TREATMENT OF TEXTILE WASTEWATER CONTAINING DYE STUFF BY FENTON OXIDATION PROCESS AND ADSORPTION

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DECLARATION

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Abstract

Environmental pollution is the most severe global issue threatening our ecosystem in the current scenario. Pollution is present in every strata of the earth, and the negative effects associated with it are a major source of concern in the modern era. Textile industry hazardous effluents are regarded as one of the major contributors to water pollutants discharged untreated into bodies of water. The discharged effluents from these industries have been demonstrated to bear a high pollution load (high dissolved solids, COD, colour and chloride content) with poor biodegradability. Therefore, untreated textile wastewater causes severe damage to the environment if discharged without treatment. Many techniques like electrochemical coagulation, reverse osmosis, nanofiltration, adsorption using activated materials etc., draw attention to treatment. With traditional approaches, treating textile wastewater, which is of great strength and complexity, has become a significant challenge.

Advanced oxidation processes represent a powerful treatment for refractory and toxic pollutants in textile wastewaters. The present investigation is focused on COD removal, using Fenton oxidation and combined treatment with materials of TiO_2, Commercial activated carbon and TiO_2 impregnated activated carbon (AT). Initial COD level of 2100mg/l decrease up to 710 mg/l through Fenton oxidation process. Further to discharge treated wastewater into the water body (<250mg/l) is achieved with 8g of TiO_2,7 g of CAC, and 6g of TiO_2 impregnated AC. CAC was selected as the best material economically for post-treatment. Many factors influenced the degradation rate in the Fenton process, such as initial hydrogen peroxide concentrations(0.65ml/l), initial iron concentration (1.5 g/l) and pH (2-3).

CAC gave maximum COD removal at pH 2. The data were fitted to the Langmuir adsorption isotherm, with a maximum adsorption capacity of 8.16 mg/g and monolayer dye adsorption to the material. The Langmuir adsorption separation factor was 0.033, indicating that the Langmuir adsorption is favourable. The reaction proceeded in a pseudo-second-order, implying chemisorption to the substance. The optimum regeneration agent was found to be NaOH, and the material was exhausted after two regeneration cycles.

From the results Fenton with CAC adsorption is most efficient treatment method at higher dye concentrations and for textile industry effluent.

Keywords: Adsorption, Fenton, COD, TiO_2, Iron

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TABLE OF CONTENTS

DECLARATION i
ABSTRACT iii
ACKNOWLEDGEMENT iv
TABLE OF FIGURES viii
LIST OF TABLES x
LIST OF ABBREVIATIONS xi
1.INTRODUCTION 1
1.1 General 1
1.2 Scope of the study 4
1.3 Objectives of the study 4
1.4 Approach 5
2.LITERATURE REVIEW 6
2.1 Properties of dyes 6
2.2 Textile Dye Classification 7
2.2.2 Basic dyes 8
2.2.3 Direct or Substantive dyes 8
2.2.4 Reactive dyes 8
2.2.5 Vat dyes 8
2.2.6 Disperse dyes 8
2.2.7 Sulphur dyes 9
2.2.8 Azoic dyes 9
2.3 Dye intermediates 9
2.4 Toxicity of dyes 9
2.5 Textile dyeing processes 10
2.5.1 Pre-treatment processes of dyeing 10
2.6 Wastewaters from textile processing 11
2.7 Treatment and disposal of textile industry wastewater 13
2.8 Primary treatment 14
2.9 Advanced oxidation process 16
2.9.1 Uses of the Fenton's reagent 16
2.10 Adsorption 22

2.11 Titanium dioxide 23
2.12 Treatment methods and their advantages and limitations 25
3.MATERIAL AND METHODS 28
3.1Textile Industry Effluent 28
3.2 Classification of dyes 29
3.3 Chemical Oxygen Demand analysis 32
3.4 Synthesis of TiO_2 34
3.5 Synthesis of TiO_2 impregnated Activated Carbon 34
3.6 Fenton Oxidation process 35
3.7 Evaluation of COD removal efficiency for different combination of synthesized TiO_2 and AC 36
3.8 Selection of Best Material for COD removal 36
3.9 Characterization of CAC using SEM, EDX, XRD, and FTIR 36
3.10 Optimization of experiment condition for the CAC for COD removal 38
3.10.1 Optimum Contact time 38
3.10.2 Optimum pH 39
3.11 Adsorption isotherms and kinetic studies for CAC 39
3.11.1 Adsorption isotherms 39
3.11.2 Kinetic studies 40
3.12 Regeneration Studies for Commercial Activated Carbon 41
4.1 Wastewater Characterization 42
4.2 Operating Parameters of Fenton Oxidation Process 42
4.3 Best pairing selection of AC: TiO_2 ratio to remove COD 44
4.4 Effect of $(AT)_{opt}$ on COD removal 44
4.5 Effect of TiO_2 loading on COD removal 46
4.6 Effect of Activated Carbon loading on COD removal 47
4.7 Selection of best material for COD removal 48
4.8 Characterization of Activated carbon using SEM, EDX, XRD and FTIR 50
4.8.1 ESEM and EDX Analysis 51
4.8.2 XRD Analysis of AC 53
4.8.3 FTIR analysis for AC 54
4.9 Optimum condition for COD removal using AC 54

4.9.1 Impact of contact time 54
4.9.2 Effects of pH 56
4.10 Adsorption Isotherms and kinetic studies 58
4.10.1 Adsorption isotherms for COD removal by AC 58
4.10.2 Kinetic studies 61
4.11 Regeneration studies for AC 64
A schematic diagram of a wastewater treatment module for dyestuffs is shown below. ... 65
5. CONCLUSIONS AND RECOMMENDATIONS 66
5.1 Conclusions 66
5.2 Recommendations 67
LIST OF REFERENCES 69

TABLE OF FIGURES

Figure 2. 1: Classification of textile dyes (Christie 2007, Hunger 2003, Sabnis 2010) 7
Figure 2. 2: The constituents and wastewater characteristics from various textile processing steps (Verma et al., 2012) 12
Figure 2. 3: Stages of wastewater treatment 13

Figure 3. 1 : Structure of Disperse red 29
Figure 3. 2: Structure of Disperse yellow 30
Figure 3. 3: Structure of Disperse orange 30
Figure 3. 4: Structure of Disperse navy blue 30
Figure 3. 5 : Structure of Sunset yellow 30
Figure 3. 6: Structure of Suncid red 31
Figure 3. 7: Structure of Disperse Rubine 31
Figure 3. 8: Structure of Disperse blue8 31
Figure 3. 9: COD reflux condenser 33
Figure 3. 10: Titration setup and color change 33
Figure 3. 11: Aerating the wastewater with Fenton reagent 35
Figure 3. 12: The laboratory setup for the batch studies on the mechanical stirrer 36
Figure 3. 13: Environmental Scanning Electron Microscopy- Energy-Dispersive X-ray Spectroscopy 37
Figure 3. 14: Fourier Transform- Infrared Spectroscopy 37
Figure 3. 15: X-Ray Diffraction spectroscopy 38
Figure 3. 16: The experimental setup for batch experiments 38

Figure 4. 1: COD Removal efficiency with different AT_{opt} dosages 45
Figure 4. 2: COD Removal efficiency with different dosage of TiO_2 47
Figure 4. 3: COD removal efficiency with different CAC dosage 48
Figure 4. 4: Final COD with different dosage of CAC, TiO_2 and TiO_2 impregnated AC 49
Figure 4. 5: Treatment cost for 1l of Fenton treated water for three materials 50
Figure 4. 6 SEM image of AC before Adsorption 51
Figure 4. 7: SEM image of AC After Adsorption 51
Figure 4. 8: The EDX image of CAC 52

Figure 4. 9: XRD analysis of AC.....53
Figure 4. 10: FTIR analysis of AC before and after adsorption 54
Figure 4. 11: Final COD vs the contact time 55
Figure 4. 12: Final COD with different pH.....57
Figure 4. 13: The Langmuir isotherm for COD removal with AC 59
Figure 4. 14: The Freundlich isotherm for COD removal with AC.....60
Figure 4. 15: Pseudo first order kinetic model for adsorption onto AC 62
Figure 4. 16: The reaction kinetic data is fitted to second order kinetic model.....63
Figure 4. 17: The COD removal efficiency of AC after each regeneration cycle 64

LIST OF TABLES

Table 2. 1: Highlights of published work on Fenton's/photo-Fenton oxidation of textile dyes/ wastewater.....17
Table 2. 2: Available COD removal methods and their advantages and limitation 25
Table 3. 1: Characteristics of textile industry effluent before treatment 28
Table 3. 2:Properties of dyes 29
Table 3. 3: Mixing weight ratio of AC and TiO_2.....35
Table 4. 1:Characteristics of effluent.....42
Table 4. 2: COD removal percentage for different ratio of AC:TiO_2.....44
Table 4. 3: COD removal percentage with different dosage of AT_{opt} 45
Table 4. 4: COD removal percentage with dosage of synthesized TiO_2 46
Table 4. 5: COD removal percentage with dosage of AC 48
Table 4. 6:The analyzing method with the relevant analyzed characteristics.....50
Table 4. 7: The weight and atomic composition of the CAC 52
Table 4. 8: The Optimum contact time for COD removal.....55
Table 4. 9: Optimum pH investigation 56
Table 4. 10: Adsorption data fitted to Langmuir isotherm 58
Table 4. 11: Adsorption data to fitted Freundlich isotherm.....60
Table 4. 12: The pseudo first order reaction results.....61
Table 4. 13: The kinetic experiment results of AC.....62

LIST OF ABBREVIATIONS

Abbreviation	Description
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
DO	Dissolved Oxygen
AOP	Advance Oxidation Process
CAC	Commercial Activated Carbon
FTIR	Fourier-Transform Infrared spectroscopy
SEM	Scanning electron microscope
EDX	Energy-dispersive X-ray spectroscopy
XRD	X-ray Diffraction Analysis

1.INTRODUCTION

1.1 General

Water is a vital element for the existence of life and a significant part of the biological world as all biochemical reactions occur in aqueous medium. Water is essential for all domestic purposes as well as for irrigation, shipping, sanitation, power generation, and different industrial operations. About unique feature, water is one of the precious assets of nature. Globally, water is present abundantly. About 71% of the earth's surface is occupied by a hydrosphere. The total estimated volume of global water is in the vicinity of 1400 million cubic kilometers present on earth; out of this amount 97% is saline ocean water and only 3% is fresh water. Of this 3% of global freshwater, 77.2% is locked as glaciers and polar ice – caps, approximately 22.4% is groundwater, 0.35% is in lakes and other wetlands, 0.04% in the land and 0.01% is in the rivers. Freshwater resources are generally classified as surface and ground water. Hydro-biological cycle is natural processes that replenish water between atmosphere, land, sea and all plants and animals.

The expected population growth rate around 2050 would make 40% of the world's population facing water stress or water scarcity (WHO, 2006). It results in the fast urbanization, industrialization and increased agricultural practices to fulfil the requirements of the population, which has put paramount pressure on the demands of water supply. The uncontrolled use of water resources beyond their restoration limit has resulted in the water crisis that the world is currently experiencing, and the generation of massive amounts of waste water on a daily basis. As water is an indispensable component of life without which life is not possible. As a result, water quality is critical for humans and the kingdoms of plants and animals.

In the current scenario, environmental pollution is the most serious global issue threatening our ecosystem. Pollution is present in every strata of the earth, and the negative effects associated with it are a major source of concern in the modern era. The majority of scientists and researchers are looking for effective ways and means to control environmental pollution. Polluted wastewater significantly contributes towards environmental pollution.

Water pollution is explained by variation in the physical, chemical, or biological qualities of water that has a negative impact on both biotic and abiotic ecosystem components (Inyinbor et al., 2018). The contaminants present in water are known as pollutants, which may be solid

suspension (sand, clay, organic matter); colloidal (soap, gel, foam) or completely soluble in water (salts, metal ions, gases, organic substances). Water pollution is classified in various categories depending upon the type of characteristic which are affected and the type of pollutant (solid, colloidal, soluble impurities). Depending upon the type of characteristics affected and nature of pollutant, water pollution is categorized as (a) Physical pollution of water affecting color, turbidity, taste and odor of water, (b) Chemical pollution of water affects pH, dissolved oxygen (DO), Biological oxygen demand (BOD), Chemical oxygen demand (COD), organic pollutant (biodegradable and nonbiodegradable) such as ketones, phenols, amines, mercaptans and hydroxyl benzenes or inorganic pollutants (free chlorine, chloramines and many dissolved metal/nonmetal ions), and (c) Biological pollution of water caused due to presence of biological pathogens. These pollutants attribute to a large number of waterborne diseases such as cholera, hepatitis, and dysentery caused due to polluted water, resulting in large scale death. About 90% of diseases are caused due to polluted water.

Textile industry hazardous effluents are regarded as one of the major contributors to water pollutants discharged untreated into bodies of water. Annually 10–15% of total dyestuff is discharged into the environment obtained from textile products (Mohamed et al., 2017) and creates contamination in our water bodies which leads to the worst effect on biotic life. There are varieties of dyestuff are used in textile industry, such as disperse red 9,Disperse violet 26,Disperse brown 1,C.I disperse blue 56,C.I disperse red 60,C.I Disperse orange 3(Nasiri et al., 2013),Direct red 28, direct black 28, direct black 38,C.I Direct red 2,C.I Reactive red 3,C.I Reactive blue 19, Vat blue 1,Vat black 25,Indico carmine, Vat yellow 1,Vat acid blue 74,Basic blue 11,Basic brown 1,acid blue 349,Acid yellow 36,acid red 337,Acid violet 17,Sulfur brilliant green, Sulfur blue dye, Phthalic anhydride, an Acid red 2 (Benkhaya et al., 2020).The effluent with color residues from dyestuff released from textile industries is toxic for living organisms and is composed of mixture of many chemical pollutants (Kartik et al., 2014). The presence of colloidal materials, as well as colors and oily scum, increases turbidity, giving the water an unpleasant appearance and odor. It stops sunlight from penetrating the plant, which is required for photosynthesis. The oxygen transport process at the air-water contact is hampered as a result of this. The most serious effect of textile waste is the depletion of dissolved oxygen in water, critical for marine life. This also obstructs the water's self-purification process. Furthermore, allowing this effluent to run in the fields blocks the soil pores, resulting in a loss of soil productivity and it affecting the growth of plant.

Interestingly, there have been numerous investigations worldwide on textile effluent treatment methods. All of the methods have drawbacks. None of them has been successful in eliminating toxic pollutants from textile wastewater; most of the existing treatments are very expensive and not much successful in the treatment effluent from textile industry. Therefore, it is important to find a reliable and efficient treatment system for treating dye-containing wastewater discharged from the textile industry.

The Fenton process is one of the most well-known AOPs, and it has been successfully used to treat a variety of resistant chemicals. Organic molecules are oxidized in the Fenton process by hydroxyl radicals produced by the interaction of H_2O_2 with iron (Walling et al., 1973). It's been frequently used to remove COD, TOC, dyes, pigments, insecticides, and other contaminants (Chamarro et al., 2001).

$$Fe^{2+} + H_2O \longrightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$$

The hydroxyl radicals further oxidize the contaminants to CO_2 and water or intermediate chemicals, which is the main mechanism of hydroxyl radical production.

In wastewater treatment processes, adsorption is a frequent technique. Adsorption, among other approaches, is quick and easy to use. The choice of adsorbent is a critical aspect of the adsorption process. A good adsorbent should have a fast kinetics of interaction with the adsorbate, and a porous structure with a large surface area and high adsorption capacity. The regeneration of spent adsorbent is another key feature of adsorptive wastewater treatment systems.

The use of AOPs for the oxidation of hardly degraded organic contaminants has been considered. The Fenton oxidation process (H_2O_2/Fe^{2+}) is one of the most successful organic pollutant decontamination methods among the many AOPs, The Fenton oxidation technique has proven to be useful in the treatment of a variety of industrial wastewaters (Sohair et al., 2014). Adsorption is one of the most effective strategies for removing colours from wastewater. Adsorption has an advantage over other procedures since it is sludge-free, clean, and removes colours completely even from dilute solutions; Activated carbon is the most widely used adsorbent for this purpose due to its huge surface area, high porosity, adsorption ability, and high degree of surface reactivity (Chand et al., 2009). So, to achieve high efficiency these two methods are combined, and experiments are carried out with conditions.

1.2 Scope of the study

The scope of the study is limits to the reduction of high COD levels present in the textile wastewater containing dyestuff using two treatment processes, i.e. Fenton Oxidation process and adsorption. Activated carbon was selected as the adsorbent for the study. An effective photocatalyst, TiO_2 and TiO_2 impregnated activated carbon were tested for the Fenton oxidation process. It aimed to establishing the optimum combination of the Fenton Oxidation process and adsorption using activated carbon for COD removal using batch mode studies.

Among the wastewater treatment techniques, adsorption studies showed the possibility of lowering the concentration of COD well below the maximum permissible levels consistently. This has been achieved by the wise application of adsorption chemistry, tuning the materials for the said application by the help of surface modification along with detailed surface characterization. Although treating pollutants using adsorbents has got a wide interest by researchers in adsorption chemistry, there commercial- scale implementation in real system is still lacking. The application of the fabricated materials in real applications and further commercialization was envisioned for cost-effective treatment of COD removal.

1.3 Objectives of the study

The specific objectives of the study include:

- To study the degradation potential of textile dyestuff by Fenton Oxidation process to achieve the permissible level of COD($\leq$ 250 mg/l) for discharge of treated wastewater to inland surface water bodies using batch studies
- To study the suitable material (adsorbents, photocatalyst) for further treatment of textile wastewater following the Fenton oxidation process
- To study the effect of the influencing parameters (adsorbent dosage, pH, contact time) on the adsorption process, isotherm models and kinetic models

1.4 Approach

Chapter 1 presents an introduction related to the treatment of textile wastewater containing dyestuff, the scope and specific objectives of the study.

