

**TREATMENT OF TEXTILE EFFLUENT CONTAINING
REACTIVE RED 120 DYE USING ADVANCED
OXIDATION**

by

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Submitted in partial fulfilment of the requirements
for the degree of Master of Applied Science

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DALHOUSIE UNIVERSITY

DEPARTMENT OF PROCESS ENGINEERING AND APPLIED SCIENCE

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ABSTRACT

Disposal of textile effluents into nature is one of the major environmental concerns of a textile industry. Several biological, physical and chemical methods for degradation of textile effluents are being followed, but the real challenge is to find a method that is effective, comparatively fast and cost effective. Advance oxidation is an emerging field that uses oxidants producing hydroxyl radicals to oxidize toxic compounds into non-harmful by-products. The effectiveness of photooxidation on reactive red 120, a widely used complex structured cotton dye, was evaluated. Dye concentrations in the range of 50-500 mg/L were treated with UV alone, TiO₂/UV and H₂O₂/UV under 12 different residence times (5.2-60 min). The best combination was selected for Chemical Oxygen Demand (COD) analysis to determine the amount of chemicals retained in the effluent after treatment. The textile industry produce effluents with a pH of 10-11 and hence, the dye pH was adjusted to 10-11. The maximum degradation obtained with UV alone was 27.01% after 60 min for the 50 mg/L dye concentration and 0.33% after 60 min for the 500 mg/L dye concentration. The maximum degradation obtained with UV/TiO₂ was 46.07% after 60 min for the 50 mg/L dye concentration and 2.84% after 60 min for the 500 mg/L dye concentration. The maximum degradation obtained with UV/ 10 ml/L was 99.83% after 25.4 min for the 50 mg/L dye concentration and 99.70% after 60 min for the 500 mg/L dye concentration. Exposure to UV/ 20 ml/L H₂O₂ resulted in 99.96% degradation after 20 min for the 50 mg/L dye concentration and 99.95% degradation after 60 min for the 500 mg/L dye concentration. Increasing the concentration of H₂O₂ from 10 to 20 ml/L improved the oxidation efficiency and reduced the reaction time. The COD analysis performed on the samples obtained after UV/ 20 ml/L H₂O₂ treatment showed a decrease in the COD (from 996 mg/L to 416 mg/L in 20 min for 50 mg/L dye concentration and from 1399 mg/L to 256 mg/L in 60 min for 500 mg/L dye concentration) indicates a much lower COD level could be attained when the effluent is exposed to UV/20 ml/L H₂O₂ for more than 60 min. Treatment of the dye effluent under acidic condition reduces the reaction time but does not justify the cost of the chemical addition to control the pH and the further treatment to remove these chemicals.

LIST OF ABBREVIATIONS USED

ADMI	American Dye Manufacturers Institute
AOP	Advanced Oxidation Process
APHA	American Public Health Association
As	Arsenic
BOD	Biochemical Oxygen Demand
CCME	Canadian Council of Ministers of the Environment
CI	Colour Index
COD	Chemical Oxygen Demand
Cr	Chromium
Cu	Copper
DS	Dissolved Solids
FEPA	Federal Environment Protection Agency
GDP	Gross Domestic Product
GDP	Gross Domestic Product
H ₂ O ₂	Hydrogen Peroxide
HE3B	Reactive Red 120
HT/HP	High Temperature/High Pressure
L	Litre
nm	Nano Meter
OH ^o	Hydrogen Ion
PVA	Poly Vinyl Alcohol
PVC	Poly Vinyl Chloride
RO	Reverse Osmosis
SS	Suspended Solids
T&C	Textile and Clothing
TiO ₂	Titanium Oxide
UV	Ultra Violet
VOC	Volatile Organic Compounds
Zn	Zinc

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Chapter 1. INTRODUCTION

Textile and Clothing (T&C) is one of the largest and oldest industries present globally (Gereffi, 2002). The T&C industry provides jobs with no required special skills, which in turn plays a major role in providing employment in poor countries like Bangladesh, Vietnam, Sri Lanka and Mauritius and therefore, plays a vital role in the increase of Gross Domestic Product (GDP) value of these countries (Keane and Velde, 2008).

The textile industry is classified into three main categories: cellulose fibres, protein fibres and synthetic fibres. The type of dyes and chemicals used in the textile industry are found to differ depending on the fabrics manufactured. Direct dyes, naphthol dyes and vat dyes are some of the dyes used to dye cellulose fibres (Lorimer et al, 2001; Burch, 2009 and Robert et al., 2008). Protein fibres are dyed using azo dyes, natural dyes and lanaset dyes (Moody and Needles, 2004, Burch, 2009, Schmidt et al, 2002 and Robert et al., 2008). Other dyes like dispersed dyes, basic dyes and direct dyes are used to dye synthetic fibres (Butkinshaw, 1995; Burch, 2009).

Textile industries produce large amounts of liquid wastes. These textile effluents contain organic and inorganic compounds (Elliott et al, 1954). During the dyeing processes, not all dyes that are applied to the fabrics are fixed on them and there is always a portion of these dyes that remains unfixed to the fabrics and gets washed out. These unfixed dyes are found to be in high concentrations in textile effluents (Dyes and Pigments, 2010). The amount of water consumed and released also varies depending on the type of fabrics produced (Moustafa, 2008). Almost 0.08 – 0.15 m³ of water is used to produce 1 kg of fabrics. It is estimated that about 1,000 – 3,000 m³ of water is let out after processing about 12 – 20 tons of textiles per day (Pagga and brown, 1986; Kdasi et al., 2004). These effluents are rich in dyes and chemicals, some of which are non-biodegradable and carcinogenic and pose a major threat to health and the environment.

Several primary, secondary and tertiary treatment processes like flocculation, trickling filters and electrodialysis have been used to treat these effluents. However these

treatments are not found effective against the removal of all dyes and chemicals used (Kdasi et al., 2004, Eswaramoorthi et al., 2008). The effluents do not only contain high concentration of dyes used in the industry, but also contain the chemicals used in the various processing stages. Some trace metals such as Cr, As, Cu and Zn are present in these effluent and are capable of causing several health problems including haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis. Textile effluents are also found to contain other organic and microbial impurities (Nese et al., 2007; Laxman, 2009).

The usage of cotton has been increasing constantly throughout the past century (UNCTAD, 2003). Manu (2003) stated that about 12.3 millions of 0.24 Ton bale of cotton was produced in India in the year 2000 which contributed to about 14.1% of the total world production. Cotton fibres are mainly dyed using azo dyes which are one of the largest groups of synthetic colorants used in the industry (Mohan et al., 2002). Azo dyes are difficult to degrade by the current conventional treatment processes. They are characterised by the presence of the nitrogen-nitrogen bond (-N=N-) in the centre and hence they are highly electron deficient (Robert et al., 2008). Due to their poor exhaustion properties, about 40% remain unfixed in the effluents (Manu, 2003). The amount of dyes present in a typical dye bath is about 1000 mg/L (Andreozzi et al, 1999, Azbar et al, 2003). A general effluent is characterised by a pH of 9-11, a COD of 1300-2000 mg/L, total dissolved solids of 4900-7000 mg/L, a colour of 1500-4500 ADMI and a temperature of 35-45°C (Manu, 2003, Eswaramoorthi et al., 2008).

These azo dyes are found to be complex in nature and have been found to show carcinogenic evidences on reductive cleavage. These dyes are capable of altering the physical and engineering properties of soil, deteriorating water bodies and causing harm to the flora and fauna in the environment (Manu, 2003). Savin and Butnaru (2008) observed that the toxic nature of dyes causes death to the soil microorganisms which in turn affects the agricultural productivity. Hence, removing the dye contents from effluents before disposal is paramount.

Advanced oxidation processes (AOPs) were developed to generate hydroxyl free radicals using different oxidants under different combinations and these radicals were found to destroy components that are not destroyed under conventional oxidation processes (Kestioglu et al., 2005; Kdasi et al., 2004). AOP using ozone, Ultra Violet, TiO₂, fenton, photo-fenton and hydrogen peroxide can be used to treat dyes. The main advantage of AOPs over the other treatment processes is its pronounced destructive nature which results in the mineralization of organic contaminants present in wastewater (Kdasi et al., 2004). AOPs are considered as a low or non-waste generation technology, which destroys the complex structures using short lived chemical species with a high oxidation power. The hydroxyl radical (OH[°]) is the main oxidative power of AOPs (Arslan et al., 1999; Kestioglu et al., 2005). The OH[°] radicals can be generated by chemical, electrical, mechanical or radiation energy. Therefore, AOPs are classified under chemical, catalytic, photochemical, photocatalytic, mechanical and electrical processes.

In this research, the production of hydroxyl radical using TiO₂, H₂O₂ and UV individually and in different combinations and their effectiveness in degrading the azo dye – Reactive Red 120 (HE3B) were evaluated.

Chapter 2. OBJECTIVES

The main aim of this study was to evaluate the effectiveness of Advanced Oxidation Process (AOP) for degradation of the textile dye Reactive Red 120 (HE3B). The specific objectives of the studies were:

1. To study the effect of UV on the degradation of reactive red 120 dye of varying concentration (50-500 mg/L).
2. To study the effect of combined UV and of H₂O₂ treatment on the degradation of reactive red 120 dye of varying concentration (50-500 mg/L).
3. To study the effect of combined UV and TiO₂ treatment on the degradation of reactive red 120 dye of varying concentration (50-500 mg/L).
4. To compare the effectiveness of the three treatments and select the most efficient treatment process.
5. Evaluate the effect of pH on the treatment efficiency and time.
6. Evaluate the pollution potential of the treated effluent using COD, temperature and pH as pollution measurement parameters.

Chapter 3. LITERATURE REVIEW

3.1. Types of Textiles and Textile Industries

The word textile means to weave. This was adopted from a Latin word ‘*texere*’. Textiles can be woven by both hand and machines. The raw materials for textiles are fibers: natural and synthetic (Elliott et al., 1954). The sources of natural fibers are minerals, animals and plants. Now with the advancement of technology, fibers can be extracted from chemicals. However, plant sources yield a large amount of fibers than those obtained from animal and mineral sources. Most of the textiles produced are as a result of spinning of fibers from the yarns (Kuusisto, 2010; Yi Ling, 2009).

