$

However, the Fe^{3+} ions produced in equation 1 can be reduced back to Fe^{2+} ions in excess H_2O_2 with the formation of more active species, the hydroperoxyl radicals (${}^{\bullet}O_2H$), in the so called Fenton-like reaction represented by equation 2. This reaction is not only far much slower than the Fenton reaction, as depicted by the rate constant, but also reflects regeneration of Fe^{2+}. The generated hydroperoxyl radicals can also destroy organic pollutants, though they possess much lower standard reduction potentials than hydroxyl radicals. The regeneration of iron implies that the iron acts as a catalyst while H_2O_2 is depleted to generate hydroxyl radicals.

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}O_2H + H^{+} k_{2.2} = 9.1\times10^{-7} \text{ L mol}^{-1} \text{ s}^{-1} \tag{2}$$

Equation 3 describes the oxidation of ferrous ions by the hydroxyl radicals to form ferric ions and hydroxyl ions.

$$Fe^{2+} + HO^{\bullet} \longrightarrow Fe^{3+} + OH^{-} k_{2.3} = 2.5\text{-}5\times10^{8} \text{ L mol}^{-1} \text{ s}^{-1} \tag{3}$$

Equation 4 describes the oxidation of ferrous ions by the hydroperoxyl radicals to form ferric ions.

$$Fe^{2+} + {}^{\bullet}O_2H \longrightarrow Fe^{3+} + HO_2^{-} k_{2.4} = 0.72\text{-}1.5\times10^{6} \text{ L mol}^{-1} \text{ s}^{-1} \tag{4}$$

Equation 5 describes the oxidation of ferrous ions by the hydroperoxyl radicals to form ferric ions and hydrogen ions and oxygen gas.

$$Fe^{2+} + {}^{\bullet}O_2H \longrightarrow Fe^{3+} + O_2 + H^{+} k_{2.5} = 0.33\text{-}2.1\times10^{6}\ L\ mol^{-1}\ s^{-1} \quad (5)$$

From the rate constants, equation 2 with the smallest rate constant representing the slowest reaction seems to be the rate limiting step. Besides the aforementioned reactions, other reactions include reported include radical–radical reaction and hydrogen peroxide–radical reaction as shown in equation 6 and equation 7, respectively.

$$HO^{\bullet} + HO^{\bullet} \longrightarrow H_2O_2 k_{2.6} = 5\text{-}8\times10^{9}\ L\ mol^{-1}\ s^{-1} \quad (6)$$

$$HO^{\bullet} + H_2O_2 \longrightarrow {}^{\bullet}O_2H + H_2O\ k_{2.7} = 1.7\text{-}4.5\times10^{7}\ L\ mol^{-1}\ s^{-1} \quad (7)$$

However, another side reaction that results in depletion of the oxidant hence increased treatment costs is the decomposition of H_2O_2 to molecular oxygen as described by equation 8 (Pignatello et al., 2006):

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \quad (8)$$

The above reactions are a testament to the complexity of the mechanistic processes of the Fenton reaction. Equation 1 represents the chain initiation step that generates the required hydroxyl radical. However, the so-generated hydroxyl radicals can be consumed by the Fe^{2+} ions, hydrogen peroxide, hydroperoxyl radicals, or may be auto scavenged as shown in equations 3 to 7. The equations also indicate that H_2O_2 acts both as radical generator (Equation 1) and as radical scavenger (Equation 7). These hydroxyl radicals are responsible for chemical destruction of the organic contaminants present in the effluent.

The Fenton process has several inherent advantages. These include; the process is spontaneous at room temperature. Additionally, the required reagents are relatively cheap, readily available, easy to store and handle and are eco-environmentally (Pignatello et al., 2006). However, the Fenton process suffers two main limitations. Firstly, the radical scavenging effect of hydrogen peroxide results to wastage of the oxidants. Secondly, the process is cumbered with continuous loss of iron ions and the formation of solid sludge. Several economic and environmental shortcomings have been associated with Fenton process generated sludge (Benatti et al., 2009). Recent studies have reported emerging technologies, equipment and experimental conditions for economical, efficient and sustainable use of oxidants, primarily hydrogen peroxide and recovery and recycling of Fe^{2+} ions.

The efficiency of any wastewater treatment process is dependent on the operation conditions. Below are factors affecting the performance of the Fenton process for organics oxidation.

The Solution pH

Solution pH is an important parameter in water treatment processes since it affects the speciation of molecules, both reagents and contaminants. However, several studies suggest that pH 3 is the optimum pH for the Fenton process regardless of the target pollutants (Ma et al., 2000; Rivas et al., 2001). The activity of Fenton reagent is significantly retarded by increased pH attributed to the formation of relatively inactive iron oxohydroxides and insoluble iron (III) hydroxide (Parson, 2004). Under these conditions, the precipitation reduces the amount of iron ions in solution resulting to production of less hydroxyl radicals. Increase in solution pH decreases the oxidation potential of hydroxyl radicals and promotes auto-decomposition of hydrogen peroxide (Szpyrkowicz et al., 2001). On the other hand, pH values below 3 impede the Fenton process efficiency due to formation of iron complex moieties $[Fe(H_2O)_6]^{2+}$, which reacts quite slowly with hydrogen peroxide relative to other moieties (Kavitha et al., 2005). Furthermore, the peroxide becomes solvated in the presence of high concentration of hydrogen (H^+) ions to form stable oxonium ion $[H_3O_2]^+$ which imbues the H_2O_2 with increased stability thus reducing its reactivity with Fe^{2+} ions (Kavitha et al., 2005). Ultimately, the ability of the Fenton reaction to oxidize and destroy organic contaminants is significantly reduced both at low and high pH. Thus an optimized pH control increases the process performance. Noteworthy, the identity of the buffer solution used for pH control affects the efficiency of the process. For example, acetic acid/acetate buffer posted the highest oxidation efficiency while phosphate and sulfate buffers revealed the least (Benitez et al., 2001). This is possibly due to generation of stable Fe^{3+} complexes formed under these conditions.

Iron (II) Ions Concentration

Lin and Lo (1997) reported that the rate of mineralization of organics increases with rise in Fe^{2+} ions concentration. However, Lin et al. (1999) observed that increment in the rate becomes minimal beyond certain limits of Fe^{2+} ions concentration. Similar observations have been reported by other researchers (Kang and Hwang, 2000). Furthermore, excess iron ions result in unused iron salts that increased the total dissolved solids (TDS) levels beyond allowable limits.

H_2O_2 Concentration

The amount of H_2O_2 is an important parameter in optimizing the efficiency of the Fenton reaction. Generally, the contaminant degradation efficiency increases with increase in the concentration of the oxidant (Kang and Hwang, 2000). However, excess H_2O_2 results to increased COD of the wastewater. Furthermore, H_2O_2 is toxic to many of the microbial organisms and would therefore impede biological degradation in systems where the Fenton process precedes biological treatment (Ito et al., 1998). Furthermore, H_2O_2 had been previously shown to be hydroxyl radicals ($HO^{\bullet}$) scavenger at high concentrations. The optimum amount of H_2O_2 should be determined empirically from small scale experiments.

Initial Contaminant Concentration

Studies show that when the initial contaminant concentration is low, then the removal efficiency is increased (Benitez et al., 2001). Nevertheless, for the Fenton reaction to be effective in treating large volumes of industrial effluents, dilution is necessary and the dilution ratio must be carefully selected.

Operating Temperature

There is paucity of data on the effects of temperature on Fenton oxidation reactions with some contradictory reports. For example, Rivas and co-workers (2001) noted that the Fenton oxidation efficiency was independent of temperature when the temperature was raised from 283 to 313 K. Furthermore, efficient consumption of H_2O_2 is significantly diminished at higher temperatures as a consequence of increased decomposition of H_2O_2 into water and molecular oxygen (Nesheiwat and Swanson, 2000). Importantly, increased temperatures invite higher operational costs and may not be practical for treatment of real industrial effluent.

Chemical Coagulation

Since the Fenton process involves utilization of soluble iron salts in the treatment process, chemical coagulation becomes a necessary step for regulation of the concentration of the total dissolved solids (TSS) below the recommended limits (Lin et al. 1999).

Effect of the Agitation Speed

Mohajeri et al. (2010) investigated the effect of agitation speed on the efficiency of Fenton oxidation of leachate and reported a strong correlation between the efficiency of the oxidation process for removal of color and the agitation speed. Increased agitation speed led to increased removal efficiencies but beyond some limit there was no significant change in removal efficiency was observed.

Effect of Contact Time

In a study evaluating the effect of reaction time on Fenton oxidation reaction, Mohajeri and co-authors (2010) noted that the removal of color increased with reaction time from 30 min through 360 min with maximum removal observed at 120 min. In a separate study, Karthikeyan et al. (2011), reported a linear increase in the percentage removal of COD with time up to 4 hours. Increase in efficiency is due to increased contact time.

Effect of Feeding Mode

According to Rui et al. (2010), feeding modes could be classified into three categories and each feeding mode influenced the removal efficiency of total organic carbon (TOC). The proposed feeding modes and their removal efficiencies are as follows:

1. When H_2O_2 was introduced in totality in the reactor at the onset of the process, the TOC removal efficiency was 56%
2. When introduction of H_2O_2 was divided into 6 hourly injections, the TOC removal efficiency was 61%
3. When introduction of H_2O_2 was divided into 12 half-hour injections, the TOC removal efficiency was 67%

The low removal efficiency with bulk introduction of H_2O_2 at the onset of the process is attributed to the radical scavenger effect of H_2O_2 when present in large quantities. Similar observation was also reported by Mohajeri et al. (2010). The results depict that stepwise addition of Fenton's reagent is recommended.

10 APPLICATIONS OF FENTON PROCESS FOR DYE REMOVAL FROM WATER

Literature is replete with data on the use of the Fenton's process for decomposition of dyes from wastewater. The mechanism of reaction, as aforementioned, entails reaction of the dyes with the hydroxyl radicals ($HO^{\bullet}$) either by removal of a hydrogen atom or addition of the hydroxyl to double bonds. Rodrigues et al. (2009) reported the removal of green cationic dyes from textile wastewater by the Fenton process. The study reported an increase in percent dye removal with increase in Fe^{2+} ions concentration. In another study, Meric and co-workers (2005) reported an effective Fenton's oxidation of four dyes, namely; Remazol Black 5, Remazol Red, Remazol Blue, and Remazol Yellow with above 99% removal efficiency. Elsewhere, Tantak and Chaudhari (2006) demonstrated that the Fenton's reaction could sequester more than 90% of RB5, RB13, and AO7 azo dyes. Badawy and Ali (2006) also achieved complete removal of colour from industrial and domestic wastewater with concomitant 90% decrease in COD using the Fenton process.

Ozonation

Ozonation is one of the most advanced method that has been applied in removal of dyes and disinfection of other pollutants found in wastewater. The common dyes used industrially are the azo derivatives. These dye molecules contain chromophore groups, which are organic compounds with conjugated double bonds. Ozone which is a powerful oxidizing agent is used to oxidize the double bonds in the dyes to form smaller molecules and decolorize the dye effluents.

Mechanism of Oxidation of Dyes by Ozone

Ozonation of dye molecules leads to the formation of benzene and naphthalene derivatives that undergo further oxidation to release aldehydes, ketones and acetic acid (Tang and An, 1995). The destruction of the azo dye molecules increases the COD value in the dye solutions because these fragments of the dye molecules do not completely mineralize during oxidation. As a result, other water treatment methods have been applied together with ozonation for complete removal of these dyes (Venkatesh et al., 2017). For instance, a study by Fahmi and co-workers (2010), demonstrated that biological treatment followed ozone oxidation could completely remove biodegradable dye fragments. The oxidation process of the double bonds by ozone has been categorized as direct ozonation or indirect ozonation. Direct ozonation involves the breaking down of double bonds using molecular ozone (Guo et al., 2012), while indirect ozonation involves the oxidation of the double bonds using the radicals such as hydroxyl resulting from the decomposition of ozone in aqueous solutions (Alvarez et al., 2011).