Chapter 2 describes a comprehensive literature review of this study including previous related research works and different methods used to treat dyestuff containing textile wastewater. The comprehensive review is carried out to provide the wastewater treatment approaches and the taxonomy in the industrial sector. This chapter provides detailed information about the problems in industries that use water at various processing stages, which motivated the present research.

Chapter 3 describes the materials and methods utilized in this research. Experimental procedures followed to realize each objective are described. Specific details on the experimental setups for each objective, methods followed to obtain optimum levels of chemicals which are used in Fenton oxidation process and chemical characteristics of adsorbent are illustrated. Further, analytical methods used the analysis of COD removal and the details of batch studies, isothermal and kinetic studies are explained.

Chapter 4 presents the results and discussion of experimental data related to each objective considered in the research. The characteristic of the textile wastewater containing dyestuff is discussed. The optimum conditions for the Fenton oxidation process, adsorption and the best combination of Fenton oxidation process with adsorption are elaborated.

Chapter 5 describes the conclusions of the research and future research scope. In this section, the overall results of the research work are explained and coordinated. The applications of the current research work are explained, and also the extension of the research work is elaborated through the future research extension.

2.LITERATURE REVIEW

2.1 Properties of dyes

Any coloring substance does not justify the definition of textile dye until unless it possesses some characteristic properties. A perfect textile dye must possess some basic properties such as coloring ability, solubility, stability, fast to light, detergents (Farah et al., 2013), a dye must have an attractive color. The material or fiber on which a particular dye is applied should possess a good affinity with the dye being applied. Various dyes have some similarities with the pigments but they are distinct from pigment in terms of their properties.

Solubility of dye compounds in water or an organic medium is a crucial characteristic, which determines their applicability during various textile processes (Anna et al., 2014), a dye must possess reasonable solubility in aqueous or organic medium so that they can be applied on to the substrate. Most azo dyes are colored and are easily soluble in aqueous medium while most of the other types of dyes such as disperse dyes are partly soluble in water (Paola et al., 2017). However, the solubility of these dyes can be improved by using organic solvents such as chloroform, cyclohexane, and dimethylformamide (Bonventre et al., 2014).

Another important property of textile dye is its affinity for the substrate to be colored (Zollinger, 2003). The dyeing process will be successful only when both the substrate and dye molecules have a high affinity for one another (Zollinger et al., 2003). Once the dyeing process is completed, the dye must be resistant to washing, light, and heat, as well as have a long life. The shade and fastness of a dye are determined by the extent to which the dye's molecular orbitals interact with the substrate (Farah et al., 2012).

The chemical architecture of the dye molecule controls the color imparting characteristics of dyes during the application process. Chemically, organic dyes only have chromogen, chromophore, and suitable auxochrome, which determine the type of color, sharpness, and intensity of color (Hunger, 2000) Chromogen is made up of chromophores and auxochromes. The appearance of color in a chemical compound is purely due to the presence of chromophore, and auxochromes both intensify the coloring ability and control the solubility of the dye (Hunger, 2000).

2.2 Textile Dye Classification

Figure 2.1 depicts the classification of dyes used in the textile industry based on their type of application.

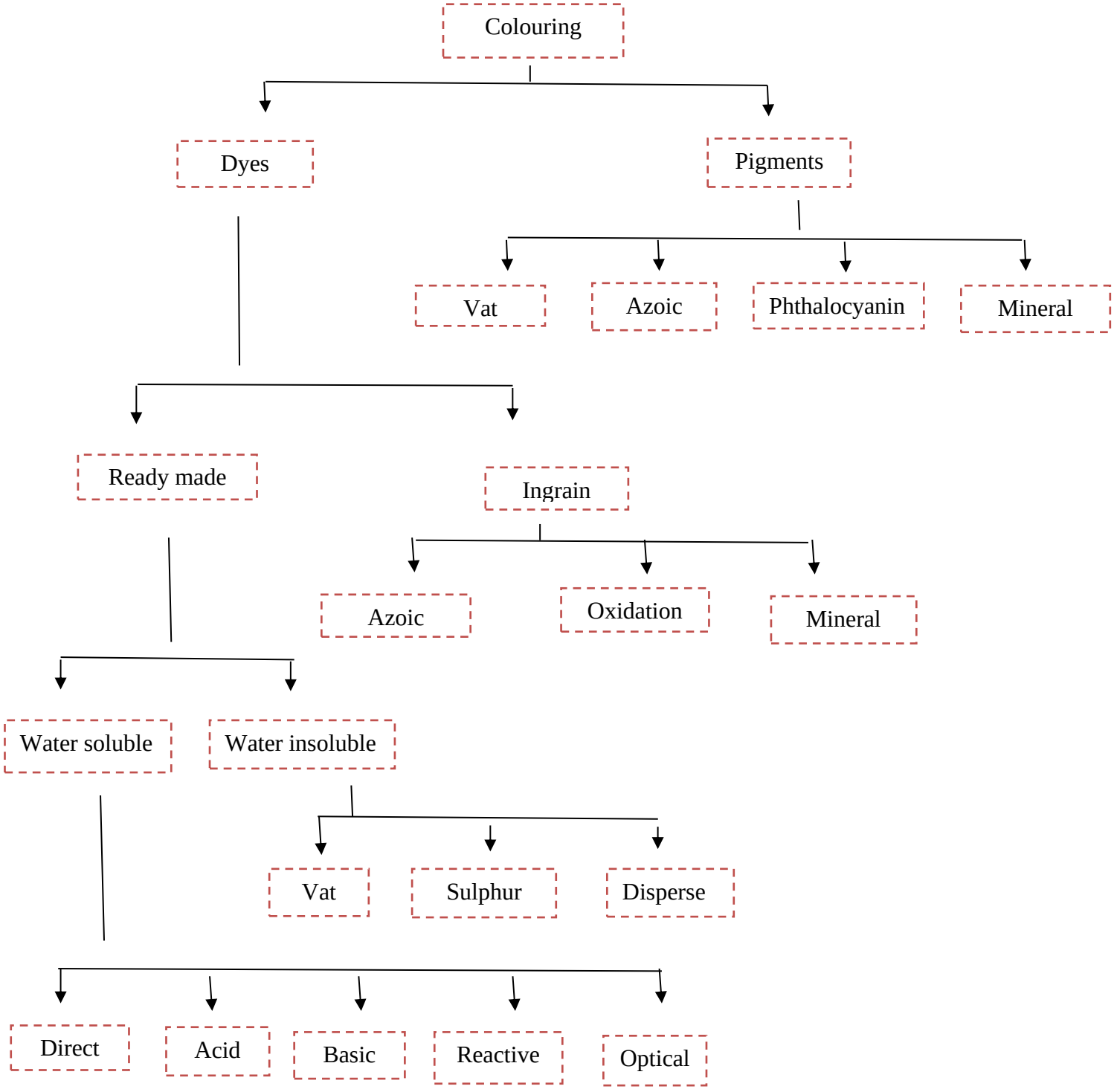


Figure 2. 1: Classification of textile dyes (Christie 2007, Hunger 2003, Sabnis 2010)

2.2.1 Acid dyes

Acid dyes are anionic dyes that are soluble in water and widely used on nylon, cotton, and wool (Benkhaya et al., 2020). The use of acid dyes accounts for approximately 30-40% of total dye consumption (Eszter et al., 2021) on other hand sulphonic acid dyes are commonly used in the textile sector due to of their rich colors and great solubility (Karadag et al., 2006).

2.2.2 Basic dyes

Basic dyes are used in wool, silk, cotton, and modified acrylic fibers. These are cationic dyes and soluble in water (Kumar et al., 2018) and these dyes have a tetra amine group, which is usually present in the formula and nitrogen is occasionally replaced by a positively charged oxygen or sulfur atom (Benkhaya et al., 2020).

2.2.3 Direct or Substantive dyes

These dyestuffs are applied to the substrate directly in a neutral or alkaline bath. Direct dyes are readily soluble in water and have a solid appearance during washing and are primarily used for coloring paper products (Jalandoni et al., 2010). Azo, stibine, oxazine, and phthalocyanine, as well as certain thiazole and copper complex azo dyes, belong to the chromophoric group of direct dyes (Benkhaya et al., 2020).

2.2.4 Reactive dyes

Reactive dyes are frequently utilized due to their durability, processing conditions, and the ability of the reactive compounds to bond with the fibers (Lewis et al., 2014). The amine or sulfhydryl groups of particular proteins contained in textile fibers can form covalent bonds with these dyes (Benkhaya et al., 2020).

2.2.5 Vat dyes

Vat dyes are employed as soluble leuco salts in the cotton, rayon, and wool industries, particularly on cellulosic fibers (Chattopadhyay et al., 2011), these dyes are recognized for their superior color fastness, as well as their light and wet fastness. They are usually soluble in hot water, although some are also soluble in a small amount of Na_2CO_3 (Benkhaya et al., 2020).

2.2.6 Disperse dyes

Disperse dyes are synthetic colorants used for hydrophobic substrates and are extensively used in textile dyeing as commercial mixtures (Daria et al., 2019) and they are frequently employed in big quantities, and substantial volumes of wastewater can be generated because of the vast

amounts of water needed in the dyeing procedures and the high proportion of dye that remains in the water bath (Hunger et al., 2003).

2.2.7 Sulphur dyes

Sulfur dyes contain high molecular weights that are produced through sulfurization based on organic compounds (Stolte et al., 2001). Sulphur dyes are commonly used to color cellulose and by reducing them, they are converted into sodium-based leuco sodium sulfide, sodium sulfide (Benkhaya et al., 2020). They have intermediate structures, and being a modest class of dyes, they are economically important due to their low cost and strong wash fastness features (Gupta et al., 2009).

2.2.8 Azoic dyes

'Azoic dyeing is a process that involves placing an insoluble azo dye immediately on or into the fiber' (Wardmen, 2017) This is accomplished by infusing both diazoic and coupling components into a fiber. When the dyebath conditions are adjusted correctly, the two components react to produce the desired insoluble azo dye. The final color of this dyeing technique is defined by the diazoic and coupling components used (Chudgar et al., 2000).

2.3 Dye intermediates

Dye intermediates are the precursors to dyes. These intermediates are highly aromatic molecules that degrade slowly in the environment that develop as a result of the fragmentation of large dye molecules during the degradation process, in addition to the dye classes listed above (Varjani et al., 2020), when harmful organic chemicals are introduced into the aquatic system, they create a wide range of health issues, as well as increased environmental dangers. Carbocycle chemistry(benzene and naphthalene) and heterocycle chemistry(pyridones and thiophenes) are the chemistry of dye intermediates (Gregory, 2000).

2.4 Toxicity of dyes

In the present scenario, dyes are extensively used in different sectors due to their coloring properties. They are stable colorants which aid the quality as well as aesthetic value of the product whether it is pharmaceutical industry, food, textile or photography sector. Inspite of such applications, they impose a huge stress on the environment due to their toxicity profile especially synthetic one. They affect aquatic systems as dye effluents are directly released into water bodies as well as human population due to the process of bioaccumulation (Khalid et al., 2020).

2.5 Textile dyeing processes

One of the most important aspects of effective textile manufacturing is the dying procedure. Aside from the design and attractive color, the consumer is usually looking for some basic product qualities, such as good light, sweat, and washing resistance, both during and after lengthy usage. To achieve these qualities, the compounds that color the fiber must have a high affinity, a uniform color, be resistant to fading, and be cost-effective (Chequer et al., 2012).

2.5.1 Pre-treatment processes of dyeing

Scouring textiles is a necessary step in the wet processing of textiles in order to generate a fabric that is adequately hydrophilic, waxes and other hydrophobic compounds are removed from fibers during scouring (Menezes and Choudhari, 2011). To saponify natural oils the textile is boiled in alkaline solution (NaOH). The use of high amounts of NaOH needs wastewater neutralization, hence it is clear that this process needs to be improved to fulfill environmental requirements.

Bleaching is the process of removing the natural colorants from the material. There is various type of bleaching agents used in this process such as hydrogen peroxide, sodium hypochlorite, sodium chlorite, and sulphureous acid (Busch et al., 2005) among this hydrogen peroxide is best bleaching agent. Textile manufacturers are now required to bleach without the use of chlorine-containing chemicals (Menezes and Choudhari, 2011).

Mercerizing is a chemical process that improve the dyeability, luster and strength, and to improve appearance. The material is treated with a caustic solution while it is under strain, and then the textile is made caustic free by several washes with hot water (Elmogahzy,2020).

Carbonizing woolen textiles is intended to eliminate grass fragments, leaf particles, and other cellulosic contaminants (Wang et al., 2016). The woolen textile is passed through sulphuric acid bath for this purpose (Moyer, 1967).

Fulling/Milling is the process of shrinking woolen fabrics to make them denser. The technique is carried out in the presence of surfactants and mechanical stirring with a hot caustic soda or acid solution(Mojsov et al., 2017).

2.6 Wastewaters from textile processing

The constituents and the wastewater characteristics from various textile processing steps are showed in Figure 2.2. A survey conducted in Thailand textile industries by Visvanathan et al., (2000) revealed 116-140 m^3 /ton of fabric processed. The wastewater generation rate for man-made fibers was reported to be between 2.7 and 27.4 m^3/ton. The main constituents of textile industry wastewaters have been identified as BOD, COD, Oil and Grease, pH, color, chromium, opper, zinc and sulphides (Visvanathan et al., 2000), In addition to these, coarse suspended solids (lint, flock, fibers, and yarns) have been found in textile wastewater. And some of other additional parameters during the monitoring of textile wastewaters identified, such as TDS, TOC, total phosphorus, TKN, conductivity, chloride, surfactants, alkalinity, sulfate, hardness, VSS, total solids, turbidity, and AOX(Adsorbable organic halides) (Bisschops and Spanjers , 2003).

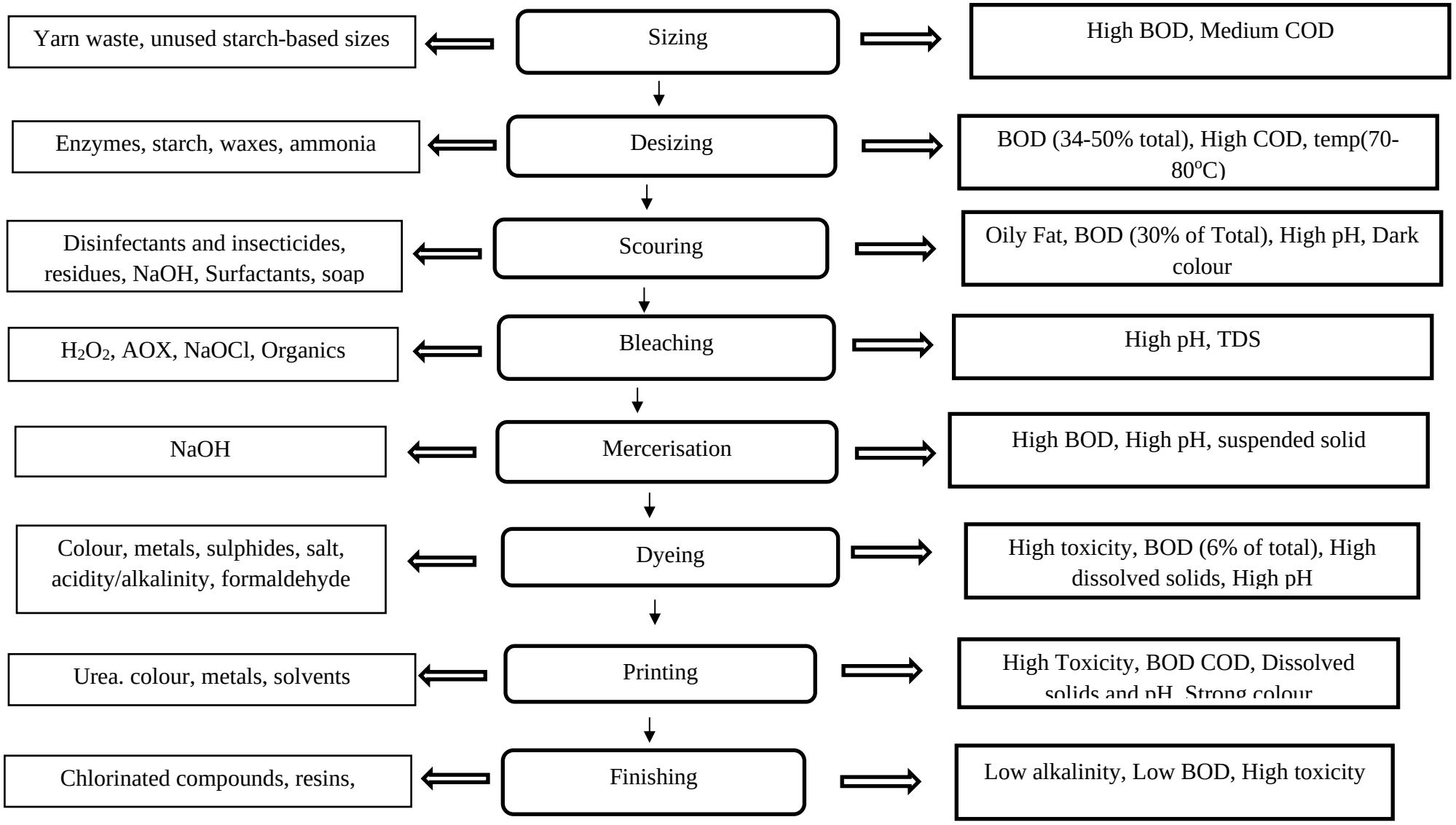


Figure 2. 2: Characteristics of components and wastewater from various textile processing stages (Verma et al., 2012)

2.7 Treatment and disposal of textile industry wastewater

Physical, chemical, and biological methods are well known methods for wastewater treatment. One of the most important aspects to evaluate treatment efficiency of different methods is the ability to reduce hazardous chemical concentrations in wastewater. Figure2.2 shows different stages of wastewater treatment.

Textile sector wastewater must be treated in order to meet applicable effluent requirements and make the wastewater suitable for disposal. Treatment is frequently performed to make the treated effluent suitable for reuse in industry as process water rather than raw water. According to the CEA's effluent standards in Sri Lanka, wastewaters should be treated for pH, TSS, BOD, COD, EC, oil & grease (CEA, Sri Lanka).