The textile industries are classified on the basis of the types of textiles they produce. These industries are mainly involved in the production of cellulose fibers, protein fibers and synthetic fibers. Cellulose fibers are obtained from plant sources, such as cotton, rayon, linen, ramie, hemp and lyocell (Bledzki and Gassan, 1999). Protein fibers are obtained from animals and include wool, angora, mohair, cashmere and silk. Polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene are artificially synthesized and are hence categorized as synthetic fibers. Most of the textiles produced are from cotton liners, petrochemicals and wood pulp. The quality of a textile depends on the type of raw material used and characteristics of the yarn spun.

China is found to be the biggest producer of almost all the textiles, followed by India and USA as shown in Table 3.1. The major producers of cotton, wool, cocoons, jute and nylon are shown in the Tables 3.2 –3.6. The world use of cotton over two decade’s are shown in Figure 3.1. The distribution of world consumption of dyes is shown in Figure 3.2.

3.2. Textile Manufacturing Process

Various manufacturing processes are carried out for different types of textiles. The production of textiles can be broadly divided into two categories: the spinning process

Table 3.1. Top 10 countries with textile manufacturers (Fashion Products, 2012).

Country	Production (%)
China	50
India	15
Hong Kong	6
USA	5
Mexico	3
Thailand	3
Philippines	2
Indonesia	2
Bangladesh	2
Sri Lanka	2
Rest of the World	10

Table 3.2. Top ten producers of cotton (LGW Limited, 2012).

Countries	Amount (Million bales)
China	25.3
India	20.5
USA	19.2
Pakistan	11.7
Brazil	7.2
Uzbekistan	5.5
Turkey	3.2
Greece	1.4
Turkmenistan	1.3
Syria	1.1

Table 3.3. Top ten producers of wool (Speer, 2006).

Country	Wool Produced (%)
Australia	25
China	18
New Zealand	11
Argentina	3
Turkey	2
Iran	2
United Kingdom	2
India	2
Sudan	2
South Africa	1
USA	0.77

Table 3.4. Top ten cocoons producers (Silkwood Silk, 2007).

Countries	Production (1000 kg)
China	290,003
India	77,000
Uzbekistan	17,000
Brazil	11,000
Iran	6,000
Thailand	5,000
Vietnam	3,000
Korea	1,500
Romania	1,000
Japan	600

Table 3.5. Top ten jute producers (IJSG, 2003).

Countries	Production (Tonnes)
India	21,40,000
Bangladesh	8,00,000
China	99,000
Cote D'Ivoire	40,000
Thailand	31,000
Myanmar	30,000
Brazil	26,711
Uzbekistan	20,000
Nepal	16,775
Vietnam	11,000
Rest of the World	32,25,551

Table 3.6. World production of nylon fiber (ICIS, 2010).

Countries	Production (Tonnes)
China	1,372,700
USA	637,304
Korea	132,305
Japan	73,578

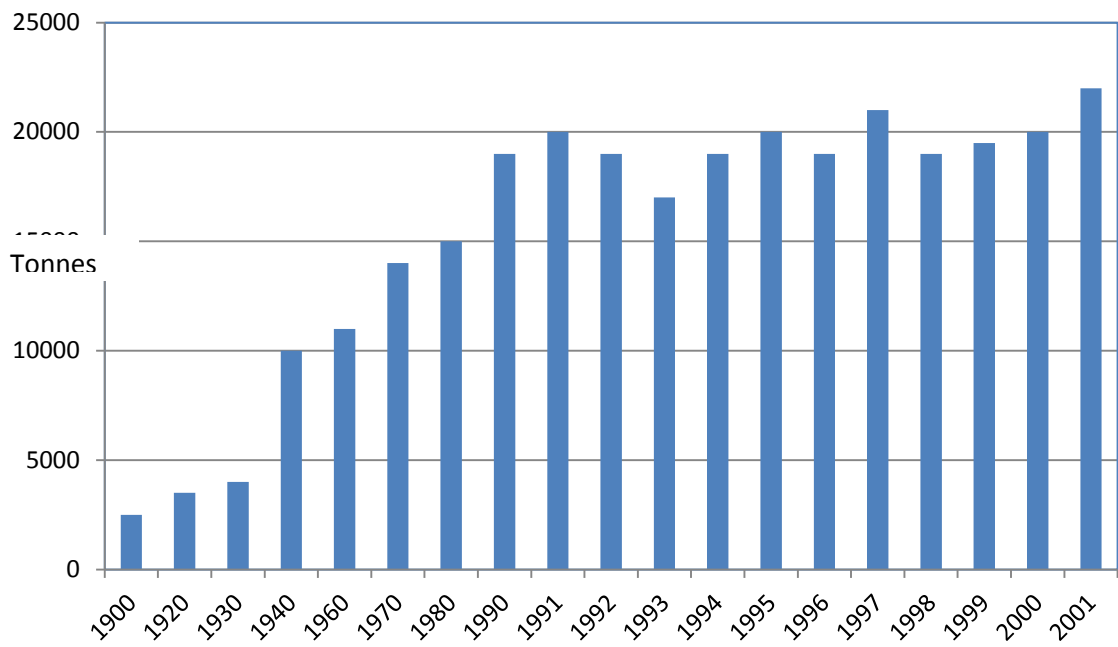


Figure 3.1. Cotton fibres in world, 1900-2001 (UNCTAD, 2003).

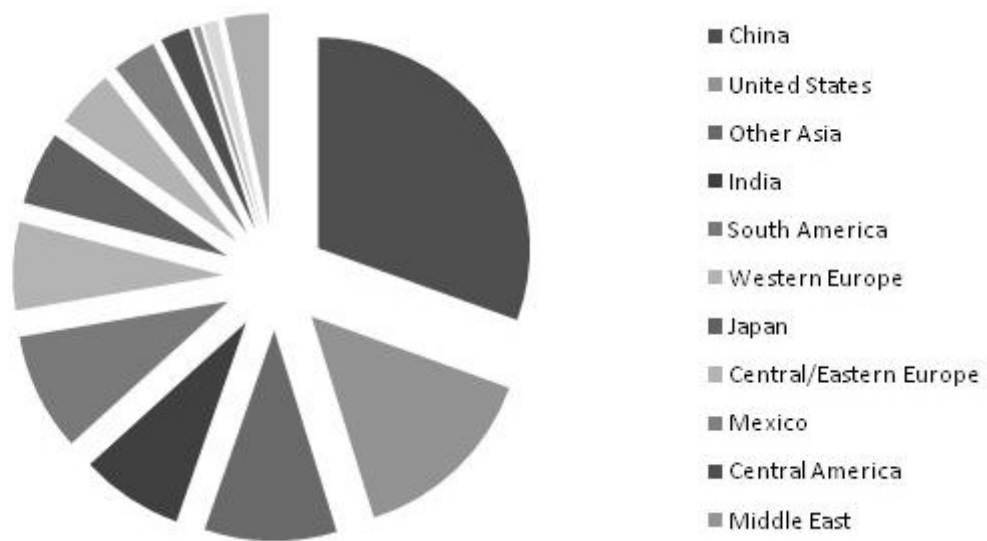


Figure 3.2. World consumption of dyes in 2007 (Sri, 2008).

(the dry process) and the wet process (involves the usage of dyes). Production of cotton textiles involves the separation of cotton fibers from the cotton seeds which are then spinned into cotton yarns (Sette et al., 1996). These yarns are weaved successfully into cloths. The cloths then undergo various wet processes including singeing, scouring. This is the part in textile making which uses a large amount of water.

Dyeing is one of the most important steps in the wet process which involves changing the colour of the textile spun using dyes. Finishing is the final step in manufacturing and uses chemicals like HS-ULTRAPHIL, ECODESIZE-PS-10 and Amino silicone fluid to treat the cloths for obtaining a better quality (Wang et al., 2002). An overall textile processing is shown in Figure 3.3.

The first step in the production of leather products involves the removal of hair, inter-fibrillary protein and epidermis using physical and mechanical methods. The leather obtained is treated with digestive enzymes to remove the non-fibrous proteins and then soaked in sulphuric acid to lower the pH. The leather then undergoes tanning process. Three main types of tanning process are used: mineral/chrome tanning, vegetable tanning and oil tanning. The leather finally undergoes dyeing and finishing processes (Dooley, 2008).

The production of silks involves the extraction of silk threads from the cocoons. The threads thus obtained have a glutinous substance on them which is removed by washing and bleaching. The threads are then weaved and undergo the dyeing procedure which gives the silks a different shade. After the dyeing process, it undergoes the finishing process (Fisher and Robertson, 1998).

3.3. Dyes Used in the Manufacturing Process

Dyes can be classified into different types depending on their chemical compositions and their properties. Different types of textiles are dyed using different types of dyes and therefore, the usage of dyes varies from industry to industry depending on the fabrics they manufacture.

3.3.1. Dyes for Cellulose Fibres

The most commonly used dye for cellulose textiles is fibre reactive dyes. These dyes are capable of forming covalent bonds with the fibre molecule and so this is considered as the most effective and permanent dye used. This is found to work well on any cellulose fibre under different required temperatures (Lorimer et al., 2001). Phillips (2005) states that the world uses of reactive dyes increased from 60,000 tonnes in 1988 to 178,000 tonnes in 2004. Some of the well known fibre reactive dyes are Procion MX, Cibacron F, Sabracron F, Drimarene K and Remazol, whose structure could be as seen in Table 3.7.