The chain reaction mechanism of the decomposition of ozone in aqueous solutions is as described by Tomiyasu et al. (1985) and Staehelin and Hoigne (1985). The Hoigne, Staehelin and Buehler (HSB) model with the reaction rates is as shown in the following equations (Staehelin and Hoigne, 1985).

$$O_3 + OH^- \longrightarrow \bullet_2OH + \bullet^-_2O\ k = 70\ L\ mol^{-1}\ s^{-1} \tag{9}$$

$$O_3 + \bullet^-_2O \longrightarrow O_2 + O_3\bullet^- k = 1.6 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{10}$$

$$H + O_3\bullet^- \longrightarrow HO_3\bullet\ pk_a = 10.3\ L\ mol^{-1}\ s^{-1} \tag{11}$$

$$HO_3\bullet \longrightarrow HO\bullet + O_2 k = 1.1 \times 10^5\ L\ mol^{-1}\ s^{-1} \tag{12}$$

$$HO_3\bullet + O_3 \longrightarrow HO_4\bullet k = 2.0 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{13}$$

$$HO_4\bullet \longrightarrow HO_2\bullet + O_2 k = 2.8 \times 10^4\ L\ mol^{-1}\ s^{-1} \tag{14}$$

$$2HO_4\bullet \longrightarrow H_2O_2 + 2O_3 k = 5.0 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{15}$$

$$HO_4\bullet + HO_3\bullet \longrightarrow H_2O_2 + 2O_3 + O_2 k = 5.0 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{16}$$

A simple form of the reaction mechanism is illustrated by Selcuk (2005) in the following equations

$$O_3 + OH^- \longrightarrow HO_2\bullet + O_2\bullet^- \tag{17}$$

$$O_3 + HO_2\bullet \longrightarrow OH\bullet + 2O_2\bullet^- \tag{18}$$

$$O_3 + OH\bullet \longrightarrow O_3\bullet + OH \tag{19}$$

$$O_3^{\bullet} \longrightarrow O^{\bullet} + O_2 \quad (20)$$

$$O^{\bullet} + H^{+} \longrightarrow OH^{\bullet} \quad (21)$$

$$OH^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O + O_2 \quad (22)$$

Factors Affecting the Ozonation Process

The ozonation process is greatly influenced by factors such as ozone dosage, pH, temperature initial dye concentration of the wastewater and the presence of initiators such UV irradiation. The effects of these variable parameters are discussed hereunder.

Ozone Dosage

The efficiency of the ozonation process depends on the ozone dosage used (Cheldy and Naser, 2011). Increase in ozone dosage results to increased efficiency in the ozonation process. The rate of oxidation is directly proportional to the ozone feed rate, implying that an increase in the pollutants leads to increased ozone consumption.

The presence of the NaCl and Na_2SO_4 in the textile effluents which are normally used to stabilize the dyes have been reported to hinder the ozonation process. According to Selvakumar (2004), more decolouration time was required when there was a higher content of these salts in the dye effluents. The presence of carbonates and bicarbonates in the effluents, which are formed as a result of the mineralization of the dyes, also reduce the ozonation efficiency because they are radical scavengers (Zhang et al., 2006).

The nature of the dye also influences the ozone dosage and hence the ozonation efficiency. For instance, as demonstrated by Davis et al. (1994), the chemical structure of the dye can influence its decomposition rate.

Operation pH

The pH of the dye solution has been observed to decrease while the electrical conductivity of the increases during the oxidation process. The decline in the pH has been attributed to the formation of organic acid intermediates (Colindres et al., 2010) and as result the increase in electrical conductivity increases is associated to the accumulation of ions (Venkatesh *et al*, 2017).

The pH of the effluent influences the ozonation mechanism. Direct oxidation, which makes use of molecular ozone, is predominantly under acidic conditions (Ku et al., 2000) while under alkaline conditions, indirect oxidation is more pronounced (Chu, 2003). The studies reported in the pH range 2-11 show that at low pH the ozone molecule takes part directly while at high pH the decomposition of ozone generates hydroxyl radicals that react with the pollutants (Glaze et al., 1987). The decolorization rate of the dye has been observed to be higher in acidic medium than in alkaline conditions. This is attributed to presence of carbonates and bicarbonates formed at high pH that act as radical scavengers resulting in decrease in the hydroxyl radicals (Song *et al*., 2009). However, other studies have observed that variation of initial pH of the solution does not show a noticeable difference in the decolorization rate (Parsa and Negahdar, 2012; Zhang et al. 2006).

Temperature

Studies show that temperature influences the ozonation efficiency. Wu and Wang (2001) reported that the decomposition of a dye increases with increase in temperature. On the contrary, Oguz et al. (2005) demonstrated that dye and COD removal decreases with increase in temperature. The study attributed this phenomenon to the decrease in ozone solubility in the dye solution as temperature increased. The increase in temperature, therefore, results to reduced degradation of the pollutants because of the decreased availability of ozone (Gotteschalk et al., 2010).

A report by Koyuncu and Afsar (1996), however, indicates that the effect of temperature on the decomposition of the azo dyes is negligible.

Initial Dye Concentration

The dye load indicates the extent of pollution in the textile wastewater. Studies on the initial dye concentration in the range of 20 mg/L to 3000 mg/L have been reported. The decolorization rate is reported to decrease with increase in the initial dye concentration this is due to the decrease in the ratio of ozone molecules to dye molecules in the solution. An increase in the initial dye concentration results to increased ozone consumption (Cuiping *et al*., 2011). It is also possible that as the dye concentration increases there is an increase in the formation of dye intermediates which may resist ozonation or require more contact time for complete removal or both.

Initiators

Oxidation process can be enhanced by use of catalysts such ultrasonic and ultraviolet (UV) irradiation (Zhang et al., 2006). Ultrasound (US) waves are used to produce hydroxyl ions through thermal decomposition of water (Naffrechoux et al., 2000). The combination of UV irradiation and ozone produces more OH radicals through photocatalysis of reactive intermediates such as hydrogen peroxide. Ozone absorbs at 260 nm strongly hence integration of UV in the ozonation system enhances

Table 3. The percent decolorization of different dyes at various conditions

Dye	Ozone Flow Rate (g/h)	Initial Concentration (mg/L)	Initial pH	Ozonation Time (min)	% Removal	Ref
Reactive Black 5	5	1500	10.13	25	93.5	Venkatesh *et al*., 2017
Rhodamine B	5	50-200	2-10	15	99.78	Cuiping *et al* 2011
Acid Blue 92	120	100	2-10	20	85	Parsa and Negahdar(2012)
CI Direct Red	5	1500		25	90	Venkatesh *et al* 2014
Methyl orange		400	5.5			Zhang *et al*., 2006

degradation of the pollutants (Ku et al., 2000; Song et al., 2011). The UV enhances the ozonation process by forming oxidants as indicated in equation 23 below:

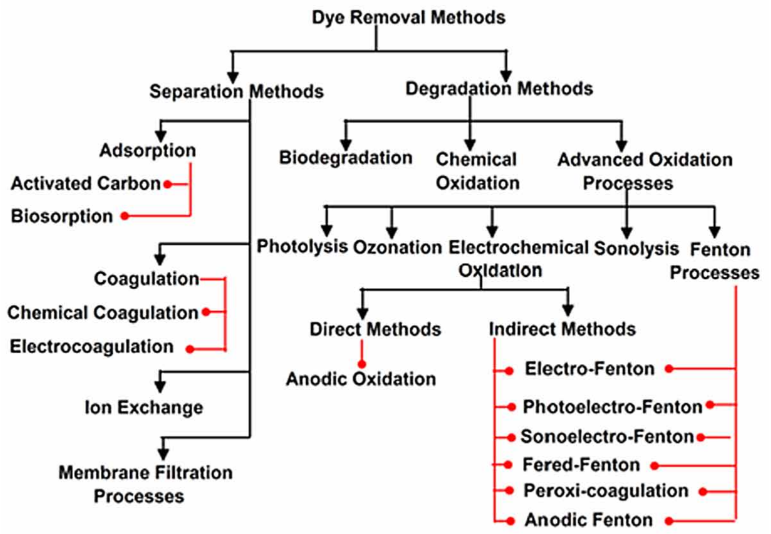
$$O_3 + H_2O + hv \longrightarrow H_2O_2 + O_2 \tag{23}$$

Cuiping et al. (2011) compared removal of Rhodamine B from aqueous solution at pH=3 using ozone, US/ozone and UV/ozone, the study reported that decolorization rates were 86.86%, 94.05% and 97.76%, respectively, during 15 min. The best combination of ozone was that with UV which recorded decolorization of 99.78% within 15 min. Studies on removal of various dyes undertaken in different operational parameters are listed in Table 3.

ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES

In the past decade, oxidative removal of various organic contaminants by electrochemically generated hydroxyl radical has received considerable attention. This section highlights, albeit in brief, some recent developments in application electrochemical advanced oxidation processes (EAOPs) dye removal from aqueous solutions. The processes that comprise EAOPs include; anodic oxidation, electro-Fenton, peroxi-coagulation, fered Fenton, anodic Fenton, photoelectro-Fenton, sonoelectro-Fenton, and bioelectro-Fenton among others (Nidheesh et al., 2018). The principles of a few of these processes have been outlined. Generally, dye removal processes can be divided into two broad classes: Separative (physical, and physicochemical) processes, and degradative (chemical and biological) processes as summarized in Figure 1 (Nidheesh et al., 2018).

Figure 1. Summary of dye removal methods



One of the major inherent limitation of separative techniques is generation of large quantities of dye laden sludge and adsorbents that present disposal challenges. Here, degradation methods, such as AOPs, are helpful for they mineralize the organic compounds to liberate CO_2, water and other inorganic ions as by-products.

Electrochemical AOPs are based on production of produced hydroxyl radicals for the mineralization of organic pollutants from an electrochemical reaction/process. This leads to the two types of EAOPs, direct and indirect EAOPs (Figure 1), depending on how the electrolytic system generates the hydroxyl radicals.

In the case of direct EAOPs, hydroxyl radicals are produced on the anode surface by direct oxidation of water as described by Equation 24 where M is the anode material:

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \tag{24}$$

The radicals' production rate depends on the catalytic activity of the anode material, diffusion rate of organic contaminants to the anodic active sites and applied the current density (Miled et al., 2010). Here, addition of reagents from external sources to generate hydroxyl radicals is not required. On the other hand, for indirect EAOPs, the hydroxyl radicals production is based on the Fenton chemistry, as previously discussed, with addition of *in situ* electrochemical generation (electro-Fenton) or externally addition of the one of the reagent (H_2O_2 or ferrous iron) (fered-Fenton) (Brillas et al., 2014).

The main advantage of the EAOPs over traditional wastewater discoloration methods is eco-friendliness since the main reagent for all the EAOPs is electron, an inbuilt clean species (Peralta-Hernández et al., 2009). Other merits include versatility, higher contaminant removal efficiency, operational safety and ease of automation (Sirés et al., 2014). Furthermore, the presence of dissolved ions in the untreated wastewater may ameliorate the process efficiency with concomitant reduction in energy consumption (Zhou et al., 2011).

Direct Electrochemical AOPs

As aforementioned, direct electrochemical AOPs produces hydroxyl radicals without the external addition of reagents. The following section is a brief description of dye removal from water by anodic oxidation.