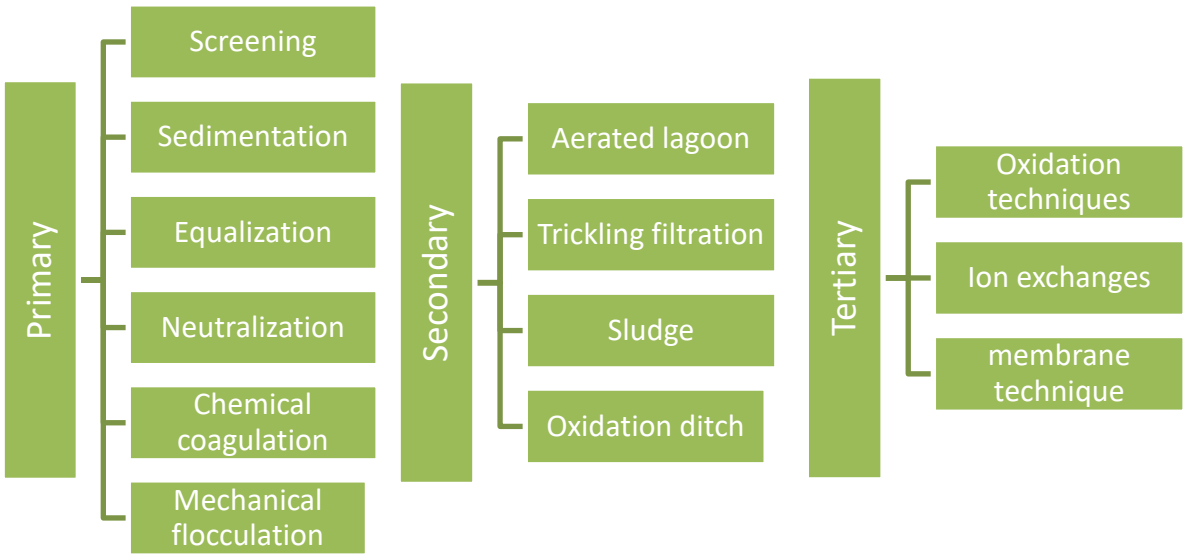


Figure 2. 3: Stages of wastewater treatment

Primary treatment

Most of the primary treatment methods involve screening, sedimentation, and floatation. Suspended and colloidal particles cannot be efficiently removed after the above processes. Therefore, in such cases chemical coagulation or mechanical flocculation is used.

Secondary treatment

Microorganisms are used in secondary wastewater treatment techniques to biologically eliminate pollutants from wastewater. Secondary biological processes can be aerobic or anaerobic, with each bacterial community used differently. Under specific conditions, coupled anaerobic–aerobic processes may be used.

Tertiary Treatment

Oxidation techniques, ion exchange and membrane technologies are involved in tertiary treatment. In the case of industrial wastewater treatment, advanced treatment technologies may be required to remove specific contaminants such as different types of dye.

2.8 Primary treatment

Neutralization, precipitation, coagulation, flocculation, and settling are the most common primary treatments. The wastewaters from the textile processing sector are usually alkaline in character and polluted with (toxic) dyes and colored pigments (Yaseen et al., 2019. The most common primary treatment concerns the correction of pH and the elimination of color. The technique used in a few cases was to adjust the pH in the first treatment, remove biodegradable organic matter in the secondary treatment, and remove color in the tertiary treatment.

The wastewaters are neutralized by adding acid or alkali. Chemical precipitation with alum, ferrous sulfate, ferric sulfate, ferric chloride, magnesium chloride, and even aeration, flocculation, and settling is used to remove color in the presence of enough alkalinity.

Among several coagulants (aluminum potassium sulphate, PAC, $FeCl_3$, and $FeSO_4$), commercial alum was shown to be the most effective and as result of hermolysis followed by coagulation is the most effective treatment approach for eliminating about 90% of COD from textile wastewater(Kumar et al., 2008). On a larger scale, $FeCl_3$ might be utilized to treat wastewater (Ali et al., 2006).

Composite of wastewater was treated with activated charcoal as an adsorbent and Alum, Ferric sulphate, and Ferrous sulphate (more competent) as a coagulant, reaching COD and color removal efficiencies of more than 80% (Patel and Vashi, 2010). Polysep3000 appears to be suitable for achieving high color removal and it was found more suitable as compared with $Al_2(SO_4)_3$ and $FeCl_3$ for sludge production (Aboulhassan et al., 2005).

Jar-tests were used to conduct chemical coagulation investigations with alum, ferric chloride, lime, and calcium carbonate and in an acidic state, the best removal efficiency 42% COD elimination was achieved by combining alum and lime (Altinbas et al., 1995).

The application of lime-ferrous sulphate significantly lowered the organic burden and Coagulation followed by sedimentation using lime and ferrous sulphate (Abo-Elela et al., 1988). Three coagulation agents ($FeCl_3.6H_2O$, Levafloc R, and Colfloc 3915) were used to perform coagulation/precipitation on wastewater samples and the addition of a 1% volume fraction of liquid Levafloc R and Colfloc 3915 virtually totally eliminated the color (Koprivanac et al., 1993).In the treatment of synthetic reactive red 24 and dispersion yellow 201 wastewater, using poly-ferric chloride dosing followed by organic polymeric coagulant epichlorohydrin–dimethylamine dual dosing (PFC/EPI–DMA) resulted in better color removal(Chee et al., 2016).

Color removal from reactive and disperse dye wastewaters using various coagulants and discovered that $MgCl_2/Ca(OH)_2$ outperformed $MgCl_2$/NaOH, $Al_2(SO_4)_3$, PAC, and $FeSO_4/Ca(OH)_2$ (Gao et al., 2007). coagulation/flocculation procedures employing ferrous sulfate and/or lime to remove the color of the effluent, lime treatment alone was shown to be quite successful in eliminating color (70-90%) and a portion of COD (50-60%) from textile effluent; Furthermore, the treatment with ferrous sulfate and lime to maintain a pH of 9.0+/-0.5 was similarly beneficial (Georgiou et al., 2003)

Alum and ferric chloride for the pretreatment of synthetic dyeing wastewater (composed of direct red dye, poly-vinyl alcohol, NaCl, and Na_2SO_4) and reported 90% removal of materials (Total concentration of the materials in the feed water was 2500 ppm) under optimum conditions (Mo et al., 2007). The efficiency of alum and poly aluminum chloride with cationic polyacrylamide was investigated utilizing a central composite design and response surface methodology, with 92% turbidity reduction and 97 % COD elimination observed (Birjandi et al., 2013). In comparison to Lime, $FeCl_3$, and $MgCl_2$, $FeSO_4$ was chosen as the best coagulant for color removal (due to its low dose required, highest decolorization, and lowest settled sludge volume) (Bidhendi et al., 2007).

2.9 Advanced oxidation process

Advanced Oxidation Process (AOP) is mainly the oxidation process which is used to degrade the organic pollutants in industrial wastewaters. Hydrogen peroxide (H_20_2) is used as the oxidizing agent in AOP. This oxidant forms hydroxyl radicals which react with organic compounds to degrade them to carbon dioxide, water and other end products. AOPs have been developed for a variety of applications. One of the most effective AOPs reported is oxidation of contaminants by Fenton's reagent (Bigda et al., 1995), which has proven to be an effective chemical oxidation process for wastewater treatment and pre-treatment (Bautista et al., 2017). According to the widely recognized Fenton's process mechanism, hydroxyl radicals are produced by reacting H_20_2 with Fe^{2+}, which is produced by reacting Fe^{3+} with H_20_2 or intermediate organic radicals (Legrini et al., 1993; Pignatello et al., 1992).

2.9.1 Uses of the Fenton's reagent

The liquid hydrogen peroxide is colorless and odorless. In all proportions, it is miscible with water. It is prepared in various purity grades that are suitable for transportation and long-term storage. The presence of a peroxo (-o-o-) group in hydrogen peroxide results in the release of active oxygen during oxidation ($H_20_2 \longrightarrow H_20 + [O]$). The catalytic activity of Fe^{2+}/Fe^{3+} ions with hydrogen peroxide results in the formation of hydroxyl radicals. The following are the primary benefits of using hydrogen peroxide as an oxidant:

- Act as in wide pH range (2-11)
- High oxidation potential
- Easy to handling
- No secondary pollutants through final products and
- Ideal reagent for an environmentally friendly process owing to the formation of water, oxygen and biodegradable residuals.

Fenton's reagent (H_20_2/Fe^{2+}) has emerged as the most effective chemical for decolorization and reduction of COD of dye and textile wastewater. Major findings of the literature review on Fenton's oxidation are summarized in Table 2.1. Most of these studies were determined in batch reactors to assess the effects of pH, temperature, H_20_2 dosage, $FeS0_4$ dosage and dye concentration.

Table 2. 1: Highlights of published work on Fenton's/photo-Fenton oxidation of textile dyes/ wastewater

Wastewater/Chemical	Experimental Condition	Major Observations	References
Retting flax wastewater	H_2O_2: COD - 0.75 H_2O_2/Fe^{2+} - 50	Detention period and Dosage was highly effected on adsorption ; Fenton's treatment followed a pseudo-first order reaction;98% COD removal efficiency	Ali et al., 2014
Dye wastewater	pH: 2-7 H_2O_2(ml/l): 0.5-4 $FeSO_4$ (mg/l): 300-700	pH-3, H_2O_2 2ml/l, $FeSO_4$ 500mg/l with 1.5 hrs. treatment time 85% of COD removal	Zou et al., 2015
Polyester and acetate fiber dyeing effluent		96% COD removal at pH=5	Azbar et al., 2003
Methyl degradation in aqueous solutions by Fenton's reagent and	Optimum pH=3 H_20_2/Fe^{2+} and H_20_2/Fe^{2+} /UV system Reaction time=30min	The degradation kinetics were found 1st order reaction rules. The photo Fenton system is more efficient than the Fenton system, achieved100 % methomyl degradation in 30 minutes of reaction time	Tamimi et al., 2008

the photo Fenton system	Kinetic study		
Cosmetic wastewater	pH= 2.5-3.0, Fe^{2+} dosage = 200 mg/l, the initial weight ratio of H_20_2 conc. to COD corresponds to the theoretical stoichiometric value. =2.12 Kinetic analysis based on TOC	At 25°C, 45% TOC is removed. At 25°C, 45% TOC is removed. COD reach to regional limit for industrial wastewater discharges. TOC conversion range up to 80-90%	Bautista et al., 2007
UV-assisted Fenton process for decomposition of an azo dye	Fenton type process has been performed (Fe^{2+}/H_20_2, Fe^{3+}/H_20_2 and Fe^0/H_20_2). The molar ratio of Fenton's reagents of 1:5 up to 1:50 at 0.5 and 1.0 mM conc of iron salt and iron powder. In batch reactor for 2hrs at pH=3	Utilization of UV-radiation with Fenton's and Fenton "like" reagents increases the degradation of azo dye. Follow the pseudo first order kinetics. Maximum decolorization of azo dye - 93.2% and TOC degradation- 76.9% using Fe^{2+}/H_2O_2=1:5 molar ratio	Koprivanac and Vujevic, 2007
Textile wastewater with high organic load	Fenton's process reaction time=4hrs Reaction time=6hrs	45% COD reduction was achieved in 4hrs 48% COD reduction was achieved in 6hrs The maximum color removal 78% was achieved	Papadopoulos et al., 2007

Polyacrylamide wastewater	pH=3 reaction temp= 40°C, Fe^{2+} dosage= 3 mmol/l, H_2O_2 dosage = 10 mmol/l, kinetic analysis	High degree of COD removal occurred about 89% Represented by the 1st order reaction model	Qiang et al., 2007
Textile wastewater	pH=3.0, Composite Fe_2O_3/Carbon heterogeneous catalysts for Fenton oxidation	Consumption of H_2O_2 is lower than required by homogeneous Fenton process	Dantas et al., 2006
Carpet dyeing wastewater	pH= 3.0, Temp.=50°C, $FeSO_4$ dosage= 5.5 g/l, H_2O_2 dosage= 385 g/l. H_2O_2/Fe^{2+} ratio constant in the range of 95-290	COD removal is 95%	Gulkaya et al., 2006
Biodegradability and oxidizing rate for hospital wastewater	Photo-Fenton process used as a pretreatment, COD:H_2O_2: Fe(ii)=1:4:0.1 at pH=3	BOD/COD ratio: increased 0.3 to 0.52, Oxidation degree of organic substance increased from -1.14 to +1.58	Kajitvichyanukul and Suntronvipart, 2006
Tannery wastewater	Fenton and photo-Fenton processes were carried out. H_2O_2/UV process at pH= 3.0.and Fenton's process at pH= 3.5	Both oxidation processes can reduce TOC content by mineralizing organic compounds	Schrank et al., 2005

Treatment of landfill leachate by Fenton reagent	Optimum pH= 2.5. H_20_2 to Fe (II) molar ratio=1.5. reaction time=30min	As the dosage increased, organic removal increased. The simultaneous addition of hydrogen peroxide and ferrous iron was more effective than the addition of only hydrogen peroxide.	Zhang et al., 2005
Color removal of Reactive Orange 4 dye	Fenton and photo-Fenton processes	Under ideal conditions, the photo-Fenton process is proven to be more efficient than the Fenton method. 2% of the color resurgence were observed at finally	Swaminathan et al., 2004
Aqueous dyes solutions	H_20_2/UV, Fe^{2+}/H_20_2 and Fe^{2+}/H_20_2/UV oxidation processes were compared.	The strongest process was Fe^{2+}/H_20_2/UV	Xu et al., 2004
Textile effluent	Conc. Of Fe (II) between 0 - 400ppm, Dose of H_20_2 between 0 - 10,000 ppm. Temperature= 251°C to 701°C.	Removal of organic load in photo-Fenton process is much greater than Fenton process	Perez et al., 2002
Disperse dyes.	Fenton process. Optimal pH= 3. H_20_2 dosage = 600 mg/dm^3, $FeS0_4$ dose = 550 mg/dm^3	The final effluent is colorless and has a residual COD of 100mg/dm^3	Szpyrkowicz et al., 2001
Wastewater from dye intermediate amine J acid plant	pH= 1-3, H_20_2:Fe^{2+}=10:1(M/M), H_20_2/COD = 2.0 g/g, BOD/COD = 0.5	Removal of total COD was 66.7%. Removal of amino was 68%	

Desizing wastewater; less than 0.2% Poly vinyl alcohol and blue G (a direct dye) or Black B (a reactive dye)	pH = 3 Temperature 30^{o}C, Chemical coagulation followed after Fenton oxidation	The two-step treatment technique was shown to be just moderately better than the single-step approach in terms of COD elimination efficiency	Cho et al., 1997
Removal of color and COD from synthetic textile wastewater		90% of color removal at 5minutes under lower dosage of H_2O_2 and Fe^{2+}	Kang et al., 2002
Color removal from azo dye Orange G(OG)	Fenton oxidation process at pH 4.0, H_2O_2 dosage 1.0×10^{-2} M and molar ratio of $[H_2O_2]/[Fe^{2+}]$ 286:1	94.6% color removal efficiency within 60 minutes for 2.21×10^{-5} to 1.11×10^{-4} M of OG, degradation reaction of OG with $Fe^{2+/}H_20_2$ follows a pseudo second-order pathway	Sheng, 2009
Synthetic dye wastewater	Application of ferrous iron-catalyzed ozonation Fe(ii) 3.6mMFe^{2+} at pH 3; Fe $^{2+}$: O_3 molar ratio 1:14	95% color and 48% COD removal and investigated that in terms of BODs/COD ratio, the biodegradability parameter of synthetic dye wastewater has been expanded six-fold	Arslan, 2001

2.10 Adsorption

The most widely used technique in water and wastewater treatment is activated carbon (AC) adsorption. Because of its high surface area, AC shows greater adsorptive capacity for dyes than the other adsorbents (Mustafa et al., 2014).

Kannan and Sundaram (2002) worked on removal of dyes using activated carbon as an adsorbent. The results showed that, when the contact time and adsorbent dose increased, the rate of adsorption increased through the decrease in pH. Neutral and basic dyes adsorption increased with the increase in pH.

Yeh and Thomas (1995) investigated Powdered AC (PAC) and Granular AC (GAC) that possess high adsorptive capacity. Removal of colour from synthetic dye (disperse red 60) wastewater, which typically emanates from the Taiwan textile industry, has been studied with PAC. The study revealed the effective diffusivity of the adsorbent material (PAC). In this work film-pore diffusion model was also attempted for the mass transfer of disperse dye from wastewater into porous sorbent material and have found that the film mass transfer co-efficient increases with the decrease in particle size. The time required to attain equilibrium for the removal of color from dye wastewater was reported to be three hours both for PAC and GAC(Zaman and Gupta, 2011). The mass transfer coefficient (106 Kf, in cm h^{-1}) increased from 26.77 to 47.08 with the increase in particle size from 100-230 to 235-400 mesh. The COD removal was found to be 95-98% for various dye concentrations (25-200 ppm).

Miao and Dai (1998) have reported that AC adsorption is a suitable method for the removal of dye(s) and colour from wastewater. The diffusion mass transfer coefficients were determined and correlated against the Reynolds number. Jia-Ming et al., (2000) have investigated the adsorption of red and yellow dyes from aqueous solution by GAC. Adsorption data were found to obey Langmuir, Freundlich and Redlich-Peterson isotherms. The fixed bed column tests were also carried out with GAC and efficient color removal with low-feed flow rates were observed.

The removal of acid yellow 36 dye by adsorption utilizing activated carbons as an adsorbent was studied, with activated carbons manufactured from low-cost mahogany sawdust and rice husk serving as adsorbents(Zaman and Gupta, 2011). The pH value of 3 was found to be preferable for adsorption, and the Langergren pseudo-first-order constant and intraparticle diffusion rate constants were determined as kinetic parameters. The rate limiting process has been identified as dye molecule intraparticle diffusion within the particle and saw dust carbon

had an adsorption capacity of 183.8 mg/g and rice husk carbon had an adsorption capacity of 86.9 mg/g. For the removal of acid dyes in wastewater treatment, saw dust and rice husk activated carbons were used as alternatives to commercially available activated carbons.