Direct dyes are applied under an aqueous bath containing electrolytes and ionic salts. These dyes do not form strong bonds and are loosely associated with the fibre molecules hence they lack the property of drying up quickly after they are applied on fabrics. These dyes are applied under a temperature of 79.4°C and 93.3°C (Lorimer et al, 2001, Burch, 2009). Textiles dyed with direct dyes should only be cold washed along with similar colours since they lack the fixative property. One of the advantages of these dyes is that they are the cheapest among all other dyes. Direct dyes are used for dyeing rayon, linen and cellulosic fibres, they could also be used to dye wool and silk by using chemical fixative agents. The usage of direct dyes was increased from 46,000 tons in 1992 to 60,000 tons in 2004 (Phillips, 2005)

Indigo is a dark blue crystalline powder that is insoluble in water. Reducing agents like sodium hydrosulfite makes it soluble in water. Normally, indigo does not have an affinity towards cotton, but in a reduced state they tend to enter the space in the cotton fibres. The dye molecules inside the fibre are then exposed to air, which makes it insoluble again and trapped inside the fibre (Prideaux, 2003, Burch, 2009). These dyes are the primary colour of blue jeans and the dye comes under the classification of vat dyes (Robert et al., 2008). Balan and Monteiro (2001) stated that the world use of indigo dyes is 3000 ton per year.

Another type of dye called the naphthol dyes is made with the combination of two different chemicals, the diazo salts and the naphthol. This combination determines the

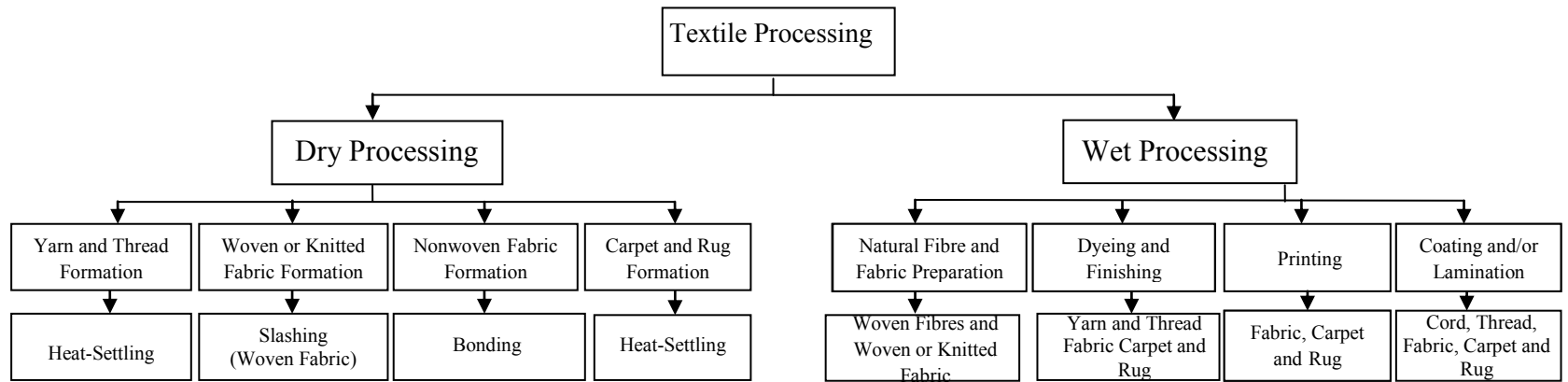


Figure 3.3. Overall basic textile processing (EPA, 1998).

colour of the dye. About 1500 tons per year of this dye was produced worldwide (Jiang et al., 2004). This dye is treated as the cold water dyes. The temperature of cold water used normally for other groups of dyes may range from 35-41°C but this type of dye can be used even with ice water (Burch, 2008).

Rayon, cotton or other cellulosic fibres as well as silk could also be dyed using naphthol dyes. A major disadvantage about this group of dye is that they are found to contain more hazardous chemicals than the fibre reactive dyes, which makes them less appropriate for home use (Hanu, 2010).

3.3.2. Dyes for Protein Fibres

All fibres obtained from animals are considered as protein fibres. Cellulose is made up of repeating sugar and glucose units, while proteins are made up of twenty essential amino acids hence more complex than cellulose. High pH denatures proteins. Acid dyes are therefore used to dye wool, angora, cashmere and silk. These dyes are applied to the fabrics along with acid solutions. The chemical reaction between the dye and the fibre results in the formation of an insoluble dye molecule on the fibre (Valko, 1957). The three most important acid dyes are azo dyes, triarylmethane dyes and anthraquinone dyes shown in Table 3.8. The class of azo dyes account for 60-70% of all the dye groups. These kind of dyes are found to contain an azo group (-N=N-) in the center. Some group of azo dyes contain two or three azo groups and are called diazo and triazo, respectively. Azo dyes are found to give out bright and high intensity colours compared to the other class of dyes (University of Brisol, 2012). Triarylmethane dyes are derivatives of triarylmethane, a hydrocarbon. Basic triarylmethane dyes are mainly used for dyeing leather, plastics and paper. They are also used in printing and stamping inks. Acidic triarylmethane dyes contains at least two SO₃H groups and are used to dye silk and wool (Farlex, 2012). Anthraquinone dyes has sulfonic acid group in them, which aid them in being dissolved in water and dye wool and silk, due to their affinity towards auxiliary binding agents. A subclass of acid dye called the food colouring dyes are used to dye protein fibres and some nylon fibres under high temperature (Robert et al., 2008; Moody

and Needles, 2004). It is estimated that about 7000 tonnes of acid dyes are produced annually (Silva et al., 2004)

Another subclass is called the fibre reactive dye and is used to dye protein fibres. The most important and distinguishing characteristics of reactive dyes are its property of forming covalent bonds during the application process with the substrates that is to be coloured (Zhang et al., 2003). Reactive dyes entered the market under the name remalan in 1952, which contained monochlorotriazinyl reactive group. Later in 1953, they were modified in a way to fix the chlorotriazine containing dye to cellulose in a basic medium which was a breakthrough for reactive dyes. Since then, the development of this dye group has been rapid (Christie, 2001). Unlike other dye groups, reactive dyes consist of a known chromophore system which contains various reactive groups. Based on these reactive groups, they are classified into (a) mono anchor dyes, (b) double anchor dyes and (c) multiple anchor dyes (Hunger, 2003)

3.3.3. Dyes for Synthetic Fibres

The commonly used dye for synthetic fibres is dispersed dyes. These dyes are mainly used in the printing of polyesters, nylon and acetates. Some dispersed dyes are also used as printing ink in industries.

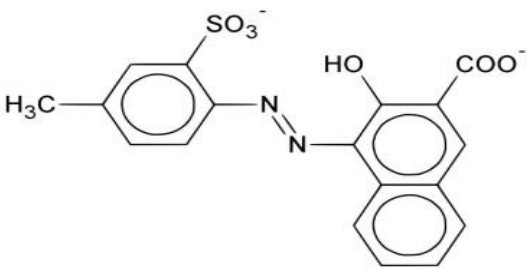
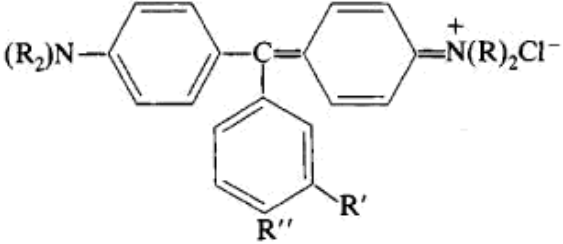
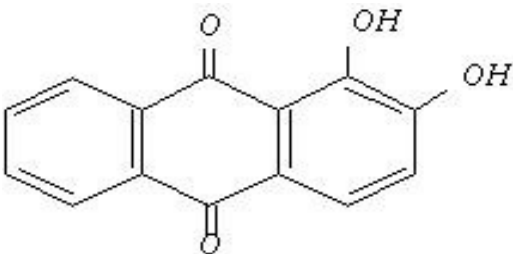
Dispersed dyes are categorised into three types based on their energy. The E type is low energy and is used in thermosol dyeing. S type is high energy and is used in HT/HP dyeing. The other SE type is suitable for all dyeing methods (Sunny, 2003; Burch, 2008). These dyes are present in a colloidal state with a low water solubility property and are applied under a dye bath condition under the required temperature which depends on the thickness of the fibre to be dyed (Butkinshaw, 1995).

Direct dyes which are used extensively to dye protein fibres can also be used to dye synthetic fibres like nylon and rayon. These dyes are applied under an aqueous bath containing electrolytes and ionic salts. Direct dyes lack the property of getting dried-up fast after they are applied on fabrics (Burch, 2009).

Table 3.7. Structures of reactive dyes (Burch, 2012).

Dyes	Structure
Procion MX	
Cibacron F	
Drimarene K	
Remazol	

Table 3.8. Structures of acid dyes.

Dye	Structure
Azo Dyes	
Triarylmethane Dyes	
Anthraquinone Dyes	 <p data-bbox="971 1115 1089 1150">Alizarin</p>

Basic dyes are also considered as cationic dyes. They form a coloured cationic salt when dissolved in water. These cationic salts are found to react with the anionic surface of the substrate. These dyes are found to be powerful colouring agents for acrylic fibres (Kiron, 2012).

3.4. Types of Textile Wastes Produced

The textile industry is considered to be one of the biggest threats to the environment. The manufacturing processes carried out in textile industries produce large amount of wastes in each stage in three forms: solid, liquid and the gas. Some of the most commonly generated wastes are listed in Table 3.9.

Most of the solid wastes are originated from the dry process while the wet process yields only a small amount of solid wastes. The majority of solid wastes are made of pieces of fabrics and packaging materials. The dried up sludge from the textile production is also a major source of solid waste. Solid wastes are not found to be hazardous in general. However the emptied chemical containers may contain traces of harmful substances (Fletcher, 2008, Georgio et al., 2003). Sources and types of solid wastes produced in each stage are listed below in Table 3.10.

The majority of the process being carried out in textile industries produces gaseous emissions. Boilers, ovens and storage tanks are the three most important sources of air pollution in the textile industry. The boilers are usually found to generate sulphur oxides and nitrogen. The high temperature textile drying process is found to emit hydrocarbons. Pollutants are also emitted from residues of fibre preparation during the heat settling process. Gases can also be emitted from the chemicals during the dyeing process (Georgio et al., 2003). Some other major gaseous pollutants are as follows in Table 3.11.

Textile industry uses a large amount of water for its manufacturing purposes. It roughly takes about 200 L of water to produce 1kg of textile. The water let out after the production of textiles contains a large amount of dyes and other chemicals which are harmful to the environment. The level of toxicity or harmfulness of the textile effluents is

Table 3.9. Types of textile wastes produced (Moustafa, 2008).