Anodic Oxidation

In anodic oxidation, the hydroxyl radical is produced at the anode surface (Panizza and Cerisola, 2009). The process is heterogeneous and the hydroxyl radicals generated are either chemisorbed (e.g on platinum anode) or physisorbed (e.g on boron doped diamond (BDD)) on the anode surface. However, the chemisorbed radicals become less available for oxidation of organic compounds unlike in physisorbed systems. The mineralization of organics by anodic oxidation has been described in literature (Scialdone, 2009) and the details are not reiterated here. In brief, heterogeneous hydroxyl radicals MOx(HO●) are produced by the oxidation of water according to equation 25 and the lead to liberation of oxygen as in equation 26 catalytically regeneration the anode surface. The MOx(HO●) together with the liberated oxygen then mineralize the organic contaminant as in equation 27.

$$MO_x + H_2O \longrightarrow MO_x(HO^\bullet) + H^+ + e^- \quad (25)$$

$$MO_x(HO^\bullet) \longrightarrow MO_x + H^+ + e^- + 0.5O_2 \quad (26)$$

$$MO_x(HO^\bullet) + RH \longrightarrow MO_x + H_2O + R^\bullet \quad (27)$$

According to Comninellis and Battisti (1996), organic contaminants can be mineralized by either electrochemical conversion into biodegradable byproducts such as short-chain carboxylic acids, or by complete electrochemical incineration into CO_2, H_2O and inorganic ions. The efficiency of anodic oxidation depends largely on the selection of the anode material.

Dye Removal by Anodic Oxidation

Many reports on dye removal by anodic oxidation exist in literature and only a few are highlighted. Faouzi et al. (2007) reported complete mineralization of alizarin red S by anodic oxidation using boron doped diamond anode. Similar findings using boron doped diamond (BDD) anode anode were reported by Panizza et al. (2007) for removal of methylene blue an aqueous solution. BBD anode was also used for oxidation of methyl orange dye with 94% decolorization efficiency (Ramírez et al., 2013). Elsewhere, Zhao and co-authors (2009) reported complete degradation of methyl orange dye in the presence of *in situ* microwave activated platinum. Canizares and others (2009) described the decomposition of Congo red, methyl orange, and eriochrome black T, using conductive-diamond anodes. Panizza and Cerisola (2008) reported a comparative study on the removal efficiencies of BDD and PbO2 electrodes. The study revealed that BDD anode had higher oxidation rate and higher current efficiency than PbO2 anode. A similar study showed that methyl orange degradation efficiency of TiRuSnO2 anode was much lower than that of BDD and PbO2 anodes (Labiadh et al., 2016). The removal efficiencies of anodic oxidation depend on several factors such as choice of anode, mode of action and design, initial dye concentration among other operational conditions. Overall, anodic oxidation processes are efficient and widely used techniques for color removal from water.

Indirect Electrochemical AOPs

In indirect EAOPs, hydroxyl radicals are generated *in situ* or by external addition of reagents. The different kinds of indirect EAOPs are shown in Figure 2. In this section, only the Fered-Fenton and Electro-Fenton processes will be considered.

The Fered-Fenton AOP

The Fered-Fenton process is an adjusted mode of the Fenton process. Here, H_2O_2 and Fe^{2+} ions are added from an external source into the electrolytic cell and the ferrous iron regenerated electrochemically from reduction of ferric ions (Fe^{3+}) formed in Fenton's reaction, (see section on Fenton reaction), to improve the process efficiency (Brillas et al., 2014). In the presence of hydrogen peroxide and ferrous ions, the standard Fenton's reaction occurs and the so produced hydroxyl radicals (●OH) mineralize the organic contaminants. Therefore, the degradation of the organics is attributed to the normal Fenton process reinforced by electrochemistry. This is because the Fenton's reaction is catalyzed by the regeneration of ferrous ions from the electrochemical reduction of Fe^{3+} ions (Brillas et al., 2014).

The Electro-Fenton AOP

Electro-Fenton process is a cost effective and co-friendly method for sequestration of organic pollutants from water. Electro-Fenton process is reported to have high organics mineralization efficiency besides the aforementioned advantages and hence has gained popularity amongst researchers over time (Sirés et al., 2014).

In principle, the electro-Fenton process is based on the *in situ* electrogeneration of a mixture of H_2O_2 and Fe^{2+} which produce hydroxyl radicals by the Fenton's reaction. At the cathode surface H_2O_2 is generated from the two electron reduction of O_2 in the acidic medium as shown in equation 28 (Özcan et al., 2009a). This is required for the production of H_2O_2 in the electrolytic system. With H_2O_2, addition of Fe^{2+} ions into the solution from external source results in generation of $\cdot OH$ according to Fenton's reaction.

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \tag{28}$$

Several studies have reported the use of electro-Fenton process removal of dyes from water and selected results are hereunder highlighted.

Dye Removal by Electro-Fenton Process

Literature is replete with studies on the use of electro-Fenton (EF) process for depollution of dyes. The factors affecting the performance of EF processes include; pH, catalyst dosage, initial dye concentration, electrode area, applied current and inner electrode spacing and the hardness in the water (dos Santos et al., 2016). Lahkimi et al. (2007) reported rapid sequestration of methylene blue, Congo red and yellow drimaren using carbon felt cathode and Pt sheet anode in single solute and mixed solutions. Elsewhere, Olvera-Vargas and co-authors (2014) achieved complete mineralization of azure B in 8 hours using electro-Fenton method. A comparative study on the efficiencies of electro-Fenton and anodic oxidation techniques for abatement of indigo dye showed electro-Fenton was more efficient in mineralization of indigo dye than anodic oxidation with total destruction achieved in 2 hours Diagne et al. (2014). A comprehensive study by Sirés et al. (2008) on removal efficiency of EF process for depollution of crystal violet (CV), fast green FCF (FCF), methyl green (MeG) and malachite green (MaG) demonstrated that the rate constants for their reaction with HO● radicals increased in the order MeG

< FCF < CV < MaG. A detailed review of studies on dye removal electro-Fenton process has been described by Nidheesh et al., (2012).

Overall, the studies show that electrochemical advanced oxidation processes are effective techniques for dye removal from wastewater subject to further on-site factors.

PHOTOCATALYSIS

The photocatalysis process is a photo induced reaction initiated by a photocatalyst. The process makes use of solar energy and atmospheric oxygen as an oxidant to completely destroy organic pollutants to carbon dioxide and water. It is an effective alternative oxidation technique because it operates under ambient conditions without the input of oxidants and does not produce harmful waste.

Mechanism

Photocatalysis is a heterogeneous process that uses various semiconductors such as TiO_2, ZnO, V_2O, ZnS, CdS among others (Chin et al., 2010). The most commonly studied photocatalyst is TiO_2 because of its photostability, availability, high photocatalytic ability, low operation temperature, low energy consumption and it is biologically inert (Shneider et al., 2014). Photocatalytic activity depends on the surface and structural properties of the semiconductor which include; crystal composition, specific surface area, particle size distribution and band gap (Testino et al., 2007). Particle size plays a crucial role in photocatalysis because it is a heterogeneous process and its efficiency is directly dependent on the specific surface area (Qi et al., 2010). There are three different polymorphs of TiO_2: anatase, rutile and brookite. Anatase is the most photoactive due to its large surface area (Chin et al., 2010). Due to the synergistic effect, TiO_2 is Degussa-P25 -which is 70% anatase and 30% rutile- is the commonly studied due to its relatively high photocatalytic activity (Hussein and Abbas, 2010).

Irradiation of the semiconductor generates electrons and holes if the energy of the incident photons is greater or equal to the metal oxide band gap energy. The electron-hole pairs created initiate photocatalytic reactions (Chen et al., 2015). The energy band gap associated with the most commonly used photocatalyst, TiO_2, is around 3.2eV (390nm). The following equations 28-38 describe the mechanism for photocatalytic oxidation (Fernandez et al., 2002; Zangeneh et al., 2014).

$$TiO_2 + hv \longrightarrow TiO_2\ (e^- + h^+) \tag{29}$$

The positive holes react with electron donors in the solutions to produce hydroxyl radicals or the electrons react with other molecules like oxygen to form superoxide anions or the charge carriers can also recombine.

$$TiO_2\ (h^+) + H_2O \longrightarrow TiO_2 + H^+ + OH^\bullet \tag{30}$$

$$TiO_2\ (h^+) + OH^- \longrightarrow TiO_2 + OH^\bullet \tag{31}$$

$$TiO_2\ (e^-) + O_2 \longrightarrow TiO_2 + O_2^{\bullet -} \tag{32}$$

$$TiO_2\ (e^- + h^+) \longrightarrow TiO_2 + \text{Heat} \tag{33}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^\bullet \tag{34}$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \tag{35}$$

$$H_2O_2 + O_2^\bullet \longrightarrow OH^\bullet + OH^- + O_2 \tag{36}$$

The positive holes can directly oxidize the organic molecules (OM) at the catalytic surface as the hydroxyl radicals generated react with the OM absorbed by the catalyst to form degradation products.

$$TiO_2\ (h^+) + OM \longrightarrow \text{degradation intermediates } TiO_2 + OM^{\bullet +} \tag{37}$$

$$OM + OH^\bullet \longrightarrow \text{degradation intermediates} + CO_2 + H_2O + \text{salts} \tag{38}$$

However, due to its wide energy band gap, TiO_2 can only be excited by UV light ($\lambda<400$ nm) which means that <5% solar energy is effectively utilized. At the same time, the rapid recombination of the electron-hole pairs as indicated in equation 33 limits its photocatalytic activity. These challenges have propelled continued research for more efficient photocatalysts (Ge et al., 2019).

In the recent past, research has focused on development of composite materials involving incorporating two or more components to form a material that has superior properties relative to the individual components. This approach has been used in designing photocatalysts with enhanced performance resulting from the synergistic effects of the constituent materials (Devi et al., 2010; Wu et al., 2018). Some of the pathways employed to enhance the performance of photocatalysts include doping with heteroatoms and morphological modifications. Doping into the lattice of photocatalytic semiconductors with heteroatoms is done to regulate metal oxide band gaps in order to improve their absorption capacity in visible light (Devi et al., 2010). Morphological modification aims at changing the photocatalytic semiconductors into nanoparticles which have larger specific surface area and are easily be functionalized with other materials to improve their performance (Wu et al., 2018).

Factors that Influence the Photocatalytic Oxidation

The photocatalysis process is influenced by various factors such as pH, temperature, UV light intensity, dissolved oxygen, amount of photocatalyst, the concentration of the dye among others.

Effect of pH

The pH of the wastewater plays an important role in the destruction of the contaminants because the surface of TiO_2 catalyst is charged and the photocatalysis process is dependent on the generation of hydroxyl radicals. The point of zero charge (pzc) of TiO_2 (Degussa P-25) is 6.8 hence, in acidic medium its surface is positively charged while in alkaline medium it is negatively charged (Poulious and Tsachpinis, 1999). At low pH the positive holes are the major oxidation particles while at neutral or high pH levels hydroxyl radicals are predominant hence photodegradation of dyes is enhanced in alkaline solution. It is, therefore, easier for hydroxyl radicals to be produced in alkaline solution (Kim and Lee, 2010). However, other studies have shown that at higher pH (11-13), photocatalytic degradation of azo dyes by titania is inhibited since the hydroxyl radicals do not have sufficient time to react with the dyes in the wastewater. Apart from the surface charge and reaction mechanism of the photocatalyst, the production of hydroxyl radicals; the nature of the organic dye (cationic or anionic) should be considered when interpreting the influence of pH on the efficiency of the photocatalytic activity (Konstantinou and Albanis, 2004).

Effect of Temperature

Increase in the temperature increases the rate of production of hydroxyl radicals resulting to increased oxidation activity of the photocatalyst this has been attributed to increased activation energy (Kim and Lee, 2010). In the photolytic treatment of textile industrial wastewater, Hussein and Abbas (2010) reported that the efficiency of the process was enhanced by increase in temperature.