2.11 Titanium dioxide

The acceleration of a photo reaction in the presence of a catalyst is referred to as photocatalysis. The photocatalytic activity is determined by the catalyst's ability to generate electron-hole pairs that undergo secondary reactions. The discovery of TiO_2 electrolysis of water made photocatalysis a practical possibility. TiO_2 is the most commonly used semiconductor as a photocatalyst because it is inexpensive and widely available. It works well as a photocatalyst when exposed to UV light and it exhibits photo catalytic activity in visible light when doped with nitrogen ions or metal oxides (Kurtoglu et al., 2011).

Naseri et al., (2013) reported the decomposition of sulfur mustard (bis2-chloroethyl sulfide), a highly toxic chemical warfare agent, by homogeneous and heterogeneous photocatalytic degradation on titania nanoparticles. Titanium dioxide is an effective photocatalytic decontaminant of sulphur mustard, converting it to relatively non-toxic products. The results showed that adsorption of substances on the surface of nano-TiO_2 increase the rate of photocatalytic degradation. They also simultaneously carried out photolysis and photocatalysis of sulphur mustard in hexane and faster sulphur mustard decontamination to various intermediate and relatively non-toxic products after 90 minutes reaction was observed with low catalyst loadings.

Kansal et al., (2007) reported the use of a heterogeneous photocatalytic oxidation process in the presence of UV light and TiO_2 for the deterioration of persistent organic pollutants, resulting biodegradable and less hazardous material. This method is based on the formation of hydroxyl radicals in the presence of oxygen, which are capable of transforming harmful organic molecules, including those that are non-biodegradable, into relatively non-toxic end products like CO_2 and H_2O (Ahmed et al., 2010).

Lia et al., (2006) studied the degradation of methyl orange using TiO_2 coated Activated carbon and concluded that by adsorption, the adsorbent supports provide a high concentration environment of particular organic compounds around the loaded TiO_2, which improves the rate of photooxidation. Organic molecules are oxidized with adsorbed states on photocatalyst surfaces, and the resultant intermediates are also adsorbed and then oxidized and catalyst amount plays major role on the degradation efficiency.

Lee (2004) studied the removal of microcystin-LR from water with TiO_2 coated Activated Carbon. Under the UV light, the majority of microcystin-LR was destroyed after 20 minutes, after being adsorbed to the surface of the activated carbon, Microcystin-LR moved constantly onto the surface of TiO_2 particles near the entrance of macropores, with a removal effectiveness of up to 96% (Lee, 2004).

2.12 Treatment methods and their advantages and limitations

Table 2. 2: Available COD removal methods and their advantages and limitation

COD removal method	Advantages	Limitations	References
Ozonation	Satisfactory color removal water reuse	Expensive Not effective for COD, BOD reduction	Lin SH et al., 1992
Photochemical	No sludge; reduce of foul odors	Production of by products	Yang et al., 1998
Biological treatment	Eliminating some metals is possible	Technology is still being developed and commercialized.	Ahmaruzzaman et al., 2011
Electrochemical destruction	Efficient and economical dye removal, break down compound are non-hazardous	High price for electricity	Ogutveren and Kaparal, 1994; Pelegrini et al., 1999
Reverse osmosis	All mineral salts are removed, and reactive dyes and chemical auxiliaries are hydrolyzed.	High pressure	Ghayeni et al., 1998

Ion exchange	A broad range of heavy metals are effectively removed	Regeneration required Cost effective	Ahmaruzzaman et al., 2011
Irradiation	Effective oxidation at lab scale	lot of dissolves 0_2 required Costly method	Ahmaruzzaman et al., 2011
Electrokinetic coagulation	Economically feasible	Much of sludge production High disposal cost	Ahmaruzzaman et al., 2011
Photocatalysis	Near complete colour removal In short detention time complete mineralization	For final polishing only Expensive	Das et al., 2011
Activated sludge	Bulk COD removal Partial nitrification	High residual COD, ammonia, color	
Ultrafiltration–microfiltration	Low pressure	Inadequate quality of treated wastewater	Ghayeni et al., 1998
Nanofiltration	Separation of low-molecular-weight organic compounds and divalent ions from monovalent salts, High-concentration treatment		Akbari et al., 2002; Tang and Chen, 2002

Biodegradation	Approximately 90% of oxidizable substances are eliminated.	Low biodegradability	Pala and Tokat, 2002; Ledakowicz et al., 2001

3.MATERIAL AND METHODS

The materials and methods used in this research project are discussed in this chapter. For achieving the objectives, planned the work with the following work elements (i) Wastewater collection from the industry, (ii) Characteristic of textile industry effluent before treatment (iii)synthesized materials (iv) experimental setup for laboratory scale (v) studies and evaluation of experimental data.

3.1Textile Industry Effluent

The effluent was collected from one of the largest textile industries of Sri Lanka, Naturab group of companies, Panadura. They are using various types of dyes for their manufacturing according to the customer's requirement. Disperse and acid dyes are the most often used dyes and they contain inorganic substances (acids, salts, alkalis) and organic substances (thickeners, finishing agents, detergents). The effluent was characterized by various physiochemical parameters. Such as pH, COD, BOD, total suspended solid, total dissolved solid, electrical conductivity and Oil and Gas. The characterization report is presented in Table no 3.1

Table 3. 1: Characteristics of textile industry effluent before treatment

Parameters	Unit	Results
pH	-	9.9
Chemical Oxygen Demand	mg/l	2100
Biological Oxygen Demand @20^{o}C	mg/l	154
Total Dissolved Solids	mg/l	1280
Total Suspended Solids	mg/l	13
Electrical Conductivity @25^{o}C	µS/cm	1615
Oil& grease	mg/l	<2

The effluent was collected from an equalization tank in pre-cleaned plastic containers, which are free of contamination and carried out to the laboratory and refrigerated and kept 4^{0}C with pH

correction until performed analysis (preserved samples were analyzed within 28 days of collection).

3.2 Classification of dyes

They are using a variety of dyes including Rhodamine for their production. Dyeing processed wastewater was collected to the equalization tank the ratio of Rhodamine: Other dye 1:9. (meaning that when rhodamine using for their process they did pretreatment process for rhodamine mixed water, then it was mixed to equalization tank with other dyestuff containing wastewater).The properties of dyes are presented in Table 3.2 (These dyes are mostly used by selected industry for study) structure of dyes is shown in Figures 3.1, 3.2,3.3,3.4,3.5,3.6,3.7 and 3.8.

Table 3. 2:Properties of dyes

Commercial dye	**Molecular formula**	**Molecular weight**
Disperse rubine RDSE	$C_{24}H_{26}IN_5O_7$	519.93
Disperse yellow RDSE	$C_{15}H_{15}N_3O_2$	269.3
Disperse orange RDSE	$O_2NC_6H_4N{=}NC_6H_4NH_2$	242.23
Disperse Navy blue RDSE	$C_{16}H_{14}N_2O_2$	266.29
Disperse red 200%	$C_{17}H_{16}ClN_5O_2$	357.79
Sunset yellow 4 GN	$C_{16}H_{10}N_2Na_2O_7S_2$	452.37
Disperse blue 100% HACE	$C_{24}H_{27}N_7O_5$	493.5
Suncid red N 2RL	$C_{22}H_{14}N_4Na_2O_7S_2$	556.48

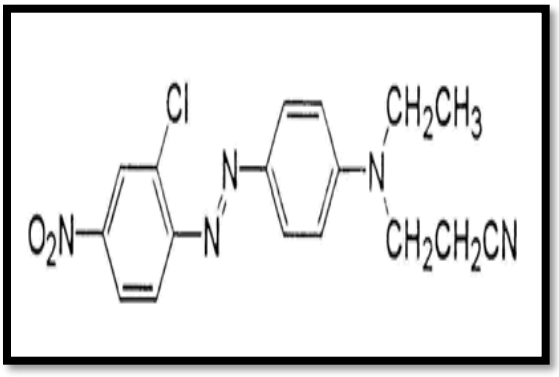


Figure 3. 1 : Structure of Disperse red

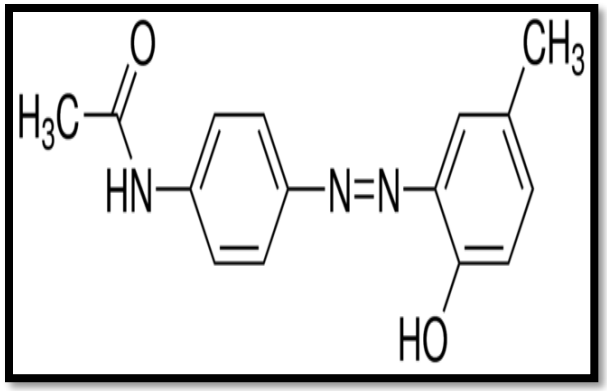


Figure 3. 2: Structure of Disperse yellow

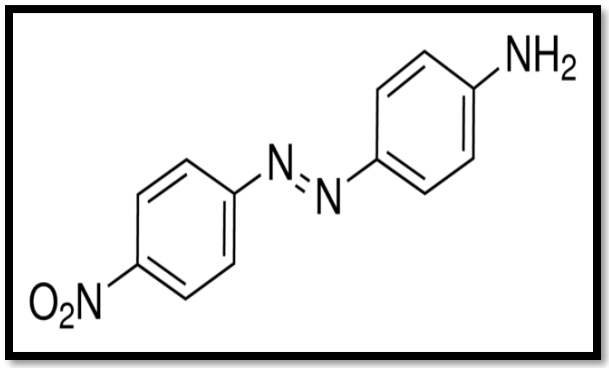


Figure 3. 3: Structure of Disperse orange

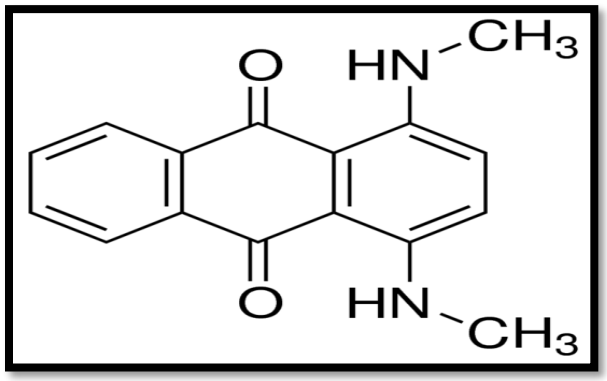


Figure 3. 4: Structure of Disperse navy blue

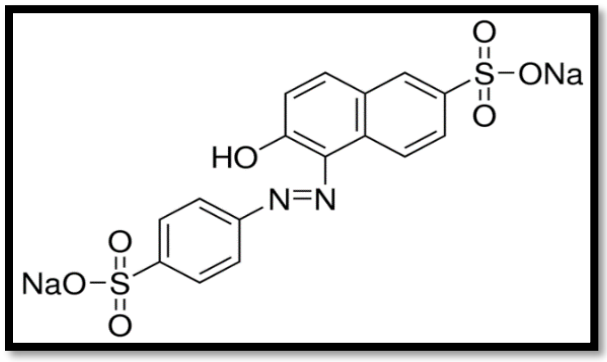


Figure 3. 5 : Structure of Sunset yellow

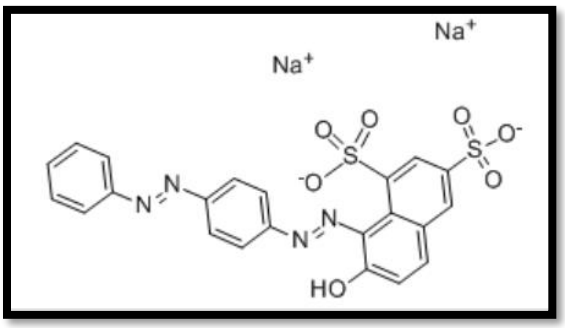


Figure 3. 6: Structure of Suncid red

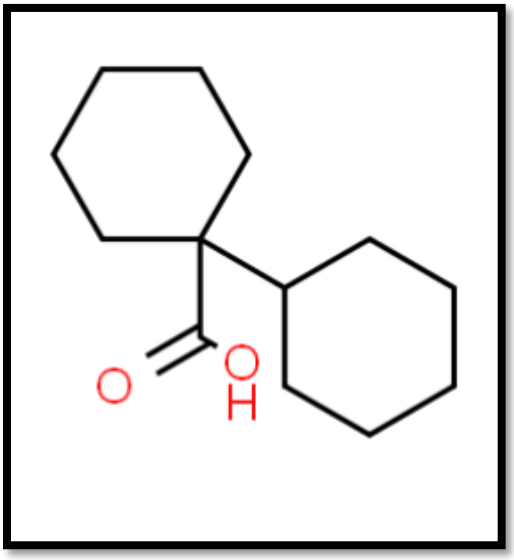


Figure 3. 7: Structure of Disperse Rubine

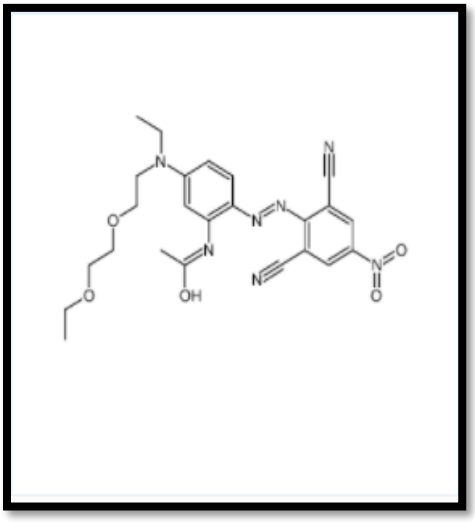


Figure 3. 8: Structure of Disperse blue8

3.3 Chemical Oxygen Demand analysis

The COD is an estimate of the quantity of oxygen necessary to oxidize the part of organic matter in wastewater, as well as the amount of oxygen used by organic matter in a boiling acid potassium dichromate solution(Khan et al., 2017). The COD was calculated using an open reflux dichromate titrimetric method, as explained in standard methods (APHA 1998) (Axán et al., 2013).

Used apparatus in this analysis

- Reflux apparatus
- Burner or plate with temperature regulator
- Titration equipment

The following reagents are used to analysis the COD

- Standard Potassium Dichromate solution (0.0417M)
- Standard Ferrous Ammonium Sulphate (0.25M)
- Conc.Sulphuric Acid Reagent
- Mercuric Sulphate
- Ferroin Indicator

Mercuric Sulphate (0.4 g) was placed in a reflux flask. Sample (20 ml) was added and mixed well. Standard Potassium Dichromate(10 ml) was added into the reflux flask. Then 30 ml of Conc.Sulfuric acid containing Silver Sulfate added slowly. (Due to the high temperature, fatty acids can escape if they are added too quickly). It was mixed well then, the flask was connected to condenser and the system was re-fluxed for two hours. It was allowed to cool then washed down the condenser with distilled water. Then it was titrated excess Potassium Dichromate with 0.5M Ferrous Ammonium Sulphate Using Ferroin Indicator. Repeat the procedure with distilled water instead of the sample. The amount of dichromate used for organic compound oxidation is given by the difference between the dichromate originally added and the remaining unreacted dichromate. COD was calculated as in equation 3.1.

$$\text{COD as mg } O_2/l = \frac{(a-b) \times M \times 8000}{\text{volume of sample(ml)}} \qquad 3.1$$

where; a- FAS amount used for control sample, b-FAS volume used for sample, M- FAS Morality

Potassium Dichromate solution (10 ml) is acidified by adding 10 ml of sulphuric acid and titrate with FAS with Ferroin Indicator. The molarity of FAS was calculated as in equation 3.2

$$\text{Molarity of FAS} = \frac{10 \times 0.25}{\text{Volume FAS used in titration, ml}} \qquad 3.2$$

Figure 3. 9: COD reflux condenser

The color shifts sharply from blue-green to reddish-brown during the titration. The image below depicts the titration's color difference.

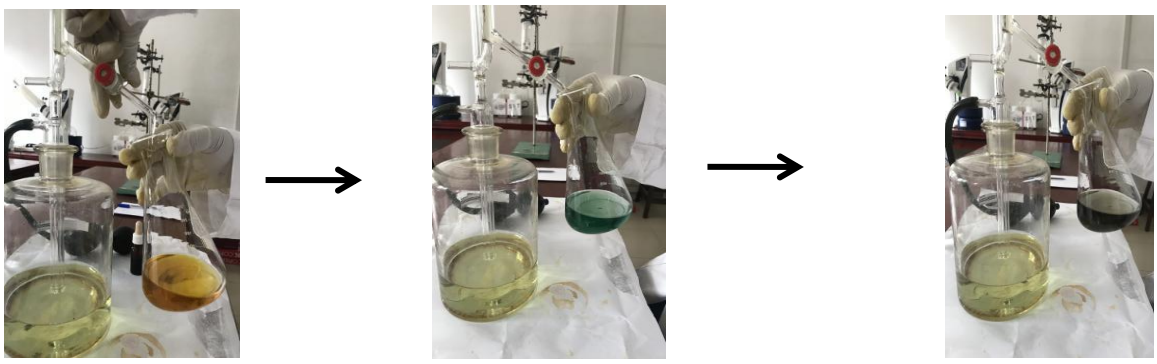


Figure 3. 10: Titration setup and color change

3.4 Synthesis of TiO_2

Titanium (IV) Isopropoxide(45.2 ml), 0.0045 g of Hydroxypropyl cellulose P.M. 100.000, and 17 ml absolute Ethanol were mixed together and stirred for 5 minutes. A mixture of methanol (5 ml) and ethanol (45 ml) with a volume ratio of 1:10 was added with 160 ml DI water and then pour into stirring solution.