Process	Emission	Wastewater	Solid Wastes
Fibre preparation	Little or none	Little or none	Fibre waste and packaging waste
Yarn spinning	Little or none	Little or none	Packaging wastes, sized yarn, fibre waste, cleaning and processing waste
Slashing/sizing	VOCs	BOD, COD, metals, cleaning waste, size	Fibre lint, yarn waste, packaging waste, unused starch-based sizes
Weaving	Little or none	Little or none	Packaging waste yarn and fabric scraps, off - spec fabric, used oil
Knitting	Little or none	Little or none	Packaging waste, yarn, fabric scraps.
Tufting	Little or none	Little or none	Packaging waste, yarn, fabric scraps, off-spec fabric
Desizing	VOCs from glycol esters	BOD from sizes lubricants, biocides, anti-static compounds	Packaging waste, fibre lint, yarn waste, cleaning and maintenance materials
Scouring	VOCs from glycol ester and scouring solvents	Disinfectants, insecticide recisues, NaOH,detergents oils, knitting lubricants, spin finishes,spent solvents	Little or none
Bleaching	Little or none	H ₂ O ₂ , stabilizers, high pH	Little or none
Singeing	Small amount of exhaust gases from the burners exhaustic with components	Little or none	Little or none
Mercerising	Little or none	High pH, NaOH	Little or none
Heat setting	Volatilisation of spin finish agents-synthetic fibre manufacture	Little or none	Little or none
Dyeing	VOCs	Metals, salt, surfactants, organic processing assistants, cationic materials, colour, BOD, COD, sulphide, acidity/alkalinity, spent solvents	Little or none
Printing	Solvents, acetic acid-drying and curing oven emission combustion gases	Suspended solids, urea, solvents, colour, metals, heat, BOD, foam	Little or none
Finishing	VOCs, contaminants in purchased chemicals, formaldehyde vapours, combustion gases	COD, suspended solids, toxic materials, spent solvents	Fabric scraps and trimmings, packaging waste

Table 3.10. Types and sources of solid wastes in textile manufacturing (Moustafa, 2008).

Source	Type of Solid Waste
<i>1. Mechanical operations of cotton and synthetics</i>	
Yarn preparation	Fibres and yarns
Knitting	Fibres and yarns
Weaving	Fibres, yarns and cloth scraps
<i>2. Dyeing and finishing of woven fabrics</i>	
Sizing, desizing, mercerizing, beaching, washing and chemical finishing	Cloth scraps
Mechanical finishing	Flock
Dyeing/printing	Dye containers
Dyeing/printing (applied finish)	Chemical containers
Dyeing and finishing of knitted fabrics	Cloth scraps, dye and chemical containers
<i>3. Dyeing and finishing of carpets</i>	
Tufting	Yarns and sweepings
Selvage trim	Selvage
Fluff and shear	Flock
Dyeing, printing and finishing	Dye and chemical containers

found to differ between the industries (Kiriakido et al., 1999). The amounts of water consumed by various types of fabrics are listed in Table 3.12

3.5. Origin of Textile Effluent Generation

The textile industry uses a variety of chemicals and a large amount of water for all of its manufacturing steps. Water is used mainly in two different ways: (a) for the application of chemical onto textiles and (b) for rinsing the manufactured textiles (Ntuli et al., 2009). Wet process usually uses a lot of chemicals and water. About 80 – 150 m³ of water is used to produce 1 kg of fabrics and, it is estimated that about 1,000 – 3,000 m³ of waste water is reproduced after processing about 12 – 20 tons of textiles per day (Atif, 2002). It has also been shown that textile industries in India use about 1608.8 L of water every day (Mishra., 2010).

However, the exact quantity of water required varies from industry to industry depending on the dyeing process and the type of fabrics produced. It is found that the longer the processing, the higher the water required. Water is also required to wash the fabrics at the end of each process (Ntuli et al., 2009). The percentages of water used during the wet processes are shown in Table 3.13. The amount of waters consumed by cotton and synthetic textile producing industries are shown in Tables 3.14 and 3.15. The amounts of chemicals used in wet processes are shown in the Tables 3.16 and 3.17.

In the textile dyeing process, there is always a portion of unfixed dye which gets washed away along with water. The textile wastewater is found to be high in the concentration of these unfixed dyes are as shown in Table 3.18.

3.6. Environmental Impacts of Textile Effluent

The characteristics of textile effluents vary and depend on the type of textile manufactured and the chemicals used. The textile wastewater effluent contains a high amount of agents causing damage to the environment and human health including suspended and dissolved solids compound, biological oxygen demand (BOD), chemical oxygen demand (COD), chemicals, odour and colour. Most of the BOD/COD ratios are

Table 3.11. Types and sources of gaseous emissions in textile manufacturing (Moustafa, 2008).

Process	Source	Pollutants
Energy production	Emission from boiler	Particulates, nitrous oxides(Nox), sulphur dioxide (SO ₂)
Coating, drying and curing	Emission from high temperature ovens	Volatile organic components (VOCs)
Cotton handling activities	Emission from preparation, carding, combing and fabrics manufacturing	Particulates
Sizing	Emission from using sizing compound (gums, PVA)	Nitrogen oxides, sulphur oxide, carbon monoxide
Bleaching	Emission from using chlorine compound	Chlorine, chlorine dioxide
Dyeing	Disperse dyeing using carriers sulphur dyeing Aniline dyeing	Carriers H ₂ S Aniline vapours
Printing	Emission	Hydrocarbons, ammonia
Finishing	Resin finishing heat setting of synthetic fabrics	Formaldehydes Carriers – low molecular weight Polymers- lubricating oils
Chemical storage	Emission from storage tanks for commodity and chemicals	Volatile organic components (VOCs)
Waste water treatment	Emission from treatment tanks and vessels	Volatile organic components, toxic emissions

Table 3.12. Average water consumption for various fabrics (Moustafa, 2008).

Processing Subcategory	Water Consumption (m³/ ton fibre material)		
	Minimum	Median	Maximum
Wool	111	285	659
Woven	5	114	508
Knit	2	84	377
Carpet	8.3	47	163
Stock/yarn	3.3	100	558
Nonwoven	2.5	40	83
Felted fabric finishing	33	213	933

Table 3.13. Total water consumed during wet process (Ntuli et al., 2009).

Process	Water Consumed (%)
Bleaching	38
Dyeing	16
Printing	8
Boiler	14
Other uses	24

Table 3.14. Water required by cotton textile industry for the wet process (Ntuli et al., 2009).

Process	Water Consumption (L/1000 kg of products)
Sizing	500-8200
Desizing	2500-21000
Scouring	20000-45000
Bleaching	2500-25000
Mercerizing	17000-32000
Dyeing	10000-300000
Printing	8000-16000

Table 3.15. Water required by synthetic textile industry for its wet process (Ntuli et al., 2009).

Process	Water Requirements (L/1000 kg of products)				
	Rayon	Acetate	Nylon	Acrylic/Modacrylic	Polyester
Scouring	17000-34000	25000-84000	50000-67000	50000-67000	25000-42000
Salt bath	4000-12000	-	-	-	-
Bleaching	-	33000-50000	-	-	-
Dyeing	17000-34000	34000-50000	17000-34000	17000-34000	17000-34000
Special finishing	4000-12000	24000-40000	32000-48000	40000-56000	8000 - 12000

Table 3.16. Chemicals used in bleaching (Eswaramoorthi et al., 2008).

Chemical	Utilization (kg/100kg of cloth)	
	Soft Flow Machine	Winch
Wetting agent	0.5	0.5
Caustic soda	2.5	4.0
Peroxide	3.0	4.0
Lubricants	0.2	0.3
Stabilizers	0.2	0.3
Peroxide killer (oxidizing agent)	1.0	1.0
Acetic acid	2.0	2.0

Table 3.17. Chemicals used In dyeing (Eswaramoorthi et al., 2008).

Chemicals	Utilization (kg/100 kg of cloth)	
	Soft Flow	Winch
Lubricants (kg)	0.3	0.4
Sequestering agent (kg)	0.6	1
Dye stuff (kg)		
Light Shade	0.150	0.150
Medium Shade	1.5	1.5
Dark Shade	10	10
Soda ash (g/L)		
Light Shade	6	6
Medium Shade	11	11
Dark Shade	20	20
Sodium chloride (g/L)		
Light Shade	15	15
Medium Shade	45	45
Dark Shade	90	90
Acetic acid (kg)	2.5	3.0
Soap (kg)	1.0	1.0
Fixing (kg)	1.0	1.0
Softener (kg)	2.0	2.0

found to be around 1:4, indicating the presence of non-biodegradable substances (Arya and Kohli, 2009). Typical characteristics of textile effluent are shown in Table 3.19. The possible pollutant and the nature of effluents released from each steps of wet process are listed in Table 3.20. The textile effluents are not only associated with dyes and chemicals but also with some trace metals like Cr, As, Cu and Zn, which are capable of harming the environment (Eswaramoorthi et al., 2008). Dyes in water give out a bad colour and can cause diseases like haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis (Nese et al., 2007). They can block the penetration of sunlight from water surface preventing photosynthesis (Laxman, 2009).

Dyes also increase the biochemical oxygen demand of the receiving water and in turn reduce the reoxygenation process and hence hamper the growth of photoautotrophic organisms (Nese et al., 2007). The suspended solid concentrations in the effluents play an important role in affecting the environment as they combine with oily scum and interfere with oxygen transfer mechanism in the air-water interface (Laxman, 2009).

Inorganic substances in the textile effluents make the water unsuitable for use due to the presence of excess concentration of soluble salts. These substances even in a lower quantity are found to be toxic to aquatic lives (Nemerow, 1997; Tholoana, 2007). The organic components are found to undergo chemical and biological changes that results in the removal of oxygen from water (Tholoana, 2007), some of the inorganic chemicals like hydrochloric acid, sodium hypochlorite, sodium hydroxide, sodium sulphide and reactive dyes are capable of being poisonous to marine lives (Blomqvist, 1996; Tholoana, 2007).