UV Light Intensity

The light absorbed by the semiconductor at a particular wavelength is determined by the intensity of the UV light and this is achieved by varying the position of the UV lamps. The rate at which the hole-electron pairs are generated in order to initiate the photocatalysis process depends on the light intensity. The separation of hole-electron pairs is efficient at high UV intensity, thus, increased intensity leads to increased production of the hydroxyl radicals resulting to increased destruction of the contaminants (Neema et al., 2009).

A study carried out by Muruganandham and Swaminathan (2006) shows that the photocatalytic degradation of Reactive Orange 4 by TiO_2 under UV irradiation was 95.1% after 60 min while the catalytic oxidation without UV caused 25% dye degradation after 30 min.

Dissolved Oxygen

The presence of dissolved oxygen in the wastewater enhances the photocatalytic oxidation process because the oxygen acts as an electron scavenger. Studies have shown UV/TiO_2 decolourisation of dyes is more efficient in the presence pure oxygen improves than in air (Nam et al., 2002).

The Amount of Photocatalyst

Increased TiO_2 load leads to increased production of hydroxyl radicals due to increased availability of active sites on the catalyst. The initial rate of degradation of azo dyes has been reported to be directly proportional to the amount of photocatalyst (Konstantinou and Albanis 2004). Very high amounts of the catalyst, however, have opposite effects because it may increase solution turbidity. The decrease in photocatalytic activity due increased turbidity has been attributed to a rise in light scattering by the excess photocatalytic particles.

The Concentration of the Dye

The rate of dye degradation increase with the initial dye concentration until a certain level where further increase in dye concentration results to a decreased in the photocatalytic degradation (Saquib and Muneer, 2003). This is because the increased concentration affects the adsorption of the reactants onto the photocatalyst's surface

Table 4. Cost estimation for advanced oxidation process unit

Item	Costs (USD)
Advanced oxidation unit	1,200,000
Piping, valves, electrical (30%)	360,000
Site work (10%)	120,000
Contractor O&P (15%)	252,000
Engineering (15%)	289,800
Contingency (20%)	444,360
TOTAL CAPITAL	2,666,160
Amortized capital	214,864
Annual O&M	207,507
Total annual cost	422,371
Total cost per 1,000 gallons treated	1.34

(Kommineni et al., 2000)

thus interfering with the amount of light penetrating the contaminants that would result to effective oxidation (Tang and An, 1995). The decreased photocatalytic activity due to increase in initial concentration has also been attributed to unavailability of active sites on the photocatalyst (Neppolian et al., 2002). Photocatalysis is therefore demonstrably a suitable technique for dye removal from water.

Cost Analysis of Advanced Oxidation Processes

The costs related to advanced oxidation processes largely depend on the characteristics physic-chemical of the wastewater to be treated and the intended use of the treated effluent. However, most studies provide scanty or no information on cost estimation of the different types of advanced oxidation processes. Furthermore, for actual cost analysis, pilot testing is required to ascertain site specific costs. Cost estimation studies indicate that the main factors influencing the prices were the removal efficiency and influent flow-rate. Here, the capital and operating costs increased with higher removal efficiency (Kommineni et al., 2000; Lin and Leu, 1999; Mahamuni and Adewuyi, 2010). Other factors to be considered in cost analysis include the physical location of the treatment plant, the residence time during treatment and environmental perturbations. For estimation purposes, Kommineni and co-workers (2000) approximations are herein reported for as a typical guideline. Noteworthy, the costs should be varied from time to time to factor in inflation rates, country and other time dependent economic changes. In the study, costs of the various AOPs were estimated and compared. The costs were divided into three categories, namely;

capital, operational, and operating and maintenance costs and the calculations are summarized in Table 4.

Mahamuni and Adewuyi (2010) proposed a method for estimation of treatment costs of various advanced oxidation processes. In the study, the rate constants obtained from the kinetic data were then used to predict the residence time needed for decomposition of the contaminant by 90% of its initial concentration. The residence time was then multiplied by the design flow rate to determine the reactor capacity. Additionally, the total energy consumed by the reactor was calculated, and the value used for estimation of the overall cost of the reactor.

CONCLUSION

Research on the performance and sustainability of advanced oxidation processes, namely Fenton oxidation, ozonation, electrochemical and photocatalysis for wastewater treatment has been on the rise in recent decades. The data on these techniques for sequestration dyes and other organic contaminants suggest AOPs are efficient and cost effective alternative techniques for wastewater treatment. Factors affecting the performance of AOPs include initial contaminant concentration, the amount of oxidizing agents and catalysts, residence time and the characteristics of the effluent (temperature, pH, presence of solids and competing ions) and oxidizing agent feeding mode. Furthermore, the operational and management costs estimation should be determined by pilot testing rather than a theoretical approach. From the assessed literature, ozonation, Fenton oxidation, electrochemical AOPs and photocatalysis are promising, economically viable alternative approaches for removal of dyes, COD and other organic contaminants from wastewater.

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KEY TERMS AND DEFINITIONS

Dye: A natural or synthetic coloring material.

Electrochemical AOPs: These are advanced oxidation processes (AOPs) involving the production of hydroxyl radicals for the mineralization of organic pollutants from electrochemical reactions.

Fenton Process: Fenton processes involve the reactions of peroxides (mostly H_2O_2) with iron ions to form active oxygen moieties that oxidize the target compounds.

Chapter 11

Removal of Dyes From Wastewater by Adsorption Onto Low-Cost Adsorbents

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ABSTRACT

This chapter describes an up-to-date critique of the use of adsorption as a wastewater treatment technique for the removal of dyes. The topics range from the classification of dyes, their occurrence in water and toxicity, various treatment methods, and dye adsorption dynamics onto agricultural wastes and inorganic adsorbents such as clay and metal oxides and adsorption onto microbial biomass under varying operational conditions. It is demonstrated that the discussed materials form alternative adsorbents for dye adsorption from aqueous solutions with comparable or better removal efficiencies relative to the non-renewable coal-based granular activated carbons; they are cheap and abundant. The relative performance of the adsorbents under different environmental parameters for dye removal has also presented. The deductions made and alluded to from various kinetic and adsorption isotherm models are also discussed. The chapter presents the past, present, and suggestions for future considerations in search of non-conventional adsorbents for dye sequestration from aqueous solution.

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INTRODUCTION

Classification of Dyes

A dye is a natural or synthetic coloring material employed for dyeing or printing of textiles, paper, leather and other materials. The color of the dyed or printed materials is anticipated not to be faded by washing, heat, light, or in other external conditions to which the material is frequently exposed. The dyes are normally applied from aqueous solution and are capable of sticking onto compatible surfaces by forming solution, a covalent bond or in situ complexes with salts or metals through physical adsorption or mechanical retention (Babatunde *et al.*, 2018). Dos Santos *et al.* (2007) and Choudhury (2018) stated that classification of dyes is based on either their application methods or chemical structures whereby a group of atoms in dye molecules known as chromophores such as azo, anthraquinone, methine, nitro, arylmethane, carbonyl are responsible for the color of dye while substituents called auxochromes, such as amine, carboxyl, sulphonate and hydroxyl, withdraw and/or donate electrons hence producing or intensifying the colour of the chromophores. Dye classes are as follows: Reactive dyes, Disperse dyes, Direct dyes, Acid dyes including metal complex, Basic or Cationic Dyes, Chrome mordant dyes, Azoic dyes, Sulphur dyes, Vat dyes, Solubilized vat dyes, and Pigment colours etc (Benkhaya *et al.*, 2017; El Harfi & El Harfi, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Reactive Dyes

Reactive dyes are made from synthetic petrochemicals, quite expensive compared to conventional dyes and currently makeup 50% of the world's total dye consumption. Reactive dyes are known to form a complex with textile fibres via covalent bonds ultimately existing as single chemical entities within the fibre. They are not only easy to apply but are also available in a wide range of colour. Although Reactive dyes require good amounts of salt and alkali they create less wastewater problems and are applied at lower temperatures (30-70ºC) than direct dyes (around 100ºC) therefore saving energy. The fastness properties of reactive dyes do not depend on the structure and molecular size of dye, unlike in other dye classes (Benkhaya *et al.*, 2017; El Harfi& El Harfi, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Sulphur Dyes

Sulphur dyes have been applied to both a chemical class of dyes and a dying class. These dyes used to dye cotton with dark colours. Sulfur black is the largest selling dye by volume. The first sulfur dyes were made from thionation of various organic materials with either sulfur or sodium polysulphide and they were all applied to cotton from sodium sulfide solution (Benkhaya *et al.*, 2017; El Harfi& El Harfi, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Disperse Dyes

Dyes generally used for dying cellulose acetate, nylon and other hydrophobic fibers are called disperse dyes. They are also known as acetate dyes. Sulphoricin oleic acid (SOA) is used as the dispersing agent. Dispersal and celliton are important dispersing agents (Benkhaya, El Harfi, & El Harfi, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Direct Dyes

These dyes are used for dyeing animal or vegetable fibers directly from a solution of the dye in water. All dyes of this class are anionic dyes having an affinity for cellulose fibers. Certain direct dyes are extensively employed in the dyeing of paper, leather, baste fibers and other substrates (Benkhaya *et al.*, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

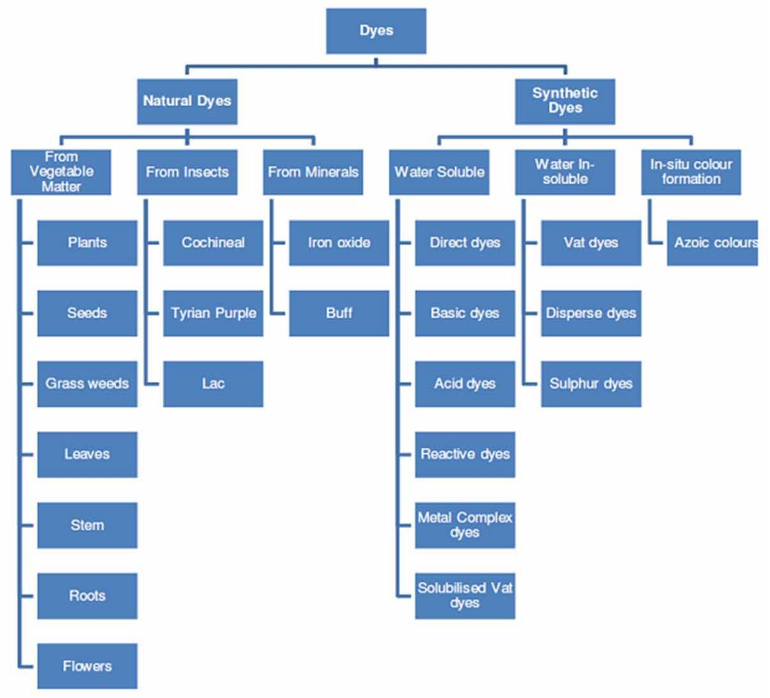
Acid Dyes

The common structural feature of this class of dyes is the chromophoric structure with a sulphonic or analogous group, which gives the dye an anionic character. Acid dyes are mainly used for dyeing wool, silk, nylon etc. These are applied from an acid dye bath (Benkhaya *et al.*, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Basic or Cationic Dyes

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually, acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the colouration of paper (Benkhaya *et al.*, 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Figure 1.



Vat Dyes

Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water-soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye. The colour of denim is due to indigo, the original vat dye (Benkhaya *et al*., 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013). The classification of dyes is summarized in Figure 1 below.

Azoic Dyes

Azoic dyes are produced by reacting two components named coupling method and diazo component contains insoluble azo group. It should be noted here that, azoic dyes are different from other dyes and the application process is also different from others. They are also known as ice colours or magic colours because they require very low temperatures during dyeing (Benkhay*a et al*., 2017; Venkataraman, 1952; Walsh, 1979; Waring & Hallas, 2013).