Then the mixture was kept for 1 hour at 550 rpm. After 1hr, 25.5 ml of Titanium (IV) Isopropoxide, 0.0725 g of Hydroxypropyl cellulose P.M. 100.000 and 11 ml absolute Ethanol were mixed together. DI water, ethanol, and methanol mixture were prepared as previous step. Then those two added together to the initial solution and kept for another 1 hour at 550 rpm. Then the final mixture kept for another 30 minutes until a white precipitate is appearing. The precipitate was then collected by centrifugation for 3 minutes at 2000 rpm. The white precipitate was washed with ethanol for three times. The final precipitate was heated at 70 ^oC for 12 hours and calcined at 550 ^oC for 5 hrs.

3.5 Synthesis of TiO_2 impregnated Activated Carbon

The method described Baolin et al., 2016 was further modified to synthesis of TiO_2 impregnated AC, Solution A - Titanium (IV) Isopropoxide was first diluted in anhydrous ethanol and acetic acid. Second, solution B was made by combining anhydrous ethanol with deionized water, then gently adding dilute nitric acid to set the pH to 2-3. Finally, with continuous shaking drop by drop, solution B was poured into solution A to make TiO_2 sol.The sol was mixed with the as-prepared AC using continuous magnetic stirring and then aged for 20 hours at room temperature to make sol-coated AC. The mixture was rinsed with ethanol and deionized water to remove untreated products. The final precipitate was heated at 70 ^oC for 12 hours and calcined at 550 ^oC for 5 hrs.

Table 3. 3: Mixing weight ratio of AC and TiO_2

Label	AC	TiO_2
AT_1	1	1
AT_2	2	1
AT_3	3	1
AT_4	1	2
AT_5	1	3

3.6 Fenton Oxidation process

Temperature, H_2O_2 concentration, and Fe^{2+} concentration are the three most important factors in the Fenton reaction. To find out the optimum operating parameters for the Fenton reagent (H_2O_2/Fe^{2+}), the Fenton process was conducted at room temperature. Wastewater sample was collected from equalization tank which includes 1:9 ratio of Rhodomine EB: Other dyes. The effluent pH was corrected to a range of 2-3 with the addition of Con H_2SO_4 prior to the chemical oxidation process. To achieve the desired Fe^{2+} concentration, $FeSO_4.7H_2O$ was added. Finally, a little amount of H_2O_2 (35%(w/v)) was carefully introduced to start the Fenton reaction. Aerated the mixture for 2 hrs. After the Fenton oxidation process, the pH of the treated wastewater was corrected to 8 by adding 10% lime. Following that, 1.4 ml of PLC flocculant was added and vigorously stirred. Finally settling on 60 minutes. The titrimetric method was used to evaluate the COD removal efficiency.

Figure 3. 11: Aerating the wastewater with Fenton reagent

3.7 Evaluation of COD removal efficiency for different combination of synthesized TiO_2 and AC

Single-solute batch trials were carried out using synthesized TiO_2 impregnated AC(AT1-AT5) to study the COD removal efficiency. Experiments were done two Ultraviolet (UV) lamps (360 nm) with 6 g of material. The contact time was 4 hours with pH 2. Initial Dye wastewater COD was 710 mg/l, the temperature was 28 ºC, and the stirring speed was 150 rpm. The material with the acceptable COD removal (COD removal below 250 mg/l) was selected and given the term as (AT)opt.

Figure 3. 12: The laboratory setup for the batch studies on the mechanical stirrer

3.8 Selection of Best Material for COD removal

Following Fenton treatment, the effluent was treated with synthesized TiO_2, $(AT)_{opt}$ and CAC. Each batch adsorption experiment was conducted at room temperature (27 ^{0}C). The sample's initial pH was 2. The 1l sample was placed in a volumetric flask and stirred for 4 hours in a mechanical shaker at 100 rpm with different weights of materials to range from 1 g to 8 g. The COD in the filtrate was evaluated after all samples were filtered by a filter paper (Whatman, No. 42). The dosage with the highest absorbance was chosen as the optimum dosage. The cost calculation was done for all three materials. Then the best material was selected considering the cost.

3.9 Characterization of CAC using SEM, EDX, XRD, and FTIR

Environmental Scanning Electron Microscopy (ESEM- Carl Zeiss, EVO 18, Secondary Electron Microscope, Germany) coupled with Energy-Dispersive X-ray Spectroscopy (EDX Z1 analyzer,

USA) was used to examine the morphology and elemental composition of AC before and after the treatment.

The phase identification of the activated carbon was performed by X-Ray Powder Diffraction (XRD-D8, ECO, Advance Bruker Diffractometer with filtered Cu,Kα radiation, Germany) (Danushika et al., 2019). To identify the functional group of activated carbon Fourier Transform-Infrared Spectroscopy (FTIR, ALPHA Bruker, Germany) was used in the adsorption mode at ambient temperature in the spectral range of 500-4000cm^{-1}

Figure 3. 13: Environmental Scanning Electron Microscopy- Energy-Dispersive X-ray Spectroscopy

Figure 3. 14: Fourier Transform- Infrared Spectroscopy

Figure 3. 15: X-Ray Diffraction spectroscopy

3.10 Optimization of experiment condition for the CAC for COD removal

A Fenton treated wastewater sample containing 710 mg/l of COD was applied for further COD removal experiment. Batch studies were carried out to determine contact time, and pH of CAC for effective COD removal.

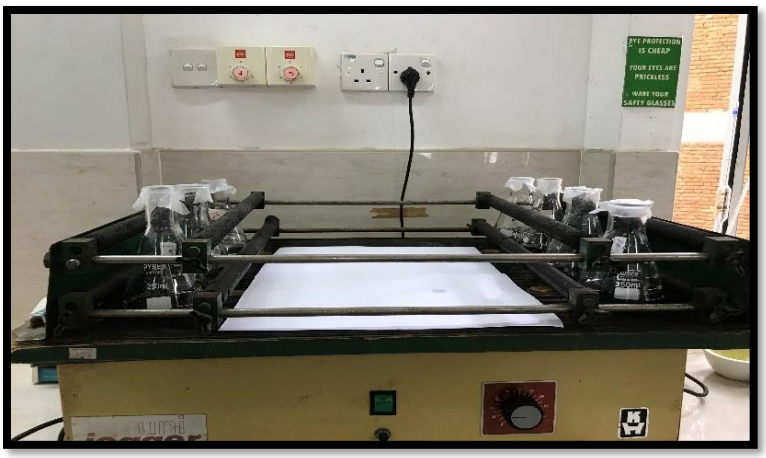


Figure 3. 16: The experimental setup for batch experiments

3.10.1 Optimum Contact time

A volume of 1 l wastewater sample was used to investigate the optimum contact time with ideal dosage of 8 g. The initial pH of the sample was 2, and the temperature was 27^{o}C. The sample was

placed into the volumetric flask and after the addition of sorbent the contents were stirred with mechanical shaker at 100 rpm with time variation 30 minutes to 12 hours. The contact time that results in the highest absorbance is chosen as the optimum contact time.

3.10.2 Optimum pH

Removal efficiency is highly depended on solution pH. A volume of 1 l wastewater sample was used to find optimum pH with optimum dosage of 8 g, optimum contact time of 2 hrs. The pH of the sample was varied from 2 to 12 used 20% of HCl and 20% of NaOH with keeping other parameters as constant. The optimum pH was chosen as to result in the maximum COD reduction percentage.

3.11 Adsorption isotherms and kinetic studies for CAC

3.11.1 Adsorption isotherms

Adsorption isotherm and kinetic model studies are essential in process of adsorption. The batch experiments were carried out to determine the sorption capacity of sorbent for COD removal. The Freundlich isotherm and Langmuir isotherms are the two most common isotherms for this study.

Equation 3.1 was used to calculate the quantity of COD removed per unit mass of the AC (Qe) in mg/g.

$$Q_e = (C_o - C_e) \times \frac{V}{W} \qquad 3.1$$

where Co and Ce are the initial and the equilibrium concentrations in the solution (mg/l) respectively, V is the volume of solution (l), and W is the mass of the adsorbent (g).

The Langmuir isotherm applies when the adsorbate coverage is confined to one molecular layer. The linear form of this isotherm follows equation 3.2. Only monolayer adsorption occurs with no interaction between adjacent adsorbed ions, and adsorbate ions tend to either adsorb or desorb, according to the Langmuir adsorption isotherm model (Miedaner et al., 2006).

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L C_e} \qquad 3.2$$

where Ce is the equilibrium concentration of adsorbate (mg/l), Qe is the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium (mg/g), Qm is maximum monolayer coverage capacity (mg/g), and K_L is the Langmuir isotherm constant (l/mg).

A dimensionless equilibrium parameter R_L also known as the separation factor. It can be used to analyze the Langmuir equation. R_L is given in equation 3.3; where Co is initial concentration (mg l^{-1}), and K_L is Langmuir constant. R_L value describes the shape of the isotherm. If ($R_L > 1$) unfavorable, linear ($R_L = 1$), favorable ($0 < R_L > 1$), or irreversible ($R_L = 0$) (Weber and Chakravorti, 1974).

$$R_L = \frac{1}{[1 + (1 + K_L C_o)]} \qquad 3.3$$

Freundlich,1906 proposed the Freundlich isotherm for multilayer adsorption from solution. The Freundlich isotherm is expressed in linear form as follows in equation 3.4. To study the adsorption of dye with CAC Freundlich isotherm was studied. There are some assumptions considered in this isotherm model. Such as the availability of heterogeneous surfaces bound to be as a multilayer in adsorbate, adsorbed ions interact with each other.

$$\log(Q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \qquad 3.4$$

Where K_f is the Freundlich constant (mg/g), which expresses the adsorbent's relative adsorption capacity in terms of bonding energy and n is the heterogeneity factor representing the deviation from linearity of adsorption. The Freundlich constant (n) indicates the adsorption mechanism and when range of 2-10 adsorption is favorable, range of 1-2 moderately difficult and $n < 1$ poor adsorption (Kakavandi et al., 2013).

3.11.2 Kinetic studies

The Kinetic data were analyzed using Lagergren's pseudo-first-order kinetic model and pseudo second-order kinetic models. Pseudo first order kinetic describes the adsorption of one ion of adsorbate to one adsorption site and the pseudo-second-order kinetic model describes the adsorption of one ion of adsorbate to two adsorption sites (Ho and McKay, 1999).The pseudo-first

order kinetic model and the pseudo second-order kinetic models equations (3.5) and (3.6) respectively as follows.

$$log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right)t \qquad 3.5$$

$$\frac{t}{q_t} = \frac{1}{[K_2 (q_e)^2]} + \left(\frac{1}{q_e}\right) t \qquad 3.6$$

Qe is the amount of adsorbate adsorbed on adsorbent (mg/g) at equilibrium, Qt is the amount of adsorbate adsorbed on adsorbent (mg/g) at time t (minutes), K_1 is the constant (min^{-1}) for pseudo-first-order kinetics, and K_2 is the rate constant (gm/g/min) for pseudo-second-order kinetics.

3.12 Regeneration Studies for Commercial Activated Carbon

The regeneration of an adsorbent is designed to decrease the amount of capital needed for material and to eliminate the deposition of additional waste. The regeneration was done to identify the best regenerating reagent for CAC. The study was conducted using HCl and NaOH solution with pH 4 and 10 respectively. The batch experiments were conducted using 7 g of CAC in 1 l of Dye wastewater with COD 710 mg/l. The contact time was 2 hours and the pH of 2 was maintained throughout the experiment. After the adsorption cycle, CAC was let to settle at the bottom of the flask before decanting the supernatant. A volume of 100 ml of regenerating reagent was then added to CAC containing flask and kept in the mechanical shaker at 150 rpm for 2 hrs. The regeneration reagent was decanted.

Then the CAC solid was washed with DI water for two times and decanted. The CAC containing flask was kept in the oven 12 hours at 105^{o}C. The weight of the flask was recorded and then another adsorption and desorption cycle were carried out. The weight loss of CAC at each step was kept to a minimum (less than 0.05 g). The COD removal was measured after every adsorption cycle. This was repeated for three regeneration cycles.

4. RESULTS AND DISCUSSIONS

4.1 Wastewater Characterization

The characteristics values of industrial dye wastewater were assessed in the laboratory using APHA standard methods. The results obtained through characteristics analysis showed that wastewater's pH value is 9.9, indicating the presence of alkaline substances. This is because the chemicals (sodium sulphate, caustic soda, soda ash, sodium hydrosulfite, etc) and softeners are involved during the dyeing process. Chemical oxygen demand is a commonly used parameter for characterizing organic matter in textile wastewaters; it is affected by the dyes used in the manufacturing process. Here the most notable are the higher BOD and COD of the wastewater.

Table 4. 1:Characteristics of effluent

Parameter	Value	Unit
pH	9.9	-
Total Dissolved Solids (TDS)	1280	mg/l
Chemical oxygen demand (COD)	2100	mg/l
Biological Oxygen Demand (BOD)	1210	mg/l
TSS	13	mg/l
Electrical Conductivity	1615	µS/cm
Oil &Grease	<2	mg/l

4.2 Operating Parameters of Fenton Oxidation Process

The initial values of operating parameters of the Fenton process determine the process efficiency. The main parameters governing the Fenton process are pH, H_2O_2 dosage and Fe^{2+} dosage. The operating parameters are interrelated with, which significantly affect the process efficiency. The interrelations between the parameters are very complex and it could be assessed only through experimental analysis. The value ranges for each parameter were chosen from the laboratory analysis and previous studies made using Fenton process for different industries.

One of the most significant parameters in the Fenton process is pH. pH is very sensitive, and it has an impact on the solubility, complexation, and redox cycling of iron in the 2+ and 3+ states (Estrada et al., 2012).The optimal pH value has been determined to be 2-3. For pH values above 4, iron precipitates as a hydroxide derivative, so Fe^{2+} availability and radiation transmission are reduced; because of this degradation is significantly reduced (Faust and Hoigne 1990; Ghaly et al., 2001). When pH is less than 2 H_2O_2 cannot be discomposed to °OH by Fe^{2+} on the other hand.In this case, by trapping one proton, H_2O_2 becomes $H_3O_2^{+}$. Because $H_3O_2^{+}$ is electrophilic, the reaction rate between H_2O_2 and Fe^{2+} slows down (Han and Xia, 2004). The dye degradation is more efficient in acidic medium because protonated form is more sensitive to the oxidation process.

The catalyst concentration ($Fe^{2+}/Fe^{3+}/Fe^{0}$) has a considerable effect on the efficiency of all Fenton processes. In general, the concentration of dye/COD removed is proportional to the catalyst concentration. Because of the concentration of hydroxyl radical, which is the principal oxidizing agent, the efficiency of the Fenton process increases as Fe^{2+} concentration increase.; Furthermore, the oxidizing capacity of hydrogen peroxide is insufficient in the absence of ferrous ions to degrade large molecules (Nidheesh et al., 2012).

The highest efficiency was recorded at Fe^{2+} value of 1.5 g/l. Fe^{2+} ions assist in the activation of H_2O_2 and in turn it also assists in the production of °OH radicals which leads to the removal percentage improvement as shown in equation 4.1 (Zhen et al., 2014).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {}^{\circ}OH$……. (4.1)

The removal efficiency increases as the concentration of H_2O_2 increases. At 0.65 ml/l, the maximum efficiency was obtained. However, an increase in H_2O_2 causes a decrease in the dye removal process because the excess H_2O_2 molecules act as a blocker of hydroxyl radicals, (equations (4.2) and (4.3)) resulting in the formation of per hydroxyl radicals with low oxidation potential (equation 4.4) (Moussavi et al., 2012).

${}^{\circ}OH + H_2O_2 \rightarrow HO_2{}^{\circ} + H_2O$……. (4.2)

$HO_2{}^{\circ} + {}^{\circ}OH \rightarrow H_2O + O_2$ ……. (4.3)

$2\ {}^{\circ}OH \rightarrow H_2O_2$..... (4.4)

The extent of decomposition or mineralization of an organic species is reflected in the reduction in Chemical Oxygen Demand (COD). For the dye sample, the percentage change in COD was investigated at optimum pH, $Fe^{2+,}$ and H_2O_2 values of 3.0, 1.5 g/l, and 0.65 ml/l, respectively. The COD value decreased from 2100 mg/l to 710 mg/l after the treatment which indicates mineralization up to 66%

4.3 Best pairing selection of AC: TiO_2 ratio to remove COD

The COD removal capacity of various weight ratios of AC: TiO_2 was investigated in order to determine the best AC: TiO_2 ratio for COD removal. The experiments were carried out with 6 g of material. The COD removal results for each combination are listed in Table 4.2.

Table 4. 2: COD removal percentage for different ratio of AC:TiO_2

AC: TiO_2 weight ratio	Initial COD (mg/l)	Final COD (mg/l)	Removal percentage %
AT_1(1:1)	710	417	41.2
AT_2(2:1)	710	254	64.2
AT_3(3:1)	710	182	74.3
AT_4(1:2)	710	344	51.5
AT_5(1:3)	710	423	40

When the AC: TiO_2 ratio was 3:1, the maximum COD removal efficiency was recorded, while the lowest COD removal efficiency was observed when the AC: TiO_2 ratio was 1:3.As a result, the AT_3 (ATopt) combination of 3:1 AC to TiO_2 was chosen as the best.