The seriousness of water pollution depends on the quantity of water and chemicals used in the wet process (Laxman, 2009). The dye concentration in a dye house range between 0.01g/L and 0.25 g/L depending on the type of the dye and the process carried out (Reife and Freeman, 1996; Helena et al; 2000; Wamburguh and Chianelli, 2008). Vat dyes are used under a concentration of 0.05-0.1 g/L (Pelegriani et al, 1999; Ren, 2000; Wamburguh and Chianelli; 2008) while indigo dyes are used under a concentration of 0.02 g/L

Table 3.18. Unfixed dyes (Dyes and Pigments, 2010).

Fibre	Dye Type	Unfixed Dye (%)
Wool and nylon	Acid dyes/ reactive dyes for wool	7-20
Cotton and viscose	Pre-metallised dyes	2-7
	Azoic dyes	5-10
	Reactive dyes	20-50
	Direct dyes	5-20
	Pigment	1
	Vatdyes	5-20
Polyester	Sulphur dyes	30-40
	Disperse	8-20
Acrylic	Modified basic	2-3

Table 3.19. Characteristics of typical untreated textile wastewater (Eswaramoorthi et al., 2008).

Parameter	Range
pH	6-10
Temperature (°C)	35-45
Total dissolved solids (mg/L)	8,000-12,000
BOD (mg/L)	80-6,000
COD (mg/L)	150-12,000
Total suspended solids (mg/L)	15-8,000
Total Dissolved Solids (mg/L)	2,900-3,100
Chlorine (mg/L)	1,000-6,000
Free chlorine (mg/L)	<10
Sodium (mg/L)	70%
Trace elements (mg/L)	
Fe	<10
Zn	<10
Cu	<10
As	<10
Ni	<10
B	<10
F	<10
Mn	<10
V	<10
Hg	<10
PO ₄	<10
Cn	<10
Oil & grease (mg/L)	10-30
TNK (mg/L)	10-30
NO ₃ -N (mg/L)	<5
Free ammonia (mg/L)	<10
SO ₄ (mg/L)	600-1000
Silica (mg/L)	<15
Total Kjeldahl Nitrogen (mg/L)	70-80
Color (Pt-Co)	50-2,500

Table 3.20. Sources of water Pollution at various stages of processing (Laxman, 2009).

Process	Possible Pollutants	Nature of Effluent
Desizing	Starch, glucose, PVA, resins, fats and waxes not exert a high BOD.	Very small volume, high BOD (30-50% of total), PVA.
Kiering	Caustic soda, waxes, soda ash, sodium silicate and fragments of cloth.	Very small, strongly alkaline, dark colour, high BOD values (30% of total)
Bleaching	Hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids.	Small volume, strongly alkaline, low BOD (5% of total)
Mercerizing	Caustic soda	Small volume, strongly alkaline, low BOD (Less than 1% of total)
Dyeing	Dye stuff, mordant and reducing agents like sulphides, acetic acids and soap	Large volume, strongly coloured, fairly high BOD (6% of total)
Printing	Dye, starch, gum oil, china clay, mordants, acids and metallic salts	Very small volume, oily appearances, fairly high BOD.
Finishing	Traces of starch, tallow, salts, special finishes, etc.	Very small volume, less alkaline, low BOD.

PVA – Poly Vinyl Alcohol

BOD – Biological Oxygen Demand

COD – Chemical Oxygen Demand

(Wamburguh and Chianelli, 2008). Textile dyestuffs are found to contain a large amount of organic substances which are difficult to degrade and are resistant to aerobic degradation. They are also found to be reduced into carcinogenic agents under anaerobic conditions (Jain et al., 2003). Some of the carcinogenic compounds produced due to the degradation of Azo dyes are as shown in Table 3.21 and the amount of pollution from wet process in textiles could be seen in Table 3.22

3.7. Standards for Textile Waste Water Disposal

Canadian Council of Ministers of the Environment (CCME) is entrusted with the protection of human health and guarding the environment from pollution. This agency has set certain limits on the disposal of effluents into the environment. Some of the CCME regulations are shown in Table 3.23. Federal Environment Protection Agency (FEPA) in USA also has its own regulation which are also shown in Table 3.23. A constant check is to be kept on these discharge limits every now and then to maintain a safe and a healthy environment. These limits are found to differ from country to country depending on their environmental conditions (Yusuff and Sonibare, 2004).

3.8. Conventional Treatments of Textile Effluents

Biological and physico-chemical treatments are used technologies for treating textile effluents. One disadvantage of biological treatment processes is the presence of toxic heavy metals in the effluent which affects the growth of microorganism. Another major disadvantage of biological treatment is that most of the dyes used are non biodegradable in nature (Eswaramoorthi et al, 2008). Physical treatments use adsorbents like activated carbon to remove soluble substances from the effluent. When the effluents are passed through activated carbon, the soluble substance in the effluents gets attached to the internal surface of activated carbon and remains trapped until removed (Lenntech, 2011). Flocculation, coagulation and ozonation are widely used chemical treatments. There are three treatment steps involved: primary, secondary and tertiary treatment.

Table 3.21. Toxic aromatic amines derivatives from azo dyes (Jain et al., 2003).

Aromatic Amine Group	Human Carcinogenic Evidences
1-Naphthylamine	Slight/Mixed
2-Naphthylamine	Good
2,5-Diaminotoluene	Slight
3,3'-Dichlorobenzidine	Slight/Mixed
3,3'-Dimethoxybenzidine	Slight/Mixed
3,3'-Dimethylbenzidine	Slight
4-Biphenylamine	Good
4-Nitrobiphenyl	Slight/Mixed
4,4'-Methylenebis (2-chloroaniline)	Slight
Auramine	Slight
Benzidine	Good
Magenta	Slight
N-Phenyl-2-naphthylamine	Slight
N,N-Bis(2-chloroethyl)-naphthylamine	Good

Table 3.22. Pollution loads from the textile wet processing (Ntuli et al., 2009).

Parameter	Pollutant Load		
	Maximum	Minimum	Average
Inorganic load (kg.day ⁻¹)	15,356	5	964
Organic load (kg COD.day ⁻¹)	7793	100	1766

Table 3.23. FEPA limits of the effluents discharged from textile mills (Yusuff, 2004).

Parameter	CCME	FEPA
pH	6.5-8.5	6-9
Temperature (°C)	30	40
Colour (Pt-Co)	100	7
TDS	2000	2000
TSS	40	30
Sulphide µg/L	200	200
Free Chlorine µg/L	1000	1000
COD	80	80
BOD ₅	50	50
Oil & Grease µg/L	-	10
Dissolved Oxygen µg/L	6000	-
Nitrate µg/L	13000	20000
Ammonia µg/L	0.1	0.2
Phosphate µg/L	<4	5
Calcium µg/L	-	200
Magnesium µg/L	200000	200000
Chromium µg/L	1	<100
Aluminium µg/L	5	<1000
Copper µg/L	<1000	<1000
Manganese µg/L	5	5.0
Iron µg/L	300	20000
Zinc µg/L	30	<10000
Mercury µg/L	0.026	0.05

3.8.1. Primary Treatment

The first step in textile wastewater treatment is the removal of the suspended solids, excessive quantities of oil and grease and gritty materials (Eswaramoorthi et al., 2008). The effluent is first screened for coarse suspended materials such as yarns, lint, pieces of fabrics, fibres and rags using bar and fine screens (Das, 2000). The effluent obtained after screening then undergoes settling for the removal of the suspended particles from the effluents. The floating particles are removed using mechanical scraping and pumping. Neutralization is done to reduce the acidic contents of the effluents Sulphuric acid and boiler flue gases are the most commonly used chemicals to alter the pH. A pH value of 5 - 9 is considered ideal for the treatment process (Babu et al., 2007, Eswaramoorthi et al., 2008).

According to Das (2000), simple sedimentation was not found to be effective because it does not remove colloidal particles. Suspended solids can be removed by mechanical flocculation and chemical coagulation processes. Mechanical flocculation is carried out by gently stirring the effluent which makes the finely dispersed solids combine with each other resulting in a heavier solid that settles down (Heukelekian, 1941). Chemical coagulants are used to alter the physical states of the colloids in the effluents and hence removing them by sedimentation. Ferrous sulphate, lime, alum, ferric sulphate and ferric chloride are some of the most commonly used chemicals. The amount of purity depends on the quality of chemical used (Chen et al., 1996). The reductions in pollution parameter of the treatment process are shown in Table 3.24

3.8.2. Secondary Treatment

The Secondary treatment process is mainly carried out to reduce the BOD, phenol and oil contents in the solution. The colour of the effluent can also be controlled using secondary treatment mechanisms. This can be biologically done with the help of microorganisms under aerobic or anaerobic conditions. Bacteria under aerobic conditions are found to use organic matters as their source of energy and nutrients. They bring out some of the changes like oxidation of dissolved organic matters to CO₂, flocculation and coagulation

of colloidal matters and degradation of nitrogenous organic matters to ammonia. On the other hand, anaerobic treatment is mainly used in the digestion of generated sludge (Das, 2000).

Aerated lagoons are one of the commonly used biological treatment processes. This consists of a large holding tank lined with rubber or polythene and the effluents from the primary treatment are aerated for about 2-6 days and the formed sludge is removed. BOD removal efficiency is up to 99% and the phosphorous removal is 15-25% (Das, 2000). The nitrification of ammonia is also found to occur in aerated lagoons. Additional TSS removal can also be achieved by the presence of algae in the lagoon (EPA, 2002). The major disadvantage of this technique is the large amount of space it occupies and the risk of bacterial contamination in the lagoons (Das, 2000; Lafond, 2008).

Trickling filters are another common method of secondary treatment that mostly operates under aerobic conditions. Water that is pre-settled to prevent clogging is trickled or sprayed over the filter. The filter usually consists of a rectangular or circular bed made up of coal, gravels, Poly Vinyl Chloride (PVC), broken stones or synthetic resins (Tilley et al., 2008). A gelatinous film comprising of microorganism is formed on the surface of the filter medium, these organisms help in the oxidization of organic loads in the effluent to carbon dioxide and water (NODPR, 1995). Trickling filters do not require a huge space, hence making them advantageous compared to aerated lagoons. However, their disadvantage is the high capital cost and odour emission (Tilley et al., 2008).