Table 1. Physical and chemical methods for dye removal from water

Method	Strength	Limitation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life
Photochemical	No sludge production	Formation of by-products
Ion-exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Membrane filtration	Removes all types of dye	Concentrated sludge production
Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Electrokinetic coagulation	Economically feasible	High sludge production
Activated carbon	Good removal of wide variety of dyes	Very costly
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity

REMOVAL OF DYES FROM WASTEWATER

The textile industry consumes a substantial amount of water in its manufacturing processes, mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition (Sen and Demirer, 2003; Dos Santos, 2005; Ben Mansour *et al.*, 2012). In addition, the increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to dye wastewater becoming one of the substantial sources of severe pollution problems in current times (Ogugbue and Sawidis, 2011). Treatment of dye-containing industrial effluents is a subject of great concern among environmentalists and researchers. There are several methods for decolouration of wastewater generally classified into three categories: chemical, physical and biological. Table 1 is a summary of the common methods for treatment of dye-containing effluents with their strengths and limitations. Research in dye removal from water is centered on the capital cost involved, operational costs and sustainability, effectiveness and longevity of the proposed technology.

Adsorption of Dyes Onto Agricultural Wastes

Agricultural byproducts are available in large quantities and are one of the most abundant renewable resources in the world. These waste materials have little or no economic value and frequently present a disposal difficulty (Adegoke & Bello, 2015). Furthermore, agricultural wastes are better than other adsorbents because they are usually used without or with a minimum of processing (washing, drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment (Adegoke & Bello, 2015; Franca *et al*., 2009). Okorocha *et al*. (2016) studied adsorption of basic and acidic dyes from aqueous media onto almond leaves powder (ALP) and observed that it had a good adsorption capacity and rapid kinetics. They also noted that coupled with the low cost of ALP, it appeared to be a promising adsorbent material for the removal of Crystal Violet (CV) and Congo Red (CR) dyes. Ansari *et al*. (2016) employed cauliflower leaf powder (CLP), a biosorbent prepared from seasonal agricultural crop waste material as a prospective adsorbent for the removal of a basic dye, methylene blue (MB) from aqueous solution by the batch adsorption method under varying conditions. The study established that CLP displayed considerable potential as a low-cost adsorbent in wastewater treatment for the removal of the basic dye, MB. Application of raw Bangalora (Totapuri) mango seed kernel powder (RMS) and surface-modified Bangalora (Totapuri) mango seed kernel powder (SMMS) for the removal of methylene blue (MB) dye from aqueous solution was investigated under ambient by Senthil Kumar *et al*. (2014). The findings convinced that both RMS and SMMS have high potential towards the removal of MB dye from the aqueous solution. A review by Bharathi and Ramesh (2013) presented a wide range of agricultural waste materials as low-cost adsorbents. The use of these low-cost biosorbents was recommended owing to their relatively cheap or of no-cost, easily available, renewable and show highly affinity for dyes. The researchers pointed out that the process of biosorption requires more investigation in the direction of modeling, regeneration of biosorbent and immobilization of the waste material for enhanced efficiency and recovery. Furthermore, they recommended that interest should be concentrated by the researchers to predict the performance of the adsorption process for dye removal from real industrial effluents. In yet another review, the efficiency of low-cost agricultural adsorbents for dye removal and the comparison between the raw and treated adsorbents were surveyed (Sharma *et al*., 2012). It was demonstrated that chemically treated agricultural waste showed better significant removal efficiency than the raw agricultural waste. It is important to note that decolourisation process is not specific and often depends upon many aspects. In addition, Sharma *et al*. (2012) observed that even though there are lots of agricultural adsorbents which can act as a surrogate for the expensive commercial activated carbon, complete replacement is not possible. However, the researchers iterated that the factors which favour the selection of agricultural adsorbents include low cost, widespread presence and organic composition which show a strong affinity for some selected dyes. Similar findings were also reported by other workers who used Rice Husk (RH) to remove methylene blue (MB), Congo red (CR), brilliant green (BG) and crystal violet (CV) from wastewater (Abbas, 2013). In summary, Nigam *et al.* (2000) proposed a pathway for the utilization of agricultural wastes as adsorbents for dye removal from water.

The agricultural wastes must be milled to increase the surface area and then dried to improve on adsorbency. The as-prepared material is the then added to the dye-laden effluent, for about 48 h residence time, allowing the decolourisation of water. The treated water can then be reclaimed and re-used. Degradation of the adsorbed dye can then be carried out by solid state fermentation is the applied to degrade the adsorbed dye while concomitantly augmenting the protein content of the substrate owing to the presence of fungal-biomass. The fermented material can then be recycled and applied as fertilizer or soil conditioner (Nigam *et al.*, 2000).

Adsorption of Dyes Onto Clays

The increasing amount of dyes in the ecosystem mainly in wastewater has propelled the search for more efficient low-cost adsorbents such as clay. Clay is a fine-grained silicate mineral made when rocks break down (Potter *et al.*, 2005). They are primarily attractive adsorbents, since they are easily accessible at low cost (Anirudhan *et al.*, 2009). A new adsorbent material developed from thermally treated waste (TTW) which can be used to remove dye from textile wastewater was suggested for adoption by Fraga *et al.* (2018). The study presented the potential of TTW as a substitute for conventional adsorbents such as activated carbon. Karim *et al.* (2017) presented results of Moroccan clay that showed that it can be used as an adsorbent for the removal of BR46, BM and GM from aqueous solutions with particular attention on its competitiveness during adsorption and the effect of inorganic ions. The researchers concluded that Moroccan clay not only showed good potential for the removal of cationic dyes but also that its use as an adsorbent for the wastewater treatment loaded with textile dyes is promoted by its natural abundance and ease of use. Moreover, the low desorption percentage exhibited by the adsorbent supports the use of clay saturated with dyes in the ceramics industry and decoration products, so, an increase and a development of the region's economy. The adsorption parameters of methyl orange (MO) from aqueous solution onto the activated clay were also evaluated in a previous study (Bendaho *et al.*, 2017). The results showed that practically 30 minutes of contact time was sufficient for the adsorption to reach equilibrium and when the amount of activated clay was increased from 1 g/L to 4 g/L, the residual dye concentration decreased. The review by Adeyemo *et al.* (2017) explored the grey areas of the adsorption properties of the raw clays and the improved performance of activated/modified clay materials with particular reference to the effects of pH, temperature, initial dye concentration and adsorbent dosage on the adsorption capacities of the clays. The review established that the development of highly efficient clay adsorbents (especially the activated/modified forms) is necessary for industrial applications. Furthermore, potential ways of improving the performance of clay adsorbents were suggested. Additional research was also recommended to achieve a better understanding of the mechanism of dye adsorption on activated clays and TiO_2 interlayer-pillared clays, especially about surface morphology after modification/activation, since the information available on the possible mechanism of dye sorption by clay materials requires further explanation. The research into the sorption of the anionic dyes (RB-81 and DB-74) onto the natural and thermally and chemically modified smectite clays showed a significant effect of the acid modification on the amount of bonded dyes. The acid-activated smectite had a strong adsorption capacity for the anionic RB-81 and DB-74 dyes in the solution. Regardless of the clay modification type, the dye sorption occurred at the $pH>pH_{PZC}$, which indicated that the particles of the clay-building minerals had a negative surface charge. It was impossible to bond the dyes by means of the electrostatic interaction with the mineral surfaces (Kyzioł-Komosińska *et al*., 2014).

Adsorption of Dyes Onto Chitin and Chitosan

Chitin is a nitrogenous polysaccharide characteristically tough and semitransparent substance forming the main component of the exoskeletons of arthropods, such as the shells of crustaceans, the cell walls of certain fungi and algae, and the outer coverings of insects (Ling *et al*., 2011). Chitosan is produced from chitin through partial deacetylation of chitin in 40-50% aqueous alkali, sodium hydroxide, at 120-150 ^{0}C under heterogeneous conditions (Crini, 2006; Kurita, 2006; Ling *et al*., 2011). Jassal & Raut (2015) reported the feasibility of crystal violet removal from wastewater using different chitosans and cross-linked derivatives. The study showed that adsorption of crystal violet (CV) onto crab shell chitosan (CSC) and medium molecular weight chitosan (MMWC) beads at pH 2–4 were not significantly affected. Moreover, the Langmuir isotherm study which provides an equilibrium parameter RL, indicated that the adsorption was favorable if R_L lies within the range $0<R_L<1$. Commercially prepared chitin and chitosan from crab and shrimp shells were investigated for their efficiency for the coagulation-flocculation of Brilliant Green (BG) dye (Chikhi & Bouzid, 2018). The utilized conditions provided a chitosan with an acceptable degree of deacetylation (75%) leading to its solubility in acetic acid, consequently charge neutralization which was responsible for the dye removal. Asgari *et al*. (2013) developed a bimetallic chitosan particle (BCP) adsorbent and examined it under various operational variables for adsorption of the Orange (O) II dye. The removal efficiency by BCP in a wide range of pH levels was remarkable, presenting a significant advantage for its practical application. In another study, chitin was prepared into beads using sodium alginate and batch adsorption of a standard dye eosin Y (Mabel *et al*., 2018). The researchers concluded that chitin-alginate beads can act as a better adsorbent for the removal of standard anionic dyes from the textile effluent and protect the aquatic environment. Iqbal *et al.* (2011) investigated the adsorption of acid yellow dye on flakes of chitosan prepared from fishery wastes and reported that the adsorbent exhibited excellent performance for adsorption of acid yellow 73. The high adsorption capacity of anionic dye on chitosan observed in the study was attributed to the strong electrostatic interaction between NH_3 of chitosan and dye anions. According to Rahman & Akter (2016) chitin which was prepared from shrimp shell by a chemical process involving demineralization, deproteinization and decolorization provided a cost-effective and environment-friendly dye removal process for textile wastewater treatment. Table 2 shows the summary of adsorption conditions for various adsorbents.

Adsorption of Dyes Onto Geopolymers

Geopolymer is a class of largely X-ray amorphous aluminosilicate materials, generally synthesized at ambient or slightly elevated temperature by reaction of a solid aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution (Provis *et al.*, 2005). This inorganic material was created by the French scientist Joseph Davidovits in 1970s. The aim of its creation was to develop a fire-resistant alternative to organic polymers in the aftermath of various catastrophic fires in France between 1970 and 1972. Since the period following the work carried out by Wastiels *et al.* (1994), the application of geopolymer shifted to uses in construction as eco-friendly alternative material to ordinary Portland cement. Presently, its plethora applications include: fire resistant materials, decorative stone artefacts, thermal insulation, low-tech building materials, low energy ceramic tiles, refractory items, thermal shock refractories, bio-technologies (materials for medicinal applications), foundry industry, cements and concretes, composites for infrastructures repair and strengthening, radioactive and toxic waste containment, arts and decoration, and adsorbent material for water treatment (Shikuku and Sylvain, 2019).