4.4 Effect of $(AT)_{opt}$ on COD removal

The COD removal was carried out with AT_{opt} under the UV light(360 nm)with 150 rpm starring speed. A weight of 1-8 g of material was used in this study as in table for 1 l of the Fenton treated wastewater sample.The initial COD was 710 mg/l. The final concentrations and COD removal percentage is shown in Table 4.3

Table 4. 3: COD removal percentage with different dosage of AT_{opt}

Dosage(g)	Initial COD (mg/l)	Final COD (mg/l)	SD	COD removal (%)
1	710	620	0.5	12.68
2	710	516	0.57	27.32
3	710	432	0.76	39.15
4	710	356	0.86	49.86
5	710	256	1	63.94
6	710	176	0.5	75.21
7	710	154	0.76	78.31
8	710	148	0.28	79.15

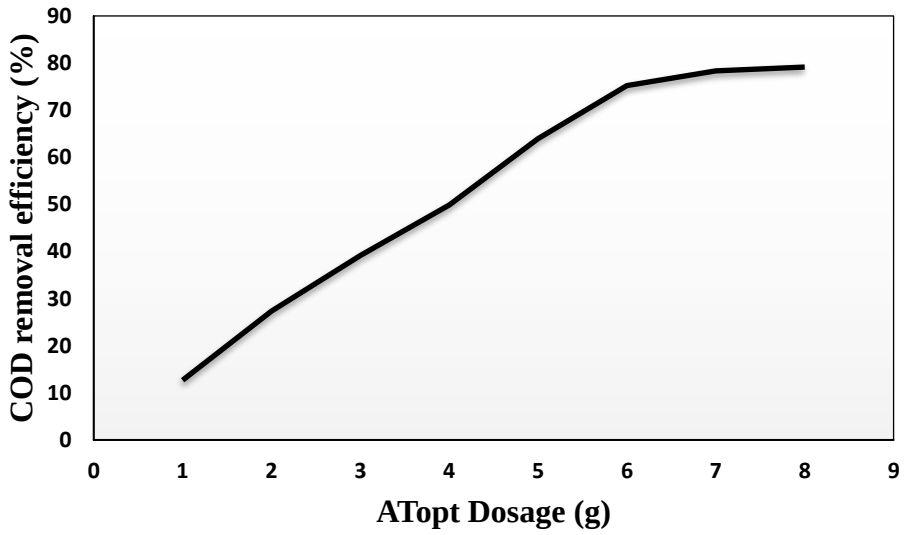


Figure 4. 1: COD Removal efficiency with different AT_{opt} dosages

When the photocatalyst was placed on the AC, it was significantly more efficient. According to the findings, the COD removal using TiO_2/AC composite was always higher than utilizing separate TiO_2 and AC particles in the solution; The best mineralization was primarily related to the proximity of photocatalyst and AC adsorption sites in TiO_2/AC composite material; Figure 4.1 shows after the 6 g of dosage the degradation level is not changed, it may be entire catalytic surface

is fully illuminated (Andriantsiferana et al., 2013).In this study, catalyst loadings 6 g/l had achieved the permissible level of COD (≤ 250 mg/l).

4.5 Effect of TiO_2 loading on COD removal

The COD removal was carried synthesized TiO_2 under the UV (360 nm) light with150 rpm starring speed. A weight of 1-8 g of materials were used in this study as in give table for 1l of Fenton treated wastewater sample. The initial COD was 710 mg/l. The final concentrations and COD removal percentage is given in Table 4.4. Increased TiO_2 dosage enhanced density of particles per unit volume, which increased the interaction between TiO_2 particles and polluting materials, resulting in high removal efficiency.

Table 4. 4: COD removal percentage with dosage of synthesized TiO_2

Dosage (g)	**Initial COD (mg/l)**	**Final COD (mg/l)**	**SD**	**COD removal %**
1	710	648	0.5	8.73
2	710	580	0.76	18.31
3	710	540	0.86	23.94
4	710	490	0.5	30.99
5	710	440	0.76	38.03
6	710	338	0.5	52.39
7	710	264	0.76	62.82
8	710	232	0.76	67.32

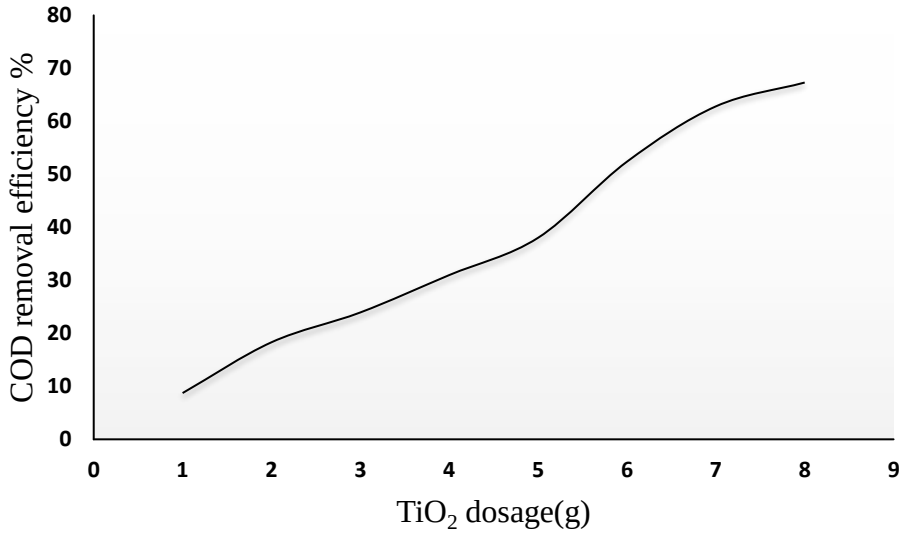


Figure 4. 2: COD Removal efficiency with different dosage of TiO_2

COD removal percentage increases with the increased dosage of TiO_2. In this study, catalyst loadings 8 g/l had achieved permissible level of COD (≤ 250 mg/l).

The removal efficiency was increased when the amount of TiO_2 was increased because of increase in total surface area for the photocatalytic reaction (Chung and Chen, 2008). However, as more photocatalyst is added, the solution gets turbid, and UV light is unable to enter it. As a result of light scattering by excess catalyst particles, photocatalytic activity can be reduced (Ghosh et al., 2018).

4.6 Effect of Activated Carbon loading on COD removal

The weight of the adsorbent is a crucial parameter for COD removal efficiency because it determines the capacity of an adsorber for a given initial effluent concentration. The effect of dosage (g of carbon/ l of wastewater) was studied, keeping all other experimental conditions constant as the dosage increased the fraction of COD removal increased as shown in Table 4.5. In this experiments, initial COD concentration (710 mg/l) was taken. The limits for the discharge of wastewater or effluents from the textile industry into inland surface water was obtained at a maximum carbon dose of 7 g per 1 l of wastewater. A larger mass of carbon could adsorb a larger amount of dye but in each case, at equilibrium, a mass of dye adsorbed per unit mass of carbon was smaller. Mckay (1982) reported similar observation that increasing carbon dosage resulted in an increase in the dye adsorbed.

Table 4. 5: COD removal percentage with dosage of AC

Dosage (g)	Initial COD (mg/l)	Final COD (mg/l)	SD	COD removal %
1	710	642	0.76	9.58
2	710	536	0.76	24.51
3	710	482	1	32.11
4	710	414	0.76	41.69
5	710	346	0.76	51.27
6	710	264	0.28	62.82
7	710	182	0.28	74.37
8	710	164	0.76	76.9

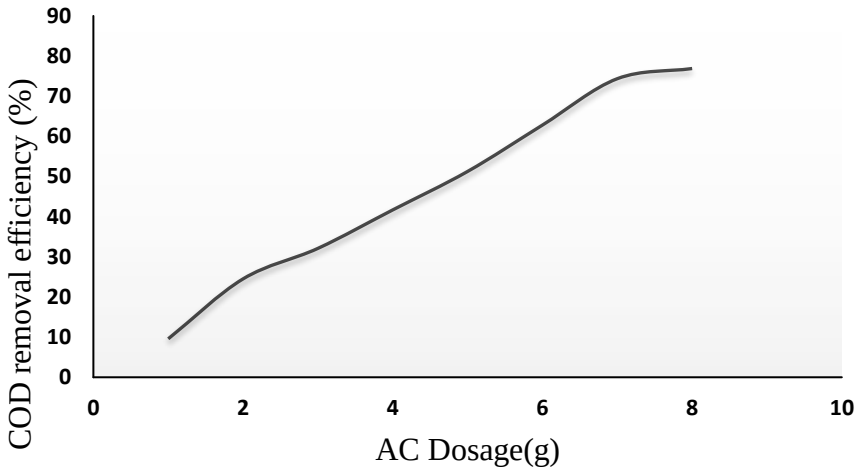


Figure 4. 3: COD removal efficiency with different CAC dosage

Permissible level of COD (≤250 mg/l) for discharge treated wastewater into the inland surface was achieved with 7 g/l of dosage. Hence 7 g selected as optimum dosage to COD removal.

4.7 Selection of best material for COD removal

Significant advantages are associated with wastewater management and treatment (avoided costs). As a result, the cost of inaction may be interpreted as benefits not realized as a result of wastewater discharge with no or inadequate treatment. In other words, costs or benefits are incurred when

untreated or improperly treated effluent is discharged directly into the environment, cost are generated.

Based on the conducted experiments, efficiency of COD removal was compared within the materials. Such as CAC, TiO_2 and TiO_2 impregnated AC. Based on the above studies and the adsorbent cost as an important factor the best material was selected.

Permissible level of COD (≤250 mg/l) to discharge treated wastewater into the water body is achieved with 8 g of TiO_2,7 g of CAC and 6 g of TiO_2 impregnated AC.

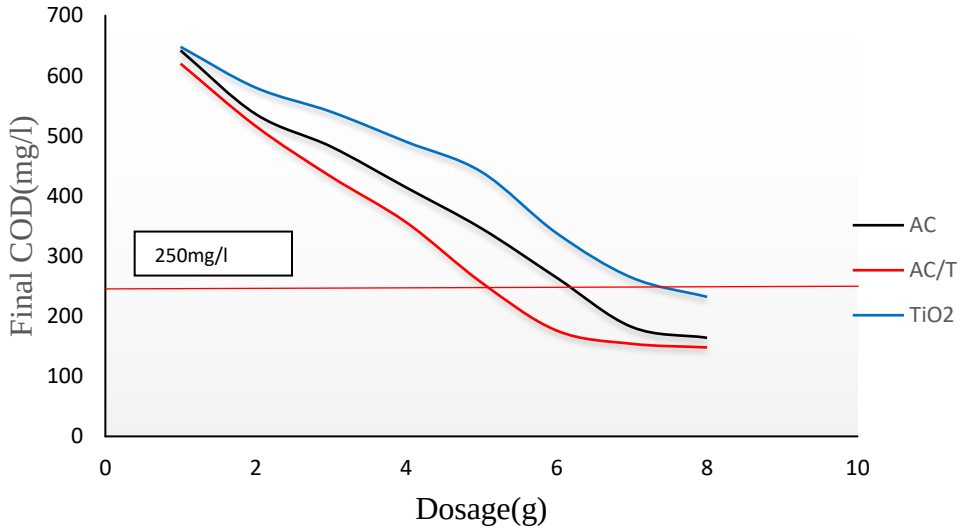


Figure 4. 4: Final COD with different dosage of CAC, TiO_2 and TiO_2 impregnated AC

Engineers face significant challenges when designing wastewater treatment plants.Both theoretical knowledge and practical expertise are required to study and select operational flows and processes that produce the highest results . Many factors must be considered, such as knowledge of required resources, required equipment, compatibility of selected design according to the operational and structural characteristics, estimation of special construction, Cost for operation and maintenance, and environmental aspects. environmental impact is a key consideration in the selection of specific treatment plant (Metcalf and Eddy, 1991).

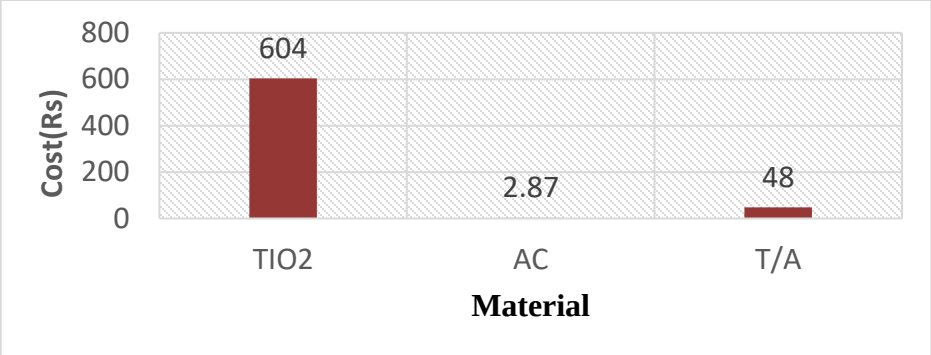


Figure 4. 5: Treatment cost for 1l of Fenton treated water for three materials

According to the cost comparison within the materials AC is selected as cost-effective method after the Fenton oxidation process for further treatment. Because it gives the better removal with less cost of material and low operating cost.

4.8 Characterization of Activated carbon using SEM, EDX, XRD and FTIR

The commercial AC was characterized using SEM, EDX, XRD and FTIR to analyze the different characteristics, enabling us to predict its morphology and structure. Table 4.6 gives the analyzing method with the relevant characteristics.

Table 4. 6:The analyzing method with the relevant analyzed characteristics

Analyzing method	**Analyzing character**
XRD	Unit cell dimensions Sample purity
FTIR	Bonding pattern Functional groups
ESEM-EDX	Morphology Chemical structure Crystal structure

4.8.1 ESEM and EDX Analysis

Morphology and elemental composition of AC were analyzed using Environmental Scanning Electron Microscopy. The morphology and distribution of pores on the activated carbon's surface are determined using these images. Depending on the magnification of the image, it also determines the nature and size of the pore.

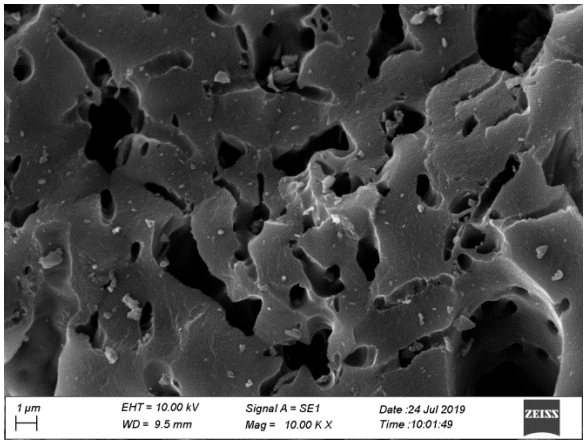


Figure 4. 6: SEM image of AC before Adsorption

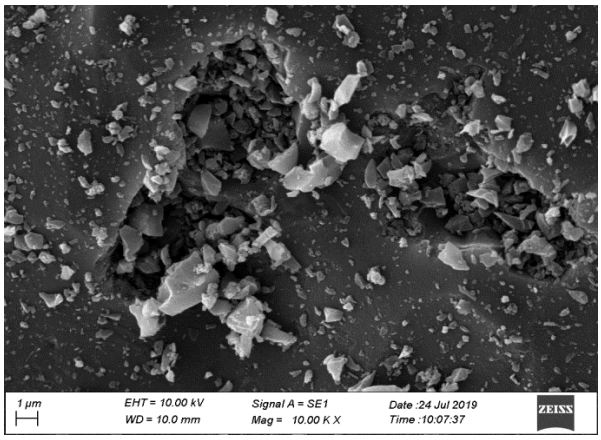


Figure 4. 7: SEM image of AC After Adsorption

The SEM images of AC before and after adsorption is shown in the above pictures. The surface structure of Figure 4.6 is revelated irregular and porous. This structure demonstrates the potential for dye penetration into these pores, improving adsorption. Figure 4.7 indicates that the porosity of the AC surface has been considerably reduced following dye adsorption, possibly due to the formation of bonds with the functional groups on the adsorbent.

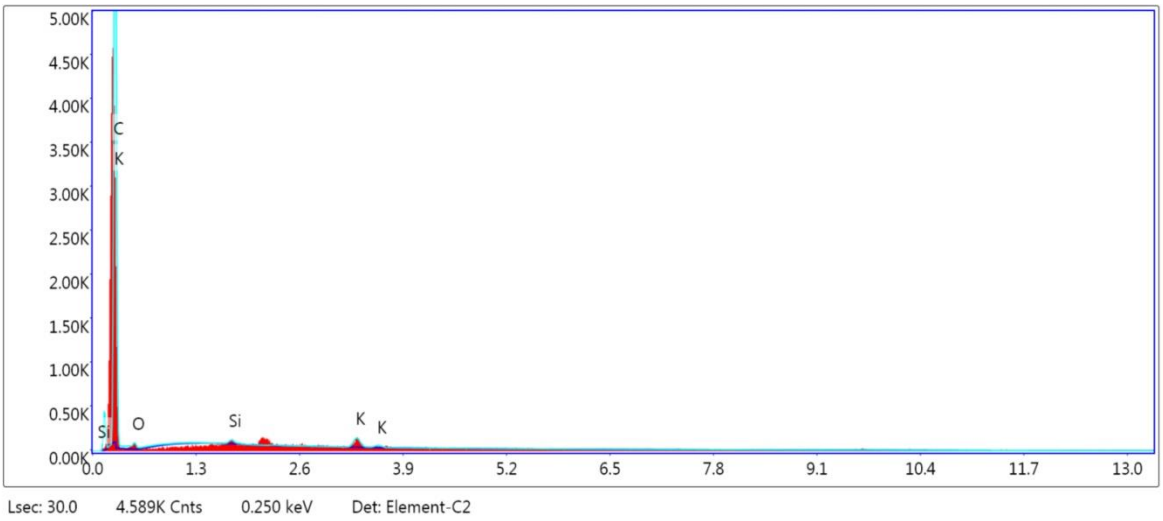


Figure 4. 8: The EDX image of CAC

Table 4. 7: The weight and atomic composition of the CAC

Element	**Weight %**	**Atomic %**
C K	86.67	90.62
O K	10.98	8.61
SiK	0.04	0.02
ClK	0.15	0.05
K K	2.16	0.69

The EDX is an analytical technique for determining the elemental composition of a sample as well as chemical characterization. The EDX spectra of activated carbon revealed that carbon and oxygen were primarily present on the surface of AC samples. Carbon had a higher ratio than oxygen in the sample and detected other elements such as silica, potassium, and chlorine were detected.