Aerobic activated sludge processes is commonly used. It involves a regular aeration of the effluent inside a tank allowing the aerobic bacteria to metabolize the soluble and suspended organic matters. A part of the organic matter is oxidized into CO₂ and the rest are synthesized into new microbial cells (Nesc, 2003). The effluent and the sludge generated from the processes are separated using sedimentation processes. Some of the sludge is returned to the tank as a source of microbes. A BOD removal efficiency of 90-95% can be achieved from this process, but is time consuming (Yasui et al., 1996).

Table 3.24. Reduction in pollution parameters after primary treatment processes (Das, 2000).

Properties	(%) Percentage of Reduction
Total suspended solids	80-90
BOD	40-70
COD	30-60
Bacteria	80-90
Total suspended matter	50-70
Organic matter	30-40

3.8.3. Tertiary Treatment

Electrolytic precipitation of concentrated textile effluents is the process of passing electric current through the textile effluent so that the impurities settle down, but it requires a high contact time between the cathodes and the effluent (Das, 2000). Electrodialysis and reverse osmosis are the well known techniques which make use of the membranes. Reverse osmosis is well known for its ability to remove the total dissolved solid contents along with the ions and larger species from the effluents. A high efficiency of >90% has been reported (Babu, et al. 2007). Dyeing process requires the use of electrolytes. NaCl is a neutral, common electrolyte that is used for cotton dyeing. These high concentrations of salts can be treated by using reverse osmosis membrane.

Electrodialysis is another method using membranes, this treatment process has the ability to separate even dissolved salts by passing an electrical potential across water. Membrane fouling has to be prevented by removing suspended solids, colloids and turbidity prior to electrodialysis (Marcucci et al., 2002).

Ion exchange method is another commonly used tertiary method which involves the passage of effluents through the beds of the ion exchange resins where the cations and anions are replaced by the hydrogen or sodium ions (Neumann and Fatula, 2009). Photocatalytic degradation is another method by which a wide range of dyes can be decolourized depending on their molecular structures (Vautier et al., 2001). Adsorption is also found to be effective in the removal of colours. Thermal evaporation using sodium persulfate is also found to have a good oxidizing potential. This process is found to be eco-friendly because they do not have the property to form sludge and also do not emit toxic chlorine fumes during evaporation (Das, 2000, NALCO, 1978).

3.9. Azo Dyes

The usage of cotton fabrics has been found to increase considerably in the past century and so is the usage of dyes (UNCTAD, 2003). The colour of a dye is due to the electronic transition between various molecular orbital, the probability of which determines the

intensity of the colour of the dye. Dyes are found to contain two groups: the chromophore eg: (N=N, C=C, C=O) and the auxochrome eg: (-OH, -NH₂, -NR₂) (Manu, 2003). Cotton in general is not found to bind well with picric acid or other anionic or cationic dyes due to the presence of hydroxylic groups in its structure. Hence simple azo dyes are found to be not that effective in the dyeing of cotton. Diazo dyes (dyes with two N=N groups) are very effective in the dyeing of cotton (Arya and Kohli, 2009). The two groups (R-N=N---N=N-R) of the diazo dyes when in a correct distance apart (usually 10.2 to 10.8 angstroms) binds strongly to cotton, but the nature of binding is not completely understood. It is assumed that when the distance between the two nitrogens of the diazo dye correlates with the distance between the hydrogen bonds of the hydroxyl group in cotton it results in an effective bonding (Tam et al., 1996).

Azo dyes in general can be defined as ones which have: (a) a chromophoric azo group (-NN-) attached to an aromatic or heterocyclic nucleus at one end and (b) an unsaturated molecule of carbocyclic, heterocyclic or aliphatic type at the other end. These dyes are found to be the largest classification of dyes with the Colour Index (CI) of more than 10,000 (Sri, 2008). CI is the systematic arrangement of colours based on their hue, brightness and saturation. Azo dyes are classified into groups (mono, di, tri, tetra etc.), based on the number of azo groups attached to its center. A mono azo dye has one N=N bond while di and tri azo groups has two and three N=N, bonds respectively. To avoid confusions, the dyes with three or more azo groups are often considered as poly azo dyes (Robert et al., 2008). The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups. The side groups attached imparts the colour to the dye and the colour index of a dye is found to vary depending on the number of azo groups attached as shown in Table 3.26 (Kirk – Othmer, 2007).

The chromogen:chromophore structure is responsible for solubility and adherence of the dye to the fibre. The bonding affinity groups are amines, hydroxyl, carboxyl and sulfonic radicals or their derivatives. The chromogen:chromophore structure of azo dyes are not effective when applied directly on cotton fibres, hence they require acidified solution along with them to bind to the fibre. The acidified solution usually contains amphoteric

protein in a combination with sulphuric acid, acetic acid, sodium sulphate and surfactants (Arslan et al., 1999). The chemical reaction between the acid and the dye molecule results in the formation of an insoluble dye molecule on the fibre (Robert et al., 2008). The aromatic ring structure of the dye coupled with a side chain is usually required for resonance and in turn imparts colour (Neill et al., 1999).

These resonance structures causing displacement or appearance of absorption bands in the visible spectrum are responsible for colour (Kdasi et al., 2004). It is found that 80-90% of the fibre reactive dyes are based on azo chromogen (Zoolinger, 1991; Manu, 2003). About 20-50% of the reactive dyes used are lost in water wash. Fiber-reactive azo dyes exhibit a high wet-fastness, due to their ability to covalently bond to substrates.

Azo dyes have the potential for toxicity on the environment and humans. A case of bladder cancer was recorded for the workers in dye manufacturing in the early 1895 and this led to further investigations of the toxic effects of these dyes (Yahagi et al., 2004). Brown and DeVito (1993) and Levine (1991) stated that the problems of azo dyes are due to the presence of benzene and the naphthalene rings attached to the azo group which are found to be carcinogenic in nature. An extensive study of hundreds of different effluent samples showed that 10% were carcinogenic under Ames test (Chung, 1983; Yahagi et al., 2004). Another study conducted on 45 combined effluents from textile finishing plants showed that 27% of the wastewater samples were mutagenic (McCarthy, 1997). Some of the toxic components and derivatives of azo dyes are as shown in Table 3.27.

Brown and DeVito (1993) developed a three-part list of the biological mechanisms thought to be responsible for carcinogenic activation of azo dye compounds. They are (a) azo dyes may be toxic only after reduction and cleavage of the azo linkage, producing aromatic amines, (b) azo dyes with structures containing free aromatic amine groups that can be metabolically oxidized without azo reduction may cause toxicity and (c) azo dye toxic activation may occur following direct oxidation of the azo linkage producing highly reactive electrophilic diazonium salts.

Table 3.25. Classifications of azo dyes (Segura et al., 2011).

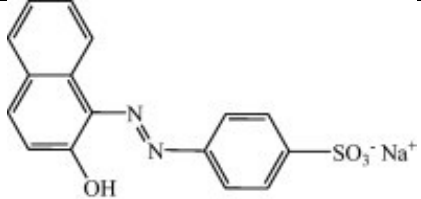
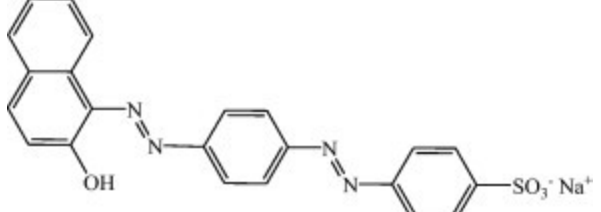
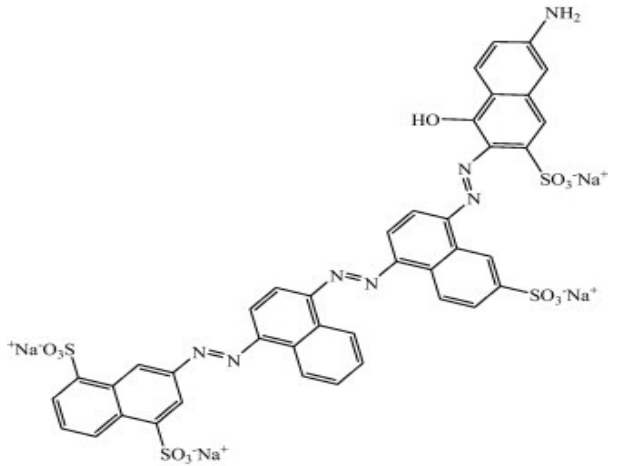
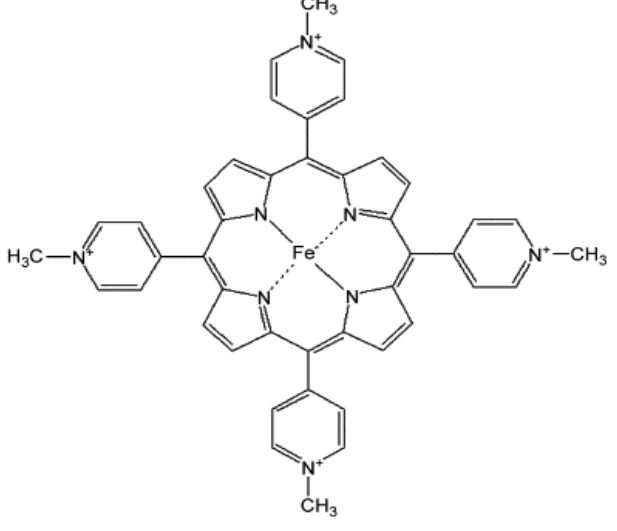
Classifications	Structure
Mono azo	
Diazo	
Triazo	
Tetrakis	

Table 3.26. Azo dyes (Kirk – Othmer, 2007).

Chemical Class	Colour Index
Monoazo	11,000-19,999
Disazo	20,000-29,999
Trisazo	30,000-34,999
Polyazo	35,000-36,999

Table 3.27. Toxic aromatic amines derivatives from azo dyes (Jain et al., 2003).