Many industrial processes, such as textile and printing, generate highly colored effluents causing environmental problems. Various methods for discoloration of effluents have been proposed. These include; aerobic and anaerobic microbial degradation, coagulation and chemical oxidation, adsorption, membrane separation, filtration, electrochemical degradation, photocatalytic degradation and reverse osmosis. Inevitably, each method has its inherent limitations. There is scarcity of literature on adsorptive removal of dyes onto geopolymers. Li *et al.* (2006) reported the application of fly ash derived geopolymeric materials for removal of methylene blue and crystal violet dyes from aqueous media. The adsorption capacity of the prepared adsorbents was demonstrated to be dependent on the preparation conditions such as fusion temperature and fly ash:NaOH ratio. The geopolymers exhibited

Table 2. Selected adsorbents for dye removal

Adsorbent	Adsorbate	Conditions	Adsorption Capacity, q_m (mgg^{-1})	Reference
Thermally Treated Waste (TTW)	Remazol Black (RB) Romazol Red (RR)	pH 4 Equilibrium time: 5mins Temp: 25^{0}C	Remazol Black (0.69) Romazol Red (2.89)	(Fraga *et al*., 2018)
Bimetallic Chitosan Particle (BCP)	Orange (O) II	pH 3 Equilibrium time: 20mins Temp: 24^{0}C	384.6	(Asgari *et al*., 2013)
Agricultural Wastes	Brilliant Green (BG) Congo Red (CR) Methylene Blue (MB) Crystal Violet (CV)	pH 8-10 Equilibrium time: 4-5hrs Temp: 30-60^{0}C	-	(Adegoke & Bello, 2015)
Almond Leaves Powder (ALP)	Congo Red (CR) Crystal Violet (CV)	CV (pH 10); CR (pH 2) Equilibrium time: 100mins for CV and CR Temp: CV (70^{0}C); CR (60^{0}C)	Congo Red (7.77) Crystal Violet (22.96)	(Okorocha *et al*., 2016)
Moroccan Clay	Basic Red (BR) 46 Methylene Blue (MB) Malachite green (MG)	pH 6 Equilibrium time: 70mins Temp: 30^{0}C, 40^{0}C, 50^{0}C, and 60^{0}C	Basic Red (BR) 46 30^{0}C (40.54), 40^{0}C (39.65), 50^{0}C (39.36), 60^{0}C (38.39) Methylene Blue (MB) 30^{0}C (46.68), 40^{0}C (46.35), 50^{0}C (47.10), 60^{0}C (47.96) Malachite green (MG) 30^{0}C (35.06), 40^{0}C (35.39), 50^{0}C (35.72), 60^{0}C (36.22)	(Karim *et al*., 2017)
Activated Algerian Clay	Methyl Orange (MO)	Natural pH Equilibrium time: 30mins Temp: 22±2^{0}C	32.3	(Bendaho *et al*., 2017)
Saudi Bentonite Clay	Acid Blue (AB) 25	pH <9 Equilibrium time: 4hr Temp: 20^{0}C, 40^{0}C, 60^{0}C, and 75^{0}C	12.7	(Alshammari, 2014)
Raw mango seed powder	Methyl Blue (MB)	pH 8 Equilibrium time: 60mins Temp: 30^{0}C	25.36	(Senthil Kumar *et al*., 2014)
Surface modified mango seed powder	Methyl Blue (MB)	pH 8 Equilibrium time: 30mins Temp: 30^{0}C	58.08	(Senthil Kumar *et al*., 2014)
Deacetylated chitin nanofibers/ nanowhiskers	Reactive Blue (RB) 19	pH 1 Equilibrium time: 20mins Temp: 20^{0}C	1331	(Liu *et al*., 2018)
Prickly bark of cactus fruit	Methyl Blue (MB)	pH >8 Equilibrium time: 60mins Temp: 20-40^{0}C	222.22	(Abdel Karim *et al*., 2017)

higher adsorption capacities than raw fly ash and natural zeolites under similar conditions. The adsorption isotherm data was best fitted to the two-site Langmuir isotherm following nonlinear regression method. Conformity to the two-site Langmuir isotherm suggests that some heterogeneous sites, such as metal oxides and unburnt carbon, in the adsorbent play a role in the adsorption process. Elsewhere, the photocatalytic properties of fly ash based geopolymer for degradation of methyl blue dye was reported (Zhang and Liu, 2013). A degradation efficiency of 92.79% was realized under UV irradiation attributed to the synergistic effects of adsorption and photocatalysis. The photocatalytic degradation process obeyed the third-order reaction kinetics. The above studies underscore the fact that geopolymers present facile materials both as adsorbents and photocatalysts for dye removal from water. A comprehensive review of the application of geopolymers for water treatment has been recently published by Shikuku and Sylvain (2019).

Adsorption of Dyes Onto Metal Oxides

Adsorptive removal of acid red 27 dye from water onto iron (III) oxide based nanoadsorbents was reported by Nassar (2010). The equilibrium data was describable using the Langmuir and Freundlich adsorption isotherm models, kinetically conforming to the pseudo-second order kinetic law while thermodynamically; the process was spontaneous, exothermic and physical in nature a testament of the feasibility of the adsorption reaction. The findings demonstrate that magnetically responsive iron (III) oxide based nanoadsorbents are potential candidates for sequestration of dyes from aqueous solutions. Zhang and Kong (2011) investigated the removal of dyes from synthetic wastewater by adsorption onto magnetic magnetite (Fe_3O_4) core–shell nanoparticles. The Langmuir monolayer adsorption density for methylene blue (MB) and Congo red (CR) were 44 and 11 mg/g, respectively while conformity to the second order kinetic model implied the rate controlling step was a chemisorption process. Reactive Blue (RB) 21 dye adsorption onto TiO_2 was reported by Srivastava *et al.* (2013). Te adsorption equilibrium data was best modeled by the Langmuir isotherm model implying monolayer adsorption while the time-dependent data was described by the pseudo-second order kinetic model. The Langmuir theoretical maximum monolayer adsorption density was about 23 mg/g. Table 3 presents a summary of selected naturally occurring inorganic materials applied as adsorbents for removal of dyes from aqueous solutions and their corresponding adsorption capacities.

Table 3. Selected inorganic adsorbents for dye removal from water

Adsorbent	Dye	Adsorption Capacity mg/g	Reference
Gypsum	Basic Red 46	39.17	(Deniz and Saygideger, 2010)
Pyrophyllite	Methylene Blue	70.42	(Gücek *et al*., 2005)
Glass fibres	Methylene Blue	2.24	(Chakrabarti and Dutta, 2005)
Charred dolomite	Dye E-4BA	950	(Walker *et al*., 2003)
Modified silica	Acid Blue 25	45.8	(Sanghi and Verma, 2013)
Raw ball clay	Methylene Blue	34.65	(Auta and Hameed, 2012)
Bentonite	Methylene Blue	175	(Hong *et al*., 2009)

Adsorption of Dyes Onto Microbial Biomass

Biosorption is the accumulation of pollutants from aqueous media onto living or inactive and dead microbial mass (Bustard *et al*., 1998). Here, adsorbents derived from biological materials, such as yeasts, fungi or bacterial biomass, are used to sorb dyes from water. The adsorptive capacity of the natural or modified biosorbents is attributed to the presence different functional groups such as carboxyl, hydroxyl, sulphate, and amino groups that form adsorption sites for diverse adsorbates. Ali (2010) notes that biosorbents are generally highly selective relative to conventional ion-exchange resins and commercial activated carbons, and can sequester dyes to molecular levels. Arief (2008) compiled a comprehensive critical review on the use of biosorption as alternative low-cost and effective technique for removal of heavy metals from water. The use of microbial mass for dye removal is not a recent concept.

As evidenced in the classification of dyes, dyes vary widely in their chemistries, and as a result their interactions with micro-organisms are a function of the chemistry of a particular dye and the specific properties of the adsorbing microbial biomass (Polman and Brekenridge, 1996). It can be demonstrated that different classes of dyes have a specific affinity for binding with certain microbial species.

In a much earlier work, Hu (1992) reported the ability of bacterial cells to adsorb reactive dyes. Zhou and Zimmerman (1993) reported decolourisation of effluents laden with azo dyes using adsorption onto actinomyces. Bustard *et al*. (1998) then showed that biosorbent developed from thermotolerant ethanol-producing yeast strain, K. *marxianus* IMB3, had high affinity for dyes removal from water (Bustard *et al*., 1998). In terms of adsorption rates, biosorption has tendency to relatively rapidly:

Table 4. Adsorption capacities of selected microbial biomass

Adsorbent	Dye	Adsorption Capacity mg/g	Reference
Green alga	Reactive red 5	555.6	(Aksu *et al*., 2005)
Caulerpalentillifera	Methylene blue	417	(Marungrueng *et al*., 2007)
Sargassummuticum	Methylene blue	279.2	(Rubin *et al*., 2005)
Dead macro fungi (P)	Methylene blue	204.38	(Maurya *et al*., 2006)
Duckweed	Methylene blue	144.93	(Waranusantigul *et al*., 2003)
Rhizopusarrhizus	Reactive Orange 16	190	(O'Mahony *et al*., 2002)
Aspergillus niger	Direct red 28	14.72	(Fu and Viraraghavan, 2002)
Living fungus	Acid Blue 29	6.63	(Fu and Viraraghavan, 2001)
Dead fungus	Methylene blue	18.54	(Fu and Viraraghavan, 2000)

a few minutes in algae to a few hours in bacteria (Hu, 1996). This is possibly due to the increased surface area resulting from cell rupture during autoclaving (Polman and Brekenridge, 1996). Table 4 presented the compilation of other relatively recent studies on microbial biomasses in the removal of dyes. Biosorption is effective in cases where the dye-containing effluent is very toxic or when the conditions are not favourable for the growth and maintenance of the microbial population.

CONCLUSION

The chapter demonstrates that physical and chemical techniques of dye removal are efficient but only effective while treating a small volume of effluent, therefore, prohibiting their application in a large scale. The driving factor limiting their sustainability is cost. On the other hand, biological treatment, namely; liquid state fermentations, is ineffective for complete removal of dyes from water in a continuous system owing to the long time needed for decolourisation-fermentation processes. Adsorption is still the most widely used method for dye treatment due to its simplicity and low-pricing in terms of technology and capital investment involved. The chapter reviews a wide range of low-cost adsorbents such as various agricultural by-products and food wastes, clays, biosorbents and inorganic metal oxides for dyes removal from aqueous solution. The literature data demonstrates that locally available and naturally occurring material are effective and inexpensive substrates for removal of dyes from aqueous solution and are potential replacement for commercial activated carbon.

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KEY TERMS AND DEFINITIONS

Adsorption: Accumulation of molecules (adsorbate) from aqueous phase onto a solid material (adsorbent).

Chitin: A nitrogenous polysaccharide that forms the main component of the exoskeletons of arthropods.

Dye: A natural or synthetic coloring material.

Geopolymer: An amorphous aluminosilicate materials synthesized by reaction of a solid aluminosilicate powder with a concentrated alkali solution.

Chapter 12

Outdoor Pollution Management by Nanotechnology

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ABSTRACT

Remediation of environmental pollution has become a hot issue in the world. Environmental pollution, mainly caused by toxic chemicals, includes air, water, and soil pollution. This pollution results not only in the destruction of biodiversity, but also the degradation of human health. Textile industrial effluent often contains the significant amount of synthetic and toxic dyes. Some dyes are water-soluble, dyes such as azo dyes, sulfonated azo dyes, etc. Hazardous effect of dyes results in the formation of tumor, cancer, liver or kidney damage, insomnia, diarrhea, nausea, vomiting, dermatitis, chronic asthma, coughing, headaches, and allergies in humans

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and also inhibit growth of bacteria, protozoan, plants, and different animals. A range of wastewater treatment technologies have been proposed that can efficiently reduce toxic dyes to less toxic forms such as nanotechnology. In this chapter, the authors give an overview of the various aspects of nanotechnology to remediate industrial textile dye effluents.

INTRODUCTION

Dye is considered as colored material which can be natural, semi-synthetic or completely synthetic. Natural dyes are of natural origin and therefore it is non-hazardous in comparison to the synthetic dyes. Plastics, textile, printing, paper, leather, rubber, and paints industries are the major sources of synthetic dyes pollution (Singh & Arora, 2011). Several dyes containing effluents are released into the water streams by these sources. Textile effluent consists of large quantity of unfixed dyes as compared to other effluents which are discharged by other industries (Ali 2010). Textile dyeing industry intensively affects the earth and is considered as first water-Polluting activity (Kant 2012, Silva 2018). Human beings along with aquatic flora and fauna are affected by the discharge of contaminated dye effluents in the water streams (Korbahti & Rauf 2008, Fernandez *et al.,* 2014, Bouaziz *et al.,* 2015, Li *et al.,* 2018). For coloring of different materials, azo dyes are frequently used (Solis *et al.,* 2012).