4.8.2 XRD Analysis of AC

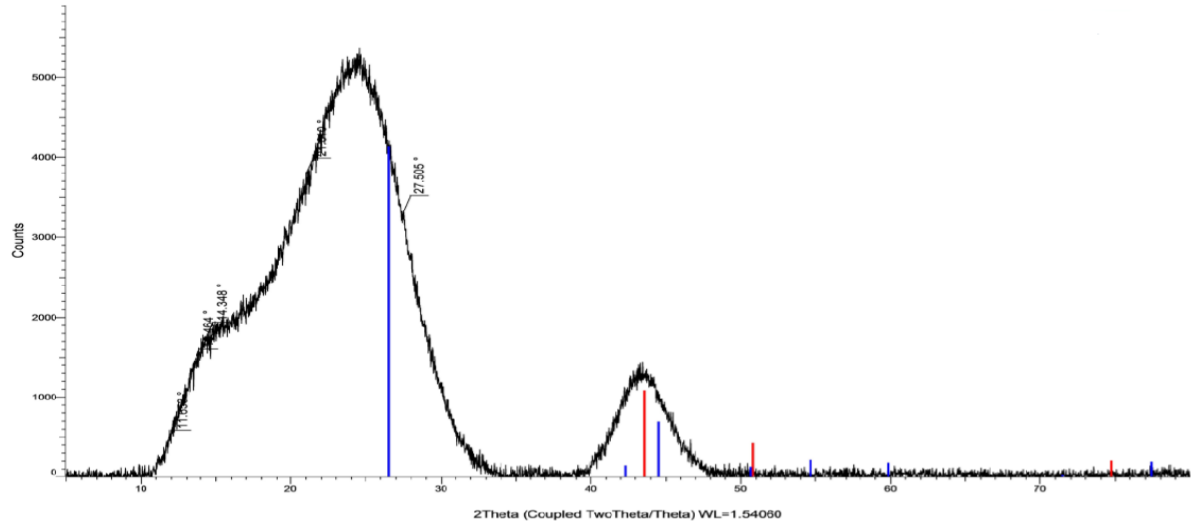


Figure 4. 9: XRD analysis of AC

AC is generally regarded as an amorphous nature with a large surface area and porosity. In the present activated carbon two weak diffraction maxima indicated that the content of the ordered crystalline phase is negligible. From the XRD spectra, it can be concluded that XRD patterns for each activated carbon had a characteristic amorphous carbon shape with broad asymmetric peaks. corresponding to 2θ ~24 and 2θ ~43.5° that are reflected by the miller indices of (002) and (101), respectively (Kumar et al., 2017; Morali et al., 2018). The peak findings at 2θ ~24 is related to(002) lattice plane of typical carbon-black graphite structure (Rahma et al., 2019). This result has good match with the date reported in literature where various researchers have reported that activated carbon has an amorphous nature (Mohamed et al., 2008).

4.8.3 FTIR analysis for AC

FTIR analysis was used to determine the bonds present in the activated carbon.

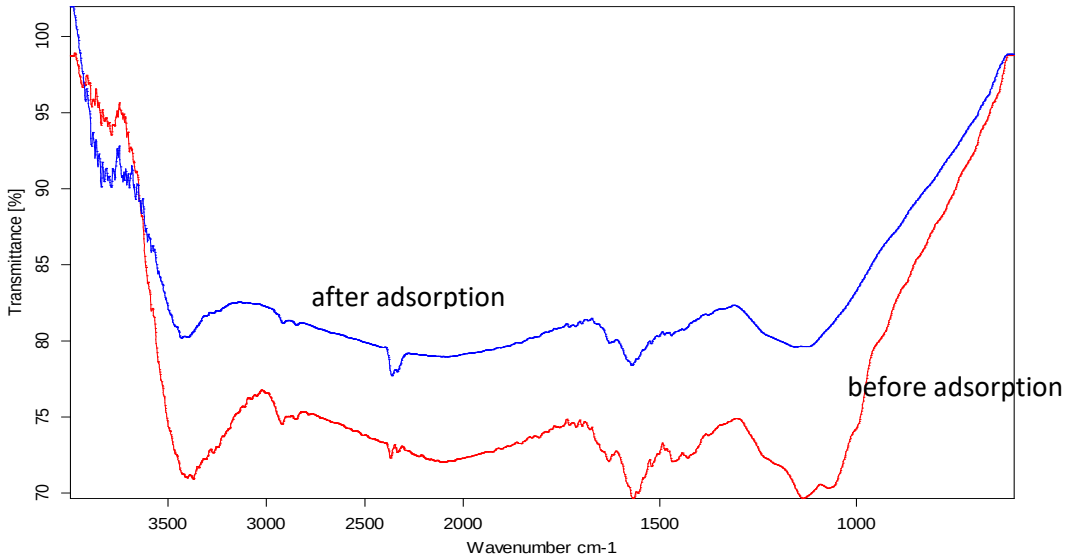


Figure 4. 10: FTIR analysis of AC before and after adsorption

The FTIR spectrum of AC shows the specific peaks reflecting the surface functional groups and the complex nature of the surface of materials. Before the removal, it reveals a broad absorption peak at 3371 cm^{-1} and coincides with the O–H stretching vibration of alcohols, phenols and carboxylic acids (Li et al., 2007). The strong peak at 2921.53 was due to the stretching vibration of -CH. The other peaks 1712,1629,1520,1136cm^{-1} are due C=O, C=C, N-O and C-O stretching respectively; After the adsorption some peaks are shifted and some of the peaks are disappeared it revealing that dye molecules interacted with the functional groups of adsorbents (Sayğıl et al., 2017).

4.9 Optimum condition for COD removal using AC

4.9.1 Impact of contact time

To determine the optimum contact time for efficient COD removal the experiments were carried out in every 30 minutes interval from 30 minutes to 720 minutes (12 hrs).And maintaining the initial COD as 710 mg/l and optimum dosage7 g, initial pH is 2 and stirring speed at 100 rpm. The absorbance results are given in Table 4.8.

Table 4. 8: The Optimum contact time for COD removal

Time(min)	Final COD (mg/l)	SD	Removal Efficiency %
30	480	0.5	32.39
60	310	0.5	56.34
90	256	0.5	63.94
120	196	0.28	72.39
180	182	0.76	74.37
240	178	0.76	74.93
360	156	0.5	78.03
480	148	0.5	79.15
720	142	0.76	80.00

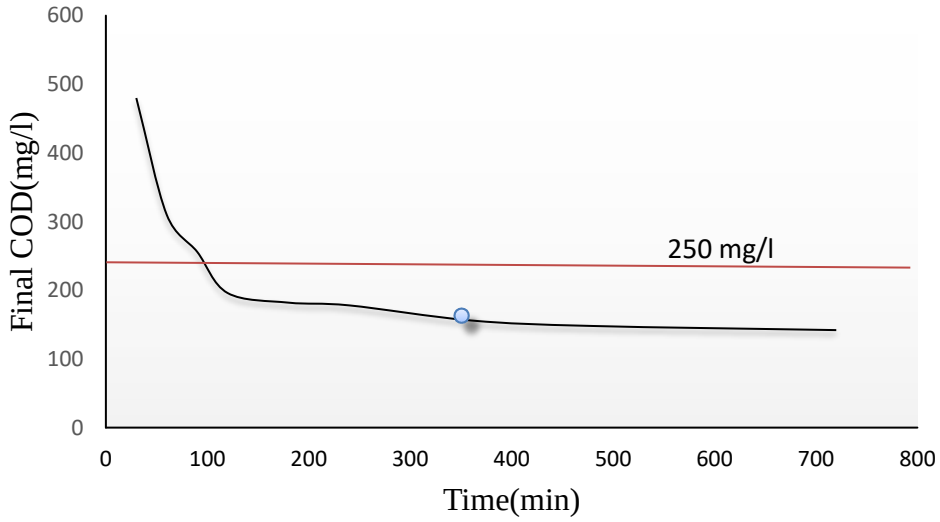


Figure 4. 11: Final COD vs the contact time

According to the optimum contact time selection from batch studies,the permissible level of COD reached 120 minutes. The final COD level reached 196 mg/l and this concentration fulfils our requirement of the permissible level for discharging treated wastewater to the water body being less or equal to 250 mg/l. When the contact time is increased further the adsorption increases. The optimum contact time was selected as 2 hours for the future batch studies. After the 2 hours of contact time, COD removal rate seems slow. At first, there isn't enough time to engage all of the adsorbate with the adsorbent when the contact period is short, the amount of COD removal is

lower. The fact that the rate of COD removal increases as contact duration increases could be attributed to the saturation of all adsorption sites with adsorbate. In this study the main focus was the final permissible level (250 mg/l or less) for discharged treated wastewater with a minimum contact time to reach the permissible level of COD.

4.9.2 Effects of pH

The pH of the wastewater is a predictable characteristic that has a considerable influence on COD removal in the sample. The optimum pH was obtained using batch studies. A weight of 7 g of AC with the contact time of two hours with a mixing velocity of 100 rpm with mechanical shaker was used for the study. The starting COD was 710 mg/l. Table 4.9 shows the result of the batch studies.

Table 4. 9: Optimum pH investigation

pH	Final COD (mg/l)	SD	Removal Efficiency %
2	186	0.28	73.80
3	206	0.76	70.99
4	248	0.28	65.07
5	300	0.5	57.75
6	300	0.5	57.75
7	314	0.5	55.77
8	332	0.5	53.24
9	352	0.28	50.42
10	364	0.5	48.73
11	372	0.5	47.61
12	372	0.28	47.61

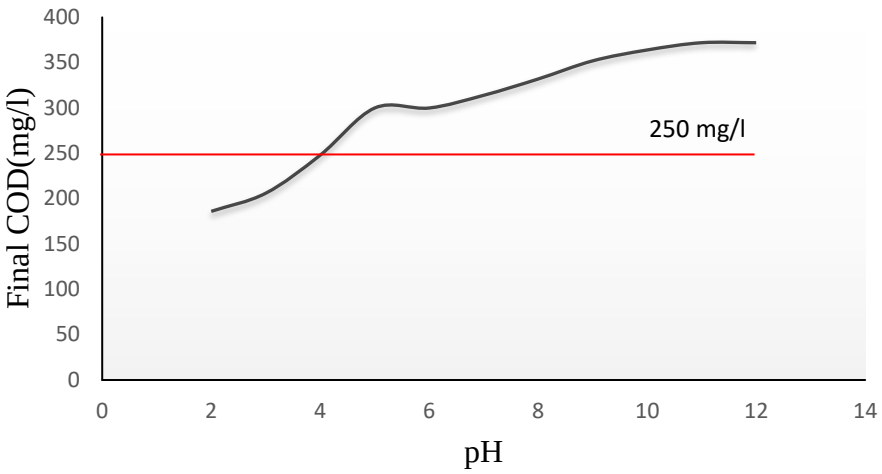


Figure 4. 12: Final COD with different pH

In the adsorption technique pH is a significant controlling factor that influences the adsorbent's surface charge during waste water treatment. It regulates the adsorbent surface's nature as well as the degree of ionization or dissociation of the aqueous adsorbate.

When the pH increases, the adsorbent surface becomes more negative, which is good for binding positive ions. Conversely, as pH decreases, the adsorbent surface becomes more positive, which provides a satisfactory condition for the uptake of negative ions. Low pH causes an increase in H^+ ion concentration in the system, and by absorbing H^+ ions, the surface of the activated carbon gains a positive charge. Because the carbon surface is positively charged at low pH, the positively charged carbon surface and the anionic dye molecule have a strong electrostatic interaction, resulting in maximum dye adsorption. As the pH of the system rises, the number of negatively charged sites increases, while the number of positively charged sites decreases (Kiwaan et al., 2021). A negatively charged surface site on activated carbon does not enhance the adsorption of anionic dye molecules due to electrostatic repulsion (Malik, 2004).

The results of the batch studies detect that the optimum pH was 2. These trends are little contrary to the reported trends in literature. When pH increases(alkalinity), adsorption of the dye decreases and percentage removal dye increases with increase in acidity. The removal of dyes from aqueous system through the process of adsorption is perfectly pH dependent, which shows better impact on charge of surface area of the adsorbent and speciation of the dye.

4.10 Adsorption Isotherms and kinetic studies

4.10.1 Adsorption isotherms for COD removal by AC

A set of batch studies were carried out to assess the adsorption isotherm behavior of AC in the adsorption of COD. The Freundlich and Langmuir isotherms are the most often used models for studying adsorbent adsorption behavior.

Freundlich and Langmuir isotherms were used to fit the experimental data, and the slope and intercept of the plotted data were used to calculate the isotherm constants. The results of adsorption studies for AC fitted to Langmuir model is given in Table 4.10. A volume of 1L of Fenton treated wastewater with 7 g of AC was used in the experiment.

Equation 4.5, 4.6 and 4.7 was used in the calculations to determine the favorability of the reaction.

$$Q_e = (C_o - C_e) \times \frac{V}{W} \qquad 4.5$$

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L C_e} \qquad 4.6$$

$$R_L = \frac{1}{[1 + (1 + K_L C_o)]} \qquad 4.7$$

Table 4. 10: Adsorption data fitted to Langmuir isotherm

Adsorbent (g)	Initial Concentration (Co, mg/l)	Final Concentration (C1, mg/l)	Co-C1	V	Qe= (Co-C1) x V/W	1/Qe	1/Ce
0	710	710	0	0.1	-	-	-
1	710	632	78	0.1	7.8	0.128	0.0016
2	710	554	156	0.1	7.8	0.128	0.0018
3	710	478	232	0.1	7.73	0.129	0.0021
4	710	404	306	0.1	7.65	0.131	0.0025
5	710	328	382	0.1	7.64	0.131	0.0030

6	710	262	448	0.1	7.47	0.134	0.0038
7	710	198	512	0.1	7.314	0.137	0.0051
8	710	154	556	0.1	6.95	0.144	0.0065

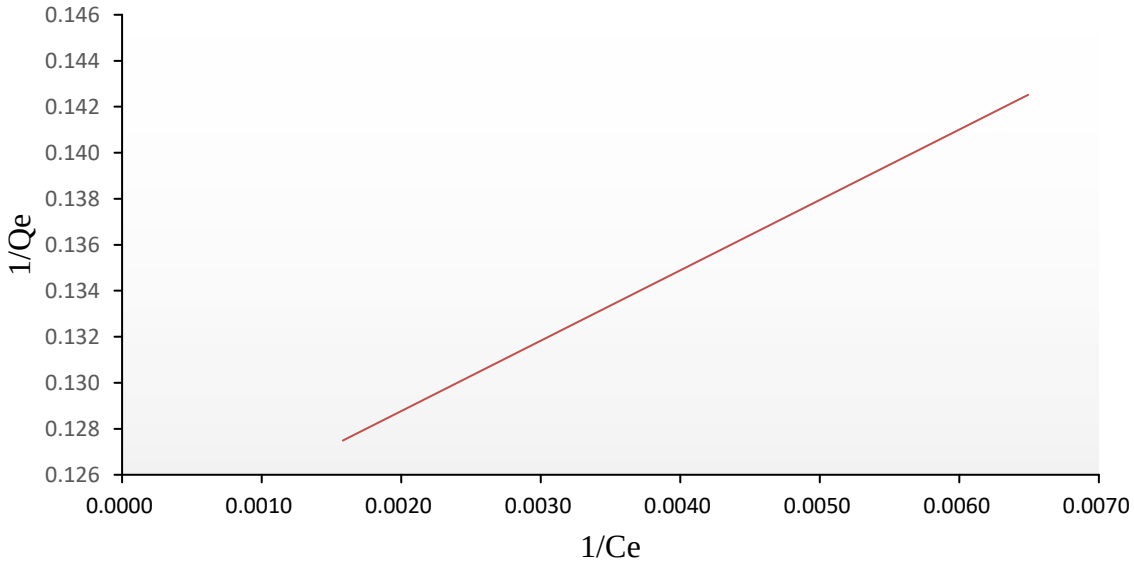


Figure 4. 13: The Langmuir isotherm for COD removal with AC

Q_m = 8.16 mg/g, K_L = 0.04 l/mg

The Maximum mono layer coverage capacity is Q_m = 8.16 mg/g and Langmuir isotherm constant is calculated as 0.04 l/mg.

The separation factor for the Langmuir constant (R_L) was calculated according to equation 4.3. The R_L value denotes that the experiment is "favourable" when $0<R_L<1$, "linear" R_L = 1 and "irreversible" R_L = 0, The shape of the isotherm is indicated by Langmuir constant (Weber and Chakravorti, 1974). The calculated Langmuir constant is in the range of "$0 > R_L > 1$" (0.033), as a result, at the given concentration, the Langmuir adsorption mechanism is favored.

The Freundlich model was used to determine the adsorption characteristics of COD removal, assuming the heterogeneous surfaces where dye molecules could bind by multilayer formation and there is an exchange between adsorbed ions. Equation 4.8 gives the Freundlich adsorption isotherm (Freundlich, 1906).

$$\log (Qe) = \log (K_f) + 1/n \log (Ce) \qquad 4.8$$

Table 4. 11: Adsorption data to fitted Freundlich isotherm

Adsorbent(g)	Initial concentration (C0)	Final concentration (C1)	C0-C1	V	Qe=(C0-C1) **x** V/W	log(Qe)	log(Ce)
0	710	710	0	0.1	0		
1	710	632	78	0.1	7.8	0.892	2.801
2	710	554	156	0.1	7.8	0.892	2.744
3	710	478	232	0.1	7.73	0.888	2.679
4	710	404	306	0.1	7.65	0.884	2.606
5	710	328	382	0.1	7.64	0.883	2.516
6	710	262	448	0.1	7.47	0.873	2.418
7	710	198	512	0.1	7.31	0.864	2.297
8	710	154	556	0.1	6.95	0.842	2.188

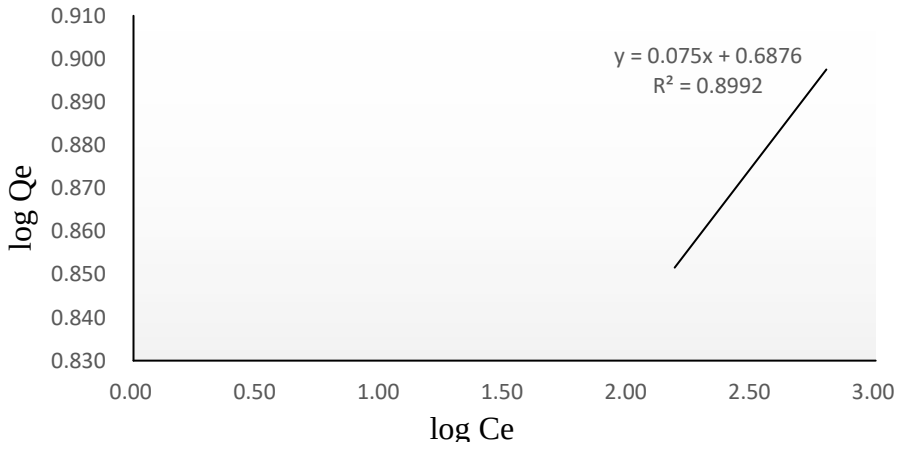


Figure 4. 14: The Freundlich isotherm for COD removal with AC

R^2 value for Langmuir adsorption isotherm model 0.9705

R^2 value for Freundlich adsorption isotherm model 0.8992

When comparing values of R^2 between Langmuir adsorption isotherm model and Freundlich adsorption isotherm model, R^2 value of Langmuir isotherm model is high; hence it can be concluded that the adsorption process favour the Langmuir model where the adsorption is unilayer or monolayer.