Aromatic Amine Group	Human Carcinogenic Evidences
1-Naphthylamine	Slight/Mixed
2-Naphthylamine	Good
2,5-Diaminotoluene	Slight
3,3'-Dichlorobenzidine	Slight/Mixed
3,3'-Dimethoxybenzidine	Slight/Mixed
3,3'-Dimethylbenzidine	Slight
4-Biphenylamine	Good
4-Nitrobiphenyl	Slight/Mixed
4,4'-Methylenebis (2-chloroaniline)	Slight
Auramine	Slight
Benzidine	Good
Magenta	Slight
N-Phenyl-2-naphthylamine	Slight
N,N-Bis(2-chloroethyl)-naphthylamine	Good

Table 3.28. Relative oxidizing power of some oxidizing species (Voglpohl and Kim, 2003).

Oxidation Species	Oxidation Power
Hydroxyl radical	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.31
Permanganate	1.24
Chlorine	1.00

Table 3.29. Oxidizable compounds by hydroxyl radicals (Momani, 2003).

Group	Compounds
Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, <i>tert</i> -butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutryaldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Esters	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

3.10. Advanced Oxidation Processes

3.10.1. Mechanism of Photo Oxidation

Advanced oxidation processes have gained attention due to their efficiency and ability to treat almost all solid components in textile effluents. Photooxidation can take place at any temperature and pressure and does not produce any secondary components (Eswaramoorthi et al., 2008). Some of the most commonly used oxidants are H₂O₂, UV, O₃, TiO₂, Fe²⁺, electron beam irradiation and ultra sound (Alfons and Soo-Myung, 2003). The oxidizing potential of the most commonly used oxidants and the components that can be oxidized by hydroxyl groups are shown in Tables 3.28 and 3.29.

The basic mechanism of advanced oxidation processes is the production of OH[°] ions (Mahmoud et al., 2007; Alfons and Soo-Myung, 2003; Kdasi et al., 2004). These are strong oxidants capable of destroying components that are hard to be oxidised. Generation of OH[°] radicals are generally accelerated by the combinations of H₂O₂, UV, O₃, TiO₂, Fe²⁺, electron beam irradiation and ultra sound (Kdasi et al., 2004).

OH[°] radicals are considered as reactive electrophiles due to their preference to electrons and hence they react rapidly towards electron rich organic compounds (Stasinakis, 2008). The radicals are found to have an oxidation potential of 2.33 V and are hence found to oxidize substances more quickly than conventional oxidants (Gogate and Pandit, 2004; Stasinakis, 2008). The organic substances are first attacked by the generated hydroxyl radicals (Equation. 3.1), followed by hydrogen abstraction (Equation.3.2) and then the electron transfer (Equation.3.3) (Stasinakis, 2008).



Where:

R Reacting organic compound

Table 3.30. Advanced oxidation processes (Kdasi, et al., 2005).

Oxidants ⁺	Use
H ₂ O ₂ / Fe ²⁺	Fenton
H ₂ O ₂ / UV / Fe ²⁺	Photo assisted Fenton
O ₃ / UV	Also applicable in gas phase
O ₃ / H ₂ O ₂	Advance Oxidation
O ₃ /UV /H ₂ O ₂	Advance Oxidation
O ₃ /TiO ₂ /Electron beam irradiation	Advance Oxidation
O ₃ /TiO ₂ /H ₂ O ₂	Advance Oxidation
O ₃ + Electron beam irradiation	Advance Oxidation
O ₃ /Ultrasonic	Advance Oxidation
H ₂ O ₂ /UV	Advance Oxidation

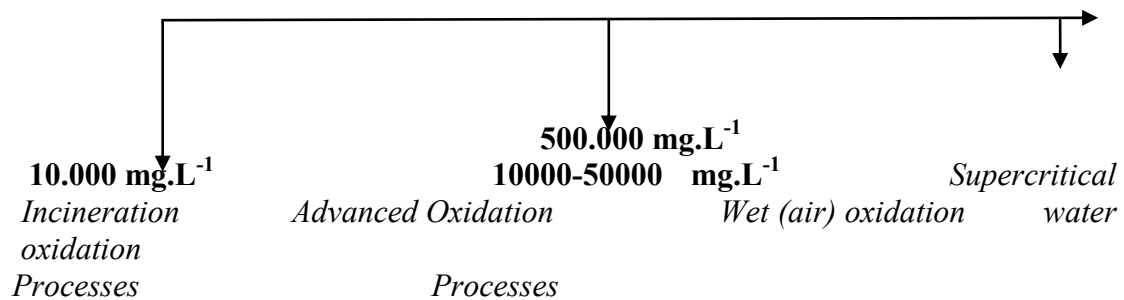


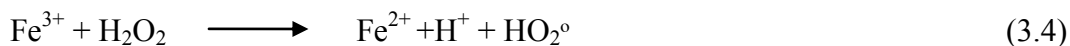
Figure 3.4. Suitability of water treatment technologies according To COD contents (Momani, 2003).

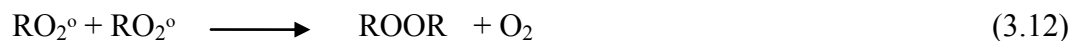
The oxidation rate depends on three main factors: (a) the concentration of the target pollutant, (b) the concentration of the radical and (c) the concentration of oxygen present in the surrounding. The maintenance of sufficient radical concentration mainly depends on the temperature, pH, the presence of ions in the solution, the presence and concentration of radical scavengers and the type of pollutant targeted (Gogate and Pandit, 2004). The combination of oxidant which gives the maximum amount of OH[°] radicals is chosen. The oxidizing reaction is a first order kinetics and has a rate constant of 10⁸-10¹⁰ M⁻¹.s⁻¹ with a hydroxyl concentration of 10⁻¹²-10⁻¹⁰ M (Momani, 2003). The type of treatment processes that is suitable is found to differ according to the amount of COD present in the effluent as shown below (Figure 3.4). Some of the different combinations of oxidants and their uses are as listed in Table 3.30

Effluents treated biologically were not found to be as efficient as those treated by advanced oxidation processes. Effluents treated biologically were found to obtain 42%, 39% and 33% COD removal when treated with *Fusarium oxysporum*, *Pleurotus ostreatus* and *Trichiderma viridae* respectively, while the effluents treated with advanced oxidation processes were found to obtain 79% COD removal (Rodriguez, 2003; Montano, 2007)

3.10.2. Treatment with H₂O₂

H₂O₂ is one of the most powerful oxidant known and is completely harmless because H₂O₂ is found to be amongst the natural metabolites of many organisms which have the ability to convert H₂O₂ into oxygen and water. H₂O₂ can be formed in nature by the action of sunlight on water and hence can be called as a natural purifier. Hydrogen peroxide as a single compound does not have the ability to split itself into hydroxyl radicals and hence is usually used in combination with ferrous salts. The reaction with ferrous salts results in the production of OH[°] which helps in the propagation of the reaction (Kos, 2002).





Where:

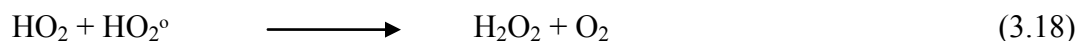
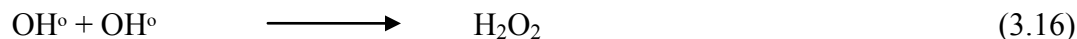
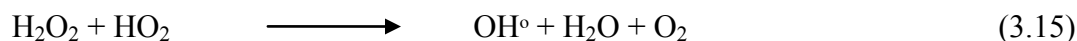
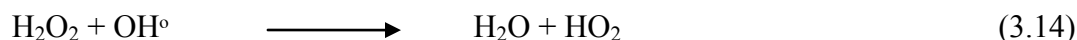
RH Organics

Equation (3.4) shows the initiation processes, which involves the reaction between the ferrous ions and hydrogen peroxide and the formation of HO_2° . Equations (3.5) and (3.6) show the chain propagation reaction by reacting with the organics present in the effluents. Equation (3.7) shows that OH° radicals are also capable of decomposing H_2O_2 resulting in the production of HO_2° radicals. Equations (3.8), (3.9) and (3.10) show that the chain propagation can be terminated by the reaction of OH° radical with the intermediates produced R° and hence resulting in the formation of H_2O_2 and O_2 , thus terminating the reaction. Equations (3.11) and (3.12) show that the chain termination can also take place by the reactions taking place between the radicals R° and RO_2° (Kos, 2002).

Hydrogen peroxide when used individually is not found to be so effective as compared to it being used under a combination of different oxidants (Goi, 2005). Alaton et al (2002) recorded that H_2O_2 when used with UV-C is found to completely decolourize the effluent containing a mixture of procion blue HERD, procion crimson HEXL, procion yellow HE4R, procion navy HEXL and procion yellow HEXL in just 10 minutes and was found to be better than O_3 when used alone. A 99% decolourization in 30 min for reactive yellow 15 dye was noted when H_2O_2 was used alongside fenton's reagent, the dye's initial adsorbance value being 2430 at 415nm (Kurbus et al., 2003). Arslan et al (1999) stated that UV catalyzed by H_2O_2 is more efficient than ozone when used alone, while $\text{H}_2\text{O}_2/\text{O}_3$ was found to be the quickest in removing colour from a dye bath which includes a mixture of seven dyes and has an absorbance of 0.47 in 40 folds at 600 nm.

3.10.3. Treatment with H₂O₂ and UV

Oxidation of textile effluent using H₂O₂ alone as known is not found to be effective on both, acids and alkalis (Kdasi et al., 2004). The combination of H₂O₂/UV is found to be very effective in the degradation of organic compounds. Wang et al. (2002) recorded that H₂O₂/UV treatment is capable of destroying the chromophore structure of azo dyes and that UV irradiation in the presence of H₂O₂ resulted in the complete decolourization of sulphonated azo and anthraquinone dyes. The production of OH° radicals in the H₂O₂/UV processes is as follows.



Equation (3.13) shows the chain initiation processes as the hydrogen peroxide present in the effluent is split into two OH° radicals. Equations (3.14) and (3.15) show the reaction between the OH° radicals formed and the hydrogen peroxide present in the system which results in chain propagation. Equations (3.16), (3.17) and (3.18) show the chain termination mechanism (Masupha, 2007).