Dyes can cause several health related problems to human body and can damage different organs such as liver, central nervous system, reproductive system, brain, and kidneys (Kadirvelu *et al.,* 2003). Water polluted by dyes at a concentration of 1.0 mg/L is not suitable for human's consumption (Malik *et al.,* 2007, Mittal & Gupta 1996). Benzidine and arylamine-based dye are harmful and found to have some carcinogenic properties (Ozcan *et al.,* 2004). Therefore, it is necessary to find economic and eco-friendly method for treatment of dye effluents (Song *et al.,* 2018).

BACKGROUND TO DYES

Colorants are basically chemicals which is responsible for imparting color to the materials on which they are applied. Pigments and dyes are the types in which dyes are classified. Both are different from each other on the basis of their solubility. The crystalline or the particulate nature of the pigments is retained during the application. But dyes on the other hand became the integral part of the material because these are soluble and can be easily diffused into the material. Polymers, paints, and inks are the materials in which pigments are used. Dyes are considered as main source for contamination of water and it is considered as ionizing, aromatic, and colored materials. These compounds which originate from hydrocarbons such as anthracene, toluene, xylene, naphthalene, and benzene which are based on coal tar are used for coloring several materials such as greases, drugs, cosmetics, paper, food, waxes, fur, plastics, leather, textile materials, hair, and other products. Factors other than solubility are required for a coloured material to be considered as dyestuff.

The Physical Basis of Color

Dyes are colored due to adsorption of light in the visible region or in the 400-700 nm range. Color –possessing group i.e chromophore and conjugate systems i.e the system consisting of alternate single and multiple bonds must be possessed by dyes. Resonance of electrons is the force of stabilization in case of organic compounds which is exhibited by dye molecules. Presence of a chromophore which is the area of the molecule where the difference of the energy between the two separate molecular orbitals lies in the range of visible region is responsible for imparting colors to the dyes. π–π^* and n–π^* transitions occurs in chromophore and the solubility of dyes are effected by auxochromes which are present in most of the dyes. Transitions of n electrons occurred in auxochromes not the π–π^* transitions. Carboxylic acid, amino, hydroxyl, sulfonic acid groups the the various auxochromes which is present in dyes and are responsible for color of the colorant. But these functional groups are not accountable for color production (Gupta *et al.,* 2013, Janaki 2014, Mallakpour 2017, Mallakpour 2018, Saini *et al.,* 2018).

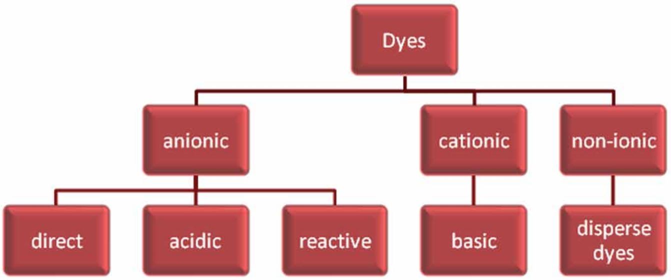
Classification of Dyes

Dyes are categorized on the basis of its chemical structure and color index (CI). Mono-azo, di-azo, tri-azo, anthroquinone, triarylmethane, and phthalocyanines are some of the general classes of the dyes. Anionic, cationic, and non-ionic are the different types of dyes which are classified on the basis of their utilization in textile industries. Yellow, orange, red, violet, blue, green, and black are the subclasses of the dyes on the basis of color.

There are generally two groups in which dyes are characterized:-

1. **Anionic Dyes:** Azine, nitroso, triphenylmethane, xanthene, and anthraquinone are the anionic dyes which are used for silk, wool, modified acrylics, nylon etc.
2. **Cationic Dyes:** Crystal violet, amaranth, and methylene blue are the cationic dyes which are used for polyacrylonitrile, modified nylons, in medicines, polyesters, and paper.

Figure 1. Classification of dyes
(Fu & Viraraghavan 2001)



Dyes are categorized according to the nature of their chromophore:-

1. **Nitro Dyes:** These dyes consist of NO_2 group (nitro group) which is attached to electron donating group such as amino and hydroxyl groups in an aromatic system.
2. **Nitroso Dyes:** These dyes are prepared on reaction of nitrous acid with naphthols or phenols. These dyes consists of nitroso group (chromophore) at orthoposition to the –OH group. These dyes are utilized in varnish industry, in paint, for rubber dyeing, and in the manufacture of pencils and wallpapers.
3. **Acridine Dyes:** These dyes are heterocyclic compounds which consist of acridine and its derivatives in their structure. These dyes are generally used for coloring mordant cotton and leather.
4. **Cyanine Dyes:** These dyes consist of delocalized charge on the two nitrogen atoms which are joined together by polymethine bridge. These dyes are used in industry, and in biotechnology for analysis and labeling because they are helpful label for nucleic acids and proteins.
5. **Oxazine Dyes:** These dyes consist of oxazine ring which act as a chromophore in which oxygen atom is attached at para-position to nitrogen atom.
6. **Thiazole dyes:** These dyes consist of thizole ring and it is mostly utilized for cotton.
7. **Anthraquinone Dyes:** These dyes are based on anthraquinone. The chromophore is provided by the resonance structure of the aromatic rings and the –CO groups. These dyes are utilized for dyeing silk, cotton, and rayon.
8. **Arylmethane Dyes:** These dyes are derived from CH_4 in which in which hydrogen atoms are replaced by aryl rings. Arylmethane dyes categorized into two subgroups:-

   a. **Diarylmethane dyes:** these dyes are derived from methane in which two hydrogen atoms are replaced by two aryl groups.
   b. **Triarylmethane dyes:** these dyes are derived from methane I which three hydrogen atoms are replaced by three aryl rings.
9. **Phthalocyanine Dyes:** These dyes consist of the derivatives of the phthalocyanine (tetrabenzotetraazoporphyrin) and its complex compounds with metals. The phthalocyanine dyes which are not soluble in water are generally used as pigments in the manufacture of printing colors, resins, plastics etc. the phthalocyanine dyes which are soluble in water are utilized for color fabrics.
10. **Indigoid Dyes:** These dyes consist of indigo as chromophore. These dyes are utilized for printing of cotton for dyeing proteins fibers and cellulose (Fabian & Hartmann 1980, Pisoni *et al.,* 2014, Raue & Corbett 2000).

Dye classification on the basis of the use or application is as follows:

There are some properties of dyes which are classified on the basis of their usage are:-

1. **Acid Dyes:**It is sodium salts of sulfonic acid and other acids like carboxylic or phenolic organic acids. Azo, nitro, nitroso anthroquinone, triphenylmethane, xanthenes, and azine are the different functional groups which are present in the acidic dyes. They are anionic dyes which are soluble in water and are used for dyeing silk, polypropylene fibers, nylon, polyamides, wools, and modified acrylics.
2. **Cationic (basic) Dyes:** They are called cationic dyes because colored cations are formed into the solution. Cationic dyes are also known as basic dyes and after the modication they can be water soluble. Hemicyanine, acridine, triarylmethane, thiazine, diazahemicyanine, oxazine, and cyanine are the different functional groups which are present in the cationic dyes. The positive charge carried by these dyes in their molecules is usually localized on the NH_4 group. These are used for cationic dyeable polyester, acrylic, cellulosic fibers, modacrylic, protein, and cationic dyeable nylon. Cationic dyes are utilized for dyeing dried flowers, jute, coir, cut flower etc.
3. **Disperse Dyes:** These dyes are free of the ionizing group and are insoluble in water which remained as suspended microscopic particles. Azo, nitro, benzodifuranone, anthroquinone, and styryl are the different functional groups which are present in the disperse dyes. Disperse dyes are mostly used for polyster dyeing and also used in form of aqueous dispersion for dyeing acrylic fibers, cellulose acetate, cellulose, and nylon.
4. **Direct Dyes:** These dyes are anionic dyes which are water soluble and coloured anions are produced due to ionization. For high affinity to cellulosic fibers,

this dye can be useful when applied with sodium sulfate and NaCl. Direct dyes are easily available in market, can be applied easily and utilized for dyeing leather, cotton, paper, nylon, and rayon. Direct dye without the help of other chemicals can easily hold on the cellulosic fibers.

5. **Reactive Dyes:** These dyes consist of atleast one reactive group which is able to form covalent bond with the fiber. The reactive group present in these dyes may be activated double bond or haloheterocycle. These dyes are generally used in the alkali situation and chemical bond is formed between reactive group of the dye and the –OH group on the cellulosic fiber. Bonding which occurs during dyeing leads to the fastness properties of these compounds. Due to the easy dyeing procedure, these dyes are used for dyeing cellulosics, some nylons, cottons, and rayons etc.
6. **Solvent Dyes:** These are characterized by its solubility in organic solvents. These dyes are nonpolar in nature and do not ionize in solution. Solvent dyes are used for coloring the waxes, organic solvents, plastics, hydrocarbon fuels, oil, lubricants, and gasoline etc. The compounds such as alcohols, chlorinated hydrocarbons, and liquid ammonia which are soluble in organic solvents are water insoluble is utilized for dyeing. Anthroquinone and azo group are the main groups present in these dyes.
7. **Sulfur Dyes:** These are called sulfur dyes because of the presence of sulfur-containing heterocyclic rings in their chemical structure. Sulfur dyes are synthetic organic molecules and it is utilized for the coloration of cotton, cellulosic fiber, and rayon due to the presence of sulfur group as chromophore. Sulfurization or thionization of organic intermediates leads to their ionization. These dyes are water insoluble and do not have affinity to cellulosic materials. Leuco compound is water soluble which is formed by treatment of sulphur dyes with weak alkaline solution of reducing agent or sodium sulfide and has affinity to cellulosic materials.
8. **Vat Dyes:** These are water insoluble dyes. These dyes polycylic compounds based on quinine structures which is utilized for the coloration of cellulosic fibers. These dyes are used generally used for color polyester and polyamide blends with cellulose fibers and also dyeing and printing cellulose fibers and cotton. These dyes are applied through the impregnation of fiber under the reducing conditions. It is further oxidized to insoluble form.
9. **Azo Dyes:** These dyes consist of aromatic compounds containing at least one azo group. These dyes are used for dyeing rayon, cotton, and polyester.
10. **Mordant Dyes:** Example of this dyes are dyes with metal chelating groups. These dyes are utilized for dyeing wool, cotton, and other protein fibers.
11. **Drug, Food, and Cosmetic Dyes:** These are natural and synthetic dyes. These are normally used in cosmetics, drugs, and foods, of which synthetic dyes

releated to anthraquinone, triarylmethane, carotenoid, and azo groups are the most commonly used (Hunger 2003, Gupta 2009, Janaki 2014, Parimalam 2012).

Nearly 1 lakh different types of dyes are synthesized with the rate of 9×10^6 tons/year nowadays. These dyes are used in numerous industries including paper, colors, foodstuffs, textiles, and printing industries etc. The dye and textile manufacturing industries are responsible for the release of the color into the water. It is not easy to evaluate the quantity of dyes discharged into the water streams. It is estimated that >10,000 tons/year of dyes are consumed in the textile industries worldwide and nearly 100 tons/year of dyes are discharged into the water. The increased usage of dye causing water contamination leads to serious environmental trouble. The water quality is changed if dye is present in very small quantity (<1 ppm). Hence, for the supply of fresh water to the society there is need to remove these contaminants from the wastewater (Mu & Wang, 2016).