4.10.2 Kinetic studies

The experimental data were fitted with pseudo-first-order kinetic models and pseudo-second-order kinetic models to find out the reaction order mechanism. The concentration of COD adsorbed at different time t, qt(mg/g) were obtained as follows:

Table 4. 12: The pseudo first order reaction results

Time (min)	Initial COD (mg/l)	Final COD (mg/l)	Log(qe-qt)
0	710	710	
30	710	480	2.362
60	710	310	2.602
90	710	256	2.657
120	710	196	2.711
180	710	182	2.723
240	710	178	2.726
360	710	156	2.744
480	710	148	2.749
720	710	142	2.754

Lagergren's pseudo-first-order kinetic model has the formula of $\log(qe-qt) = \log qe-(K_1/2.303)\ t$

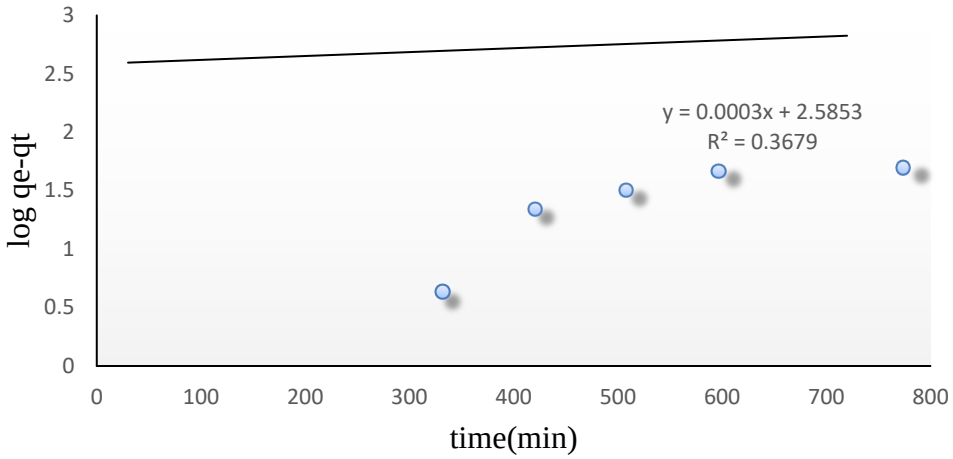


Figure 4. 15: Pseudo first order kinetic model for adsorption onto AC

in The Pseudo first-order model was observed the correlation coefficient (R^2 - 0.3679). The data are not fitted to pseudo-first order; therefore the reaction is not followed the first-order kinetics. As a result, the reaction rate is not proportional to the reactant concentration's first power.

Table 4. 13: The kinetic experiment results of AC

Time (min)	Initial COD (mg/l)	Final COD (mg/l)	Removal efficiency	v/m	Qt	t/qt
0	710	710	0.0	0.0143	0.000	-
30	710	480	32.4	0.0143	3.286	9.13
60	710	310	56.3	0.0143	5.714	10.5
90	710	256	63.9	0.0143	6.486	13.88
120	710	196	72.4	0.0143	7.343	16.34
180	710	182	74.4	0.0143	7.543	23.86
240	710	178	74.9	0.0143	7.600	31.58
360	710	156	78.0	0.0143	7.914	45.49
480	710	148	79.2	0.0143	8.029	59.79
720	710	142	80.0	0.0143	8.114	88.73

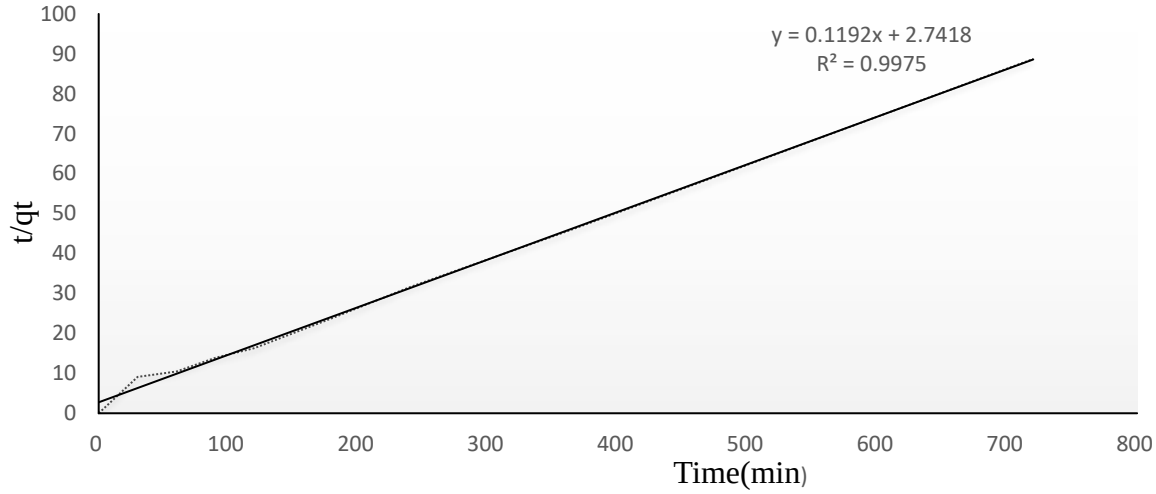


Figure 4. 16: The reaction kinetic data is fitted to second order kinetic model

To calculate the parameters of the pseudo-second-order model intercept and slope of the graph were used (Figure 4.16). The R^2 value was calculated to be 0.99, Qe-8.39 mg/g and K_2 -0.0052 mg^{-1} min^{-1}.

The pseudo-second-order model fitted the experimental data better than the pseudo first-order model. As a result, in this kind of adsorption, the chemical reaction appears to be essential in the rate-controlling step; The best correlation of experimental data is provided by pseudo second order chemical reaction kinetic, and the adsorption's mechanism is chemically rate regulating, it is referred to as chemisorption. Sorption kinetics should correlate to a reversible second order in this process (Kundari et al., 2020).

Equation 4.9 can be used to calculate the Gibbs free energy of the reaction.

$$\Delta G = -RT\ lnK$$

K - adsorption constant at equilibrium calculated from Langmuir's equation at corresponding temperature, R - gas constant (8.314 J/mol/K), T - absolute temperature (K). when ΔG value is negative the adsorption process can conduct spontaneous; according to the calculation Gibbs free energy value is (-8028), so reaction is spontaneous.

4.11 Regeneration studies for AC

Many inorganic and organic regenerants were successful in regenerating activated carbon that had been exhausted by organic compounds, according to Martin and Ng (1984, 1985, 1987). Part of this research also attempted to regenerate dye-exhausted activated carbon using a variety of acidic and alkaline media. Understanding the affinity of the regenerant with the dye material helps in the selection of an appropriate regenerant for dye desorption (Mittal et al., 2009). Because of its non-polar structure, dye molecules can be successfully adsorbed on the non-polar surface of activated carbon, and different polarities of organic solvents may compete with dyes for adsorption sites on activated carbon (Lu et al., 2011).

Various eluting agents such as HCl (pH 2), and NaOH (pH 12) was used to regenerate the saturated CAC. The aim of testing the ability of AC to regenerate using various eluting agents at various pH values is to identify the most effective regeneration medium. The ability of AC to regenerate with NaOH resulted in a greater COD removal efficiency. Because acidity of dyes exhibits good attraction toward basic medium. AC regenerated with NaOH effective up to 3 cycles. Hence, COD elimination effectiveness declined when the number of cycles was increased. The cause due to saturation of adsorption sites and variation of the chemical and physical properties on surface of adsorbent.

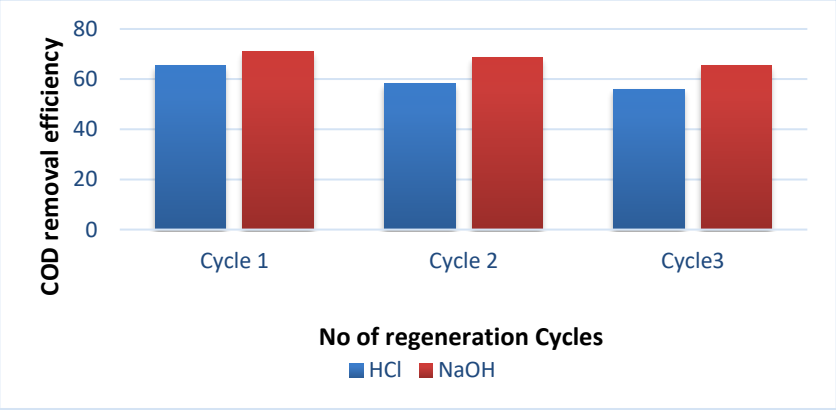
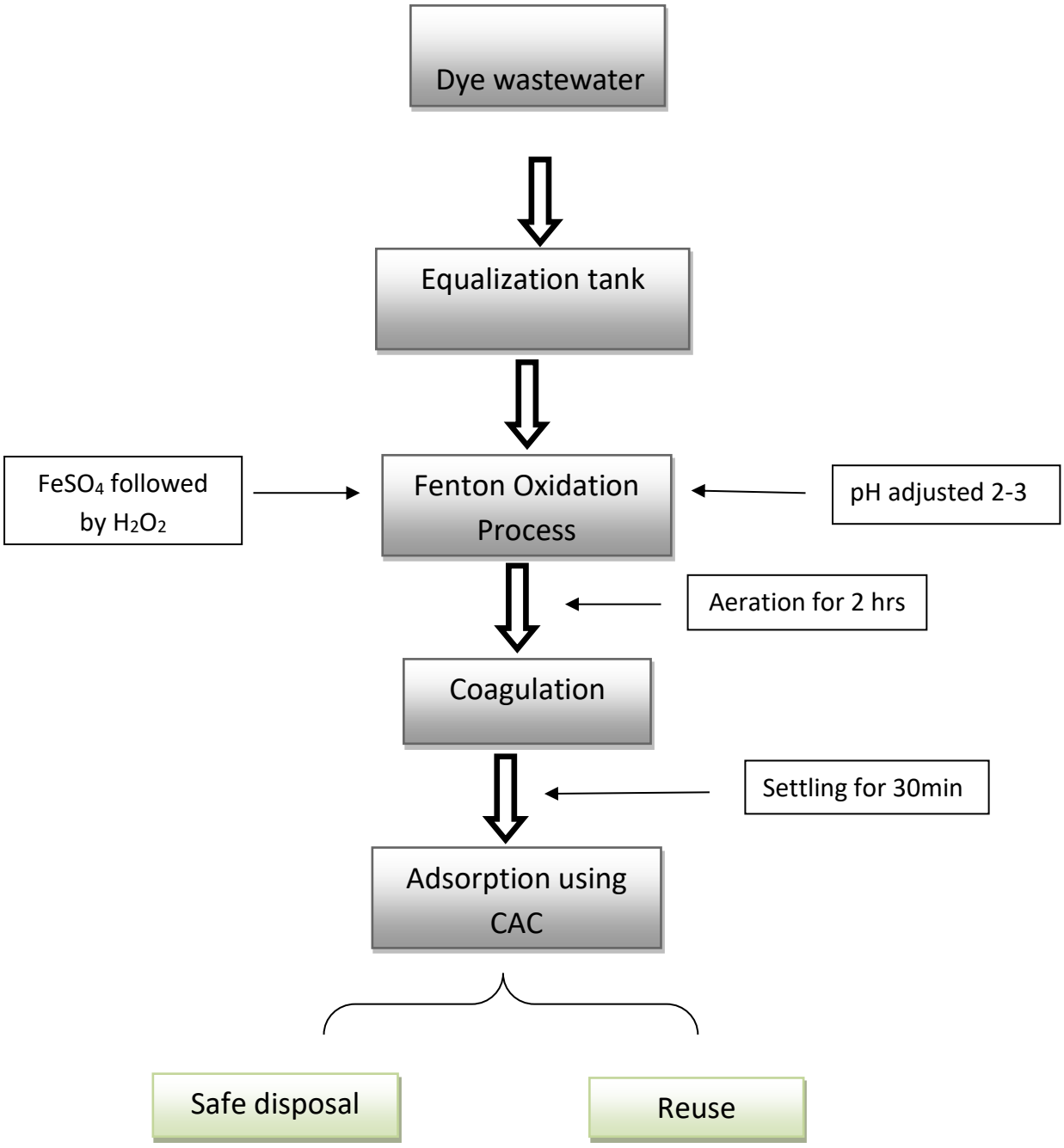


Figure 4. 17: The COD removal efficiency of AC after each regeneration cycle

A schematic diagram of a wastewater treatment module for dyestuffs is shown below.



5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Dye is one of the major pollutants that negatively impact our ecosystem. They are highly damaging to all species on the planet. When they are not treated before entering the aquatic system, they harm the ecosystem. One of the most effective methods for eliminating pigments from wastewater is the Fenton process.

AOPs are environmentally friendship processes for decolourization and removal of organic substances of natural dyeing wastewater. Advanced oxidation methods are a powerful tool for removing refractory and hazardous contaminants from wastewater. Different AOPs have been developed, allowing us to select the best solution for each treatment problem.

The findings of these studies demonstrate the need to select the best COD removal factors to achieve high efficiency, which is essential for any practical use of the system. The efficiency was influenced by many factors, such as initial iron concentrations and initial hydrogen peroxide concentrations.

These investigations clearly state the significance of selecting the optimal parameters to achieve high removal efficiency, which is critical for any practical application of the system. The COD removal efficiency was influenced by many factors such as pH (2–3), initial iron concentrations (1.5 g/l) and initial hydrogen peroxide concentrations(0.65ml/l).

Removal of COD in Fenton treated dye wastewater from the CAC,TiO_2 and ATopt has been studied. Permissible level of COD ($\leq$ 250mg/l) to discharge treated wastewater into the water body is achieved with 8g of TiO_2,7 g of CAC , and 6g of TiO_2 impregnated AC. Best material was selected among these for the post-treatment. CAC was selected as the best material economically. Batch adsorption experiments were performed at different reaction variables such as pH, contact time, adsorbent dose of the medium.

The adsorption of dye onto the CAC rises with rise in contact time and reaches an equilibrium at about 120 min. The increase in removal efficiency is, because the adsorbate has more time to coordinate with the adsorbent. Beginning expulsion happens punctually when the AC has contact

with the solution. When some readily available active sites become inaccessible, the dye requires time to find new active sites for binding.

The removal efficiency was pH-dependent. Adsorption of dye occurs mainly in acidic pH. pH 2 is selected as optimum. There was no critical increment in the dye expulsion while increasing the alkalinity.

Adsorbent doses also influence percentage uptake. With the rise in amount of adsorbent, the percentage uptake of dye increases gradually. The increase in adsorption was due to more surface area or active sites were available for adsorption. The Langmuir adsorption isotherm model was used to fit the adsorption mechanism. As a result, adsorption surface is homogeneous with the sorption site. The adsorption mechanism is chemisorption because the reaction follows pseudo second- order kinetics.

The tolerance limit of TDS gazetted on 27.1.2022, to discharge the treated wastewater into the inland surface water, the maximum TDS level is 1000mg/l. The effluent TDS level was 1280mg/l. So, it is recommended to reduce the TDS level. There are few treatment methods available in industry to reduce the TDS level, such as reverse osmosis system, water filters, and softeners. Reverse osmosis is widely regarded as one of the most effective methods for lowering TDS levels and meeting various treated water quality criteria.

The process is used by evaporation lagoon in many industries to manage the regenerated wastewater. In this case, salt contamination was discovered in the groundwater. So, treat regenerated wastewater, it is recommended effluent may be filtered, including RO, and recirculated as process water in the factory.

5.2 Recommendations

Water is essential part of human life. Fresh water is limited natural source on the earth. Due to a scarcity of fresh water, wastewater treatment techniques have rapidly been used in practically all industries. Different methods for wastewater treatment are employed, and energy efficient technologies must be used to reduce overall energy use. In this research work the proposed system is efficient COD removal for complex dye stuff containing wastewater, and the selected material

is economically feasible compared with other materials. The sludge may typically be placed in landfills or sprayed on agricultural fields directly because generated sludge is quite well stabilized.

The experiments were conducted a laboratory scale, and it is possible to scale up to the industrial stage. Attention should be focused on activated carbon can be improved with alternative low-cost synthesized material and experiments could be conduct with the photo the Fenton process instead of the Fenton process. It is recommended that must measure final TDS level, and the reverse osmosis system is to be introduced. Residual colour of effluent and treated water wants to be measured.

Use the adsorption material with low-cost media such as coconut shell powder, tea waste ash, etc as Sri Lanka is a major producer of these products. The study was limited to one particular industry, and it is suggested that implement the method in all types of textile industry.

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