TECHNOLOGY FOR THE TREATMENT OF DYE EFFLUENTS

Various techniques are employed for the treatment of dye effluents such as adsorption (Baeza *et al.,* 2017), activated carbon (Yu *et al.,* 2016), osmosis (Luo *et al.,* 2017), clay-based adsorbent coating (Ab Kadir *et al.,* 2017, Azha *et al.,* 2017), membrane filtration (Dickhout *et al.,* 2017), electrochemical oxidation (Anglada *et al.,* 2007), organic resin (Nabi *et al.,* 2011a), coagulation/ flocculation (Shahadat *et al.,* 2017b), biodegradable nanocomposite (Shahadat et al., 2017b), hybrid ion-exchange adsorbents, incineration (Lin & Wu 2006), biomass (Rahman *et al.,* 2016), and nanocomposite material (Dong *et al.,* 2015). The techniques mentioned above characterized as conventional methods which involves elimination and recovery methods. Out of these techniques, adsorption is considered as most important technique for the treatment of dye effluents. Various adsorbents such as organic resin, graphene oxide, activated carbon, polyaniline, etc are used for the recovery and removal of dye effluents from the wastewater (Cazetta *et al.,* 2018, Banerjee & Chattopadhyaya 2017).

Nanomaterials

Nanotechnology refers to the study of extremely small structures in the range of 0.1 to 100 nm. The particle which lies in the range of 1-100 nm is termed as nanoparticles. Harmful pollutants including dyes, polychlorinated biphenyls, furans and dioxins, pharmaceutical and personal care products, phthalates, inorganic pollutants, polycyclic aromatic hydrocarbons, viruses and bacteria, agrochemicals and pesticides, volatile organic compounds etc can be removed from the wastewater by using several cost effective, efficient and eco-friendly nanomaterials (Abdolmaleki *et al.,* 2017, Mallakpour *et al.,* 2017, Zare *et al.,* 2018, Prathna *et al.,* 2018, Tyagi *et al.,* 2018). Nanomaterials due to tunable pore size, high specific surface area (SSA) and related sorption sites, surface chemistry, short intraparticle diffusion distance have rapid adsorption rates and better efficiencies over wide range of pH as compared to conventional adsorbents. Low cost is needed for the fabrication of nanomaterials and only its small amount is utilized for efficient and effective dye removal. Hence for the adsorption use, these are effective in comparison to activated carbon due to less cost. Carbonaceous nanomaterials are one of the major class of nanomaterials, which comprise carbon nanofibers, fullerenes, graphene, and CNTs (carbon nanotubes). Carbonaceous nanomaterials due to higher affinity, high adsorptions kinetic and capacity are effective for dye removal from wastewater as compared to conventional activated carbon. Dyes are removed from the wastewater by π–π stacking, hydrogen bonding, covalent interaction, electrostatic interaction, and hydrophobic effect (Cai *et al.,* 2017, Shan *et al.,* 2017).

Coagulation–Flocculation

Sulfur and disperse dyes presented high coagulation and flocculation capacity while this method is not effectively applied for the color removal of acid, vat, direct and reactive dyes. Ethylediene dichloride, penta ethylene, and hexamine are the various co-polymers and ferric chloride, aluminum sulfate, copper sulfate, ferric, ferrous sulfate, and calcium chloride are the several coagulant agents which are generally used for color removal of colorants. The floc formed with the dyes is the mechanism behind the coagulation process and can be separated using filtration or sedimentation. The ability of settling of floc can be increased by dosing the polyelectrolyte during the phase of flocculation (Forgacs *et al.,* 2004). It is economic that only the separation of colorants is taking place. But the disadvantage of coagulation and flocculation process is the production of sludge (Valh *et al.,* 2011).

The characteristics of the suspended particles are changed in the coagulation method and floc are formed which sinks rapidly. The colloidal suspensions with negative charge are not effectively separated by conventional physical process. In coagulation process, electro kinetic repulsion between the particles is decreased by the addition of positive charge. Marmagne and Coste reported that in coagulation process, there is efficient removal of colour of sulfur dyes. The experiment was performed in bench flocculators, pH, temperature, and chemicals are the factors which affects the process of coagulation (Nguyen & Juang 2013).

Filtration Technology

For wastewater treatment, filtration technology is considered as a major part. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverses osmosis (RO) are the different filtration technology. Several promising results are shown by this technology for the color removal and for the process of water treatment, individual membrane is important. Various sorts of dyes are removed efficiently by the help of NF and UF but MF due to its large pore size is not sufficient for the treatment of wastewater. High membrane cost, high pressure, short life span, and momentous energy consumption are some of the limitations of this process and removal of organic contaminants or treatment of dyestuff are hindered by these properties. Salts rejections is better in case of RO. It is applied for recycling and gives improved results against several dye effluents in desalting and decolorizing.

Micro-Filtration

Dye baths consisting of pigment dyes as well as for rinsing baths are treated by this technique (Babu *et al.,* 2007). Chemical will remain in the dye bath which are not filtered by MF. Colloids, suspended solids or macromolecules having pore size of 0.1 to 1 micron are separated using MF and it is the pretreatment for NF or RO (Ghayeni *et al.,* 1998). For silt density index or turbidity, the performance of microfiltration is greater than 90. Poly (Vinylidene Difluoride), Poly (Ether Sulfone), Polycarbonate, Poly (Vinylidiene Fluoride), Poly Tetrafluoroethylene (PTFE), Poly (Sulfone), Polypropylene etc are the specific polymers from which MF membranes are formed. Operation at high temperature or where extraordinary resistance for chemicals are needed; carbon coated with zirconia, ceramic, carbon, alumina and sintered metal membranes, glass have been used. The operational velocities for micro and ultra filtration is 20 to100 cm/s and pressure is 20 to 100 (Ptm) (Naveed *et al.,* 2006).

Ultra-Filtration

This technique is used for the separation of macromolecules and particles, but only 31-76% dye is removed from this method. For reuse of treated wastewater for sensitive process such as textile dyeing is not permitted but for washing, rinsing etc where salinity is not a issue, the treated wastewater can be reused. UF can be used in combination with biological reactor, as pretreatment process for RO, and for metal hydroxide elimination (Naveed *et al.,* 2006). Polyvinyl chlorides (PVC), polytetrafluoroethylene (PTFE), polysulfone, acrylic copolymer, polypropylene, and nylon-6 are the various polymeric materials which are used for the formation of ultrafiltration membranes.

Nano-Filtration

This technique is used for the decoloration of effluents from the textile industries. Nanofilteration membranes are able to retain divalent ions, dyeing auxiliaries, organic compounds with low-molecular weight, hydrolized reactive dyes, large monovalent ions and they are normally made of aromatic polyamides and cellulose acetate. Nanofilteration and reverse osmosis membranes are manufactured by inorganic materials including carbon based membranes, ceramics, and zirconia. 5 to 30 Gross Flow per Day (GFD) is the flux rates for nanofilteration. By single nanofiltration, amount of removal of color greater than 90% were reported. Toxic effects of high concentration of dye > 1.5 g/L and mineral salts > 20g/L in the dye household effluents regularly reported (Tang & Chen 2002). The discharge of treated effluents in water streams is approximately unfeasible due to accumulation of dissolved solids. Textile decolorization of effluents by nanofilteration is fairly satisfactory.

Reverse Osmosis

Hydrolized reactive dyes, many types of ionic compounds, and chemical auxiliaries are removed by this technique in a single step and high quality of permeate is produced. Careful pretreatement of influent must be done because reverse osmosis is sensitive to fouling like nanofilration. Reverse membranes are generally made up of aromatic polyamides, inorganic materials, and cellulose acetate. In comparison to conventional treatments, membrane processes in combination with physio-chemical treatment has several advantages, such as decreasing the consumption of fresh water and the cost for wastewater treatment, decrease of regulatory pressure, capability to recover materials, costs of waste disposal can be decreased due to small disposal volumes. Several cost-effective applications in textile industries are associated with membrane processes (Naveed *et al.,* 2006).

Adsorption of Dyes

Adsorption is considered as an important method over other conservative approaches for dye removal from wastewater (Aljeboree *et al.,* 2014). Physical and chemical forces are responsible for the attachment of dissolved molecules to the surface of adsorbent in the process of adsorption. Wastewater treatment by activated carbon is widely employed. Combined adsorption and ion exchange or simply adsorption process is responsible for the removal of dye using activated carbon. Cost of operation, availability of adsorbents at low costs, and low initial capital are the factors which makes the wide applications of adsorption process for the elimination of textile contaminants. Various properties such as mechanically stable, ecofriendly, suitable pore size, less processing procedures, easy accessibility, economic, compatibility, higher adsorption capacity due to large surface area, and regeneration capacity should be consisted by superlative adsorbent for adsorption of dyes (Vakili *et al.,* 2014).

Agricultural by-product, natural and modified clay (Ahmadishoar *et al.,* 2017), polymeric sorbent (Popescu & Suflet 2016), activated carbon (Tze *et al.,* 2016), industrial by-product, chitosan-based adsorbent (Çınar *et al.,* 2017), and resin (Naushad *et al.,* 2017) are the various adsorbents which are used for the removal of colouring agents.

Adsorbents

The contaminant which is absorbed is called adsorbate and the phase on which it is getting adsorbed is called adsorbent (Yagub *et al.,* 2014). Adsorbent plays a very important process in adsorption process. Great adsorption efficiency, low cost, long life, great selectivity, and broad availability are the necessary properties for the good adsorbents. Nanomaterials, activated carbon, and several low-cost adsorbents are utilized as adsorbents for removal of contaminants from wastewater (Toor 2010).

Activated Carbon

It is mostly used adsorbent for the elimination of wide variety of dyes from the contaminated water. It is non-graphitic form of carbon, internally porous microcrystalline. Micropore structures, great adsorption capacity, large extent of surface reactivity, large surface area are the factors which makes the adsorbents efficient for dye removal but the cost of fabrication and regeneration of adsorbent is too high. Extra effluent is generated during the regeneration by means of refractory method which causes loss of removal efficiency of adsorbent due to 10%–15% loss of adsorbent (Adeyemo *et al.,* 2017).

Low-Cost Adsorbents

Soluble organic dyes from wastewater are transferred to the adsorbent which is highly porous and solid surface. Adsorption is most effective and economic process for decolorization of textile effluents or dye elimination. Temperature, interaction of dye/adsorbent, pH, surface area of adsorbent, size of particle, and contact time are the main factors for the adsorption of dyes. There is need for the low-cost adsorbents due to low regeneration capacity and high cost of adsorbents. These adsorbents must present in considerable amount in nature, need minimum processing, and must be effective.

There are three categories in which low-cost adsorbents are divided:

1. By-products of industries and agriculture wastes like sugar industry mud, wood sawdust, fly ash, coal ashes, teak wood bark, wood chips, peels (banana, pomelo, garlic, jackfruit), papaya seeds, grounded sunflower seed shells, coconut tree flower, rice husk, grass waste, ground nut shell powder, rubber seed shell, neem leaf powder.
2. Various bioadsorbents like microbial, biomass, and fungi.
3. Various natural materials like glass wool, clay.

Mixed results are shown by these adsorbents and in very few cases these have adsorption capacity larger than activated carbons (Teng & Low 2012, Servos 2014, Suteu *et al.,* 2011a, Nazarzadeh *et al.,* 2018).

CONCLUSION

Dyes are natural and synthetic materials which impart color to the products and make the environment more beautiful but it is considered as harmful and can contaminant the water streams. From the literature review it is observed that there is increase in production and use of textile dyes in last few decades which cause threat to the environment. Textile sector due to large consumption of water sources is found to be considered as an important area. The presence of dyes even in small quantity is toxic to environment and should be eliminated before entering into the water stream. By mechano-physico-chemical and biological treatment procedures, dye removal from textile effluents can be achieved. Removal techniques for dye effluents from wastewater have drawn considerable interest.

Adsorption is considered as a cost effective and efficient technique for the removal of dye effluents from wastewater and hence can generate high-quality treated effluent. This chapter highlights on the removal of dye effluents from wastewater by using nanotechnology.

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KEY TERMS AND DEFINITIONS

Dye: Dye is a colored substance which provides color to another substrate through chemical bond with the substrate.

Effluent: Effluent is an outflowing of water or gas to a natural body of water, from a structure such as a wastewater treatment plant, sewer pipe, or industrial outfall, etc.

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Index