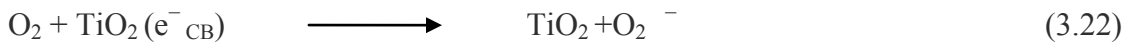
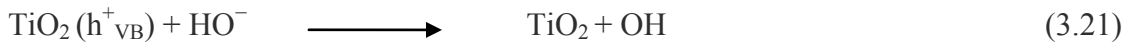
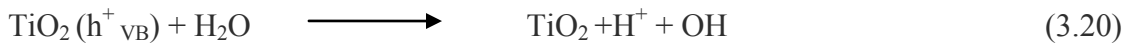
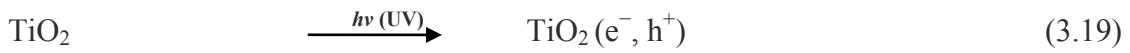
The decolourization efficiencies of the combination are found to increase as the concentration of H₂O₂ increases in the effluent (Amin et al., 2008). Kdasi et al. (2004) found that 99.9% decolourization of remazol brilliant blue dye was obtained when a H₂O₂ concentration of 12.5 mL L⁻¹ was used and temperature did not play any significant role in the removal of colour. Mahmoud et al, (2007) stated that excess concentration of H₂O₂ added to the effluent was not found to cause problems due to their property to react with the OH° radicals resulting in the formation of H₂O and O₂.

Some of the advantages of UV/H₂O₂ combination are (a) it lacks the property of developing any chemical sludge, (b) it is effective in the removal of phenolic compounds

(Stasinakis, 2008), chlorinated compounds and chlorophenols (Munter, 2001) from effluents (c) UV acts as a disinfectant and (d) it is effective in removal of TOC, 80-82% removal efficiency after 1-2 hours of exposure (Kdasi et al., 2004; Amin et al., 2008; Alton et al., 2002).

3.10.4. Treatment with TiO_2 and UV

Galindo et al. (1999) states that the first step of Photocatalytic degradation of the aromatic compounds results in the formation of hydroxyl derivatives, which in turn modifies the product distribution in the solution. Photocatalytic degradation is carried out by two types of oxidizing species: the hydroxyl radicals and the positive holes (Halmann et al, 1992)



Where:

$TiO_2(h^+_{VB})$ - Valence-band holes

$TiO_2(e^-_{CB})$ - Conduction-band Electrons

Oxidation of TiO_2/UV is found to have a larger advantage over H_2O_2/UV , this is because titanium dioxide is found to absorb light up to 385 nm which is greater than that absorbed by H_2O_2 (Al-Sayyed et al, 2001). Halmann et al. (1992) reported that the dye Acid Orange 5 which is normally found in effluents in concentrations of 10^{-4} to 10^{-6} M can be completely degraded using black-light mercury lamp as a UV radiation source.

Chapter 4. MATERIALS AND METHODS

4.1. Experimental Apparatus

The experiments were carried out using a custom built photo oxidation system. The system (Figure 4.1) consists of a reactive red 120 dye feeding tank, a peristaltic pump, a photo reactor and an effluent collection tank.

The dye feeding tank was a 20 cm diameter Poly Vinyl Chloride (PVC) container, with a working volume of about 12 L. The PVC container has a detachable top and a fixed bottom made out of 4 mm thick Poly Methyl Methacrylate (PMMA or PlexiglasTM). The detachable top has a 4 mm diameter opening to equalize the pressure caused by pumping out the dye from the container by allowing the air flow into the container. A 4 mm outlet port is located in the lower end of the feeding tank and connected to the feeding pump.

Masterflex precision tubing (06409-14 TYGON) was used along with a peristaltic pump (Digi-Staltic, Masterflex Model No: 7523-60, Head Model 77200-50. Barnant Company, Division of Cole Parmer Instrument.Co., Barrington, IL) to control the flow of dye solution into the reactors at required flowrates. The pump was connected to the feeding tanks and the photo reactor using tygon tubing. Masterflex precision tubing was used with pump to provide the required flow rate.

The photo reactor is shown in Figure 4.2. The outer and the inner diameters of the reactor were 61 and 55 mm, respectively. A low pressure mercury lamp, which emits UV light at 380 nm enclosed in a 21 mm diameter quartz tube, was used. The 3 mm stainless steel chamber provides a gap of 17 mm (distance between the quartz sleeve and the inner surface of the reactor casing). A coil (448 mm long and 0.85 mm thick) made out of stainless steel with an internal diameter of 21 mm and a pitch of 20 mm was used to create spiral motion of the liquid. The working volume of the reactor was 840 mL. The treated effluent was collected using another 20 mm diameter PVC container with a working volume of 12 L. The PVC container had a detachable top and a fixed bottom made out of 4 mm thick Poly Methyl Methacrylate (PMMA or PlexiglasTM).

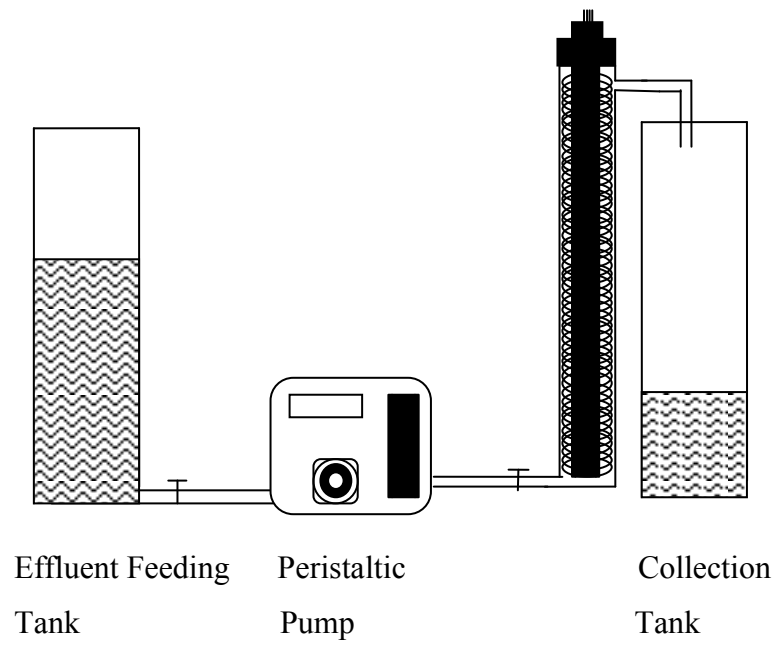
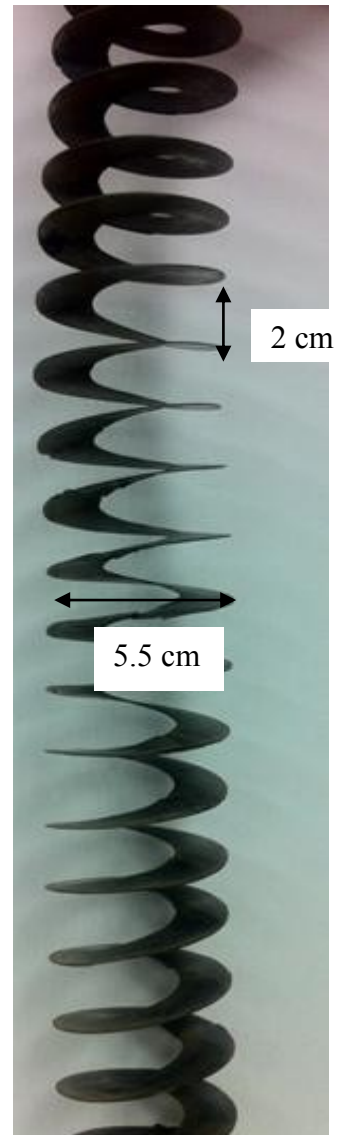


Figure 4.1. A Model of the synthetic dye wastewater feeding and effluent collection system.



(a) Reactor



(b) Stainless steel coil

Figure 4.2. Photo oxidation system

4.2. Chemicals

The chemicals used in this study are reactive red 120 Dye (HE3B), Hydrogen peroxide (H_2O_2 , 30%), tetrabutylorthotitanate ($Ti(OBu)_4$), diethanolamine ($NH(C_2H_4OH)_2$), anhydrous ethyl alcohol, sodium hydroxide (NaOH) and hydrochloric acid (HCl). The reactive red 120 dye was obtained from Sigma Aldrich (R0378-50G, CAS# 61951-82-4, Sigma-Aldrich Inc., St-Louis, MO, USA). Hydrogen peroxide and Tetrabutylorthotitanate (Titanium (IV) butoxide) were obtained from Fisher Scientific (Ca #H-325-500 and CAS # 5593-70-4 respectively, Fisher scientific, Montreal, Quebec, Canada).

4.3. Dye Preparation

Reactive red 120 (or Red HE3B) comes under the class of dye known as recalcitrant due to the sulphonic group attached on to it. This is one of the most commonly used cotton dyes, but it poses a potential threat to aquatic system because of its poor biodegradability. These dyes are non-volatile, thermally unstable and are used in an alkaline pH of 10-11. The structural formula can also be explained as 4,4'-[1,4 – phenylenebis [imino (6-chloro-1,3,5-triazine-4,2-diyle) imino]] bis [5-hydroxy-6-[(2-sulphophenyl) azo]naphthalene-2,7-disulphonic acid (An et al., 2007). The properties of the dye are listed in Table 4.1. The molecular structure of the dye is shown in Figure 4.3.

The desired concentration (50-500 mg/L) of the Reactive dye 120 was weighed using a digital balance (Model No: PI 314, Denver Instruments, Bohemia, New York, USA) and dissolved in the required amount of water. A good stirring was given to the mixture using a magnetic stirrer (Model No: 120S, Fisher Scientific, Ottawa, Ontario, Canada) to ensure that the dye was dissolved completely. The resulting dye solution had a neutral pH and the pH was, therefore, adjusted to 10-11 (as that of the textile effluent) using a pH meter (UB-10 Denver Instruments, Bohemia, New York, USA).

Table 4.1. Properties of reactive red 120 (Red HE3B) (Vinitnantharat et al., 2003).

Properties	Value
Chemical formula	$C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$
Molecular weight	1338.09
Molar Mass	1470
Charge	Negative
Functional group	Diazo
Colour	Bright red
λ_{max} (nm)	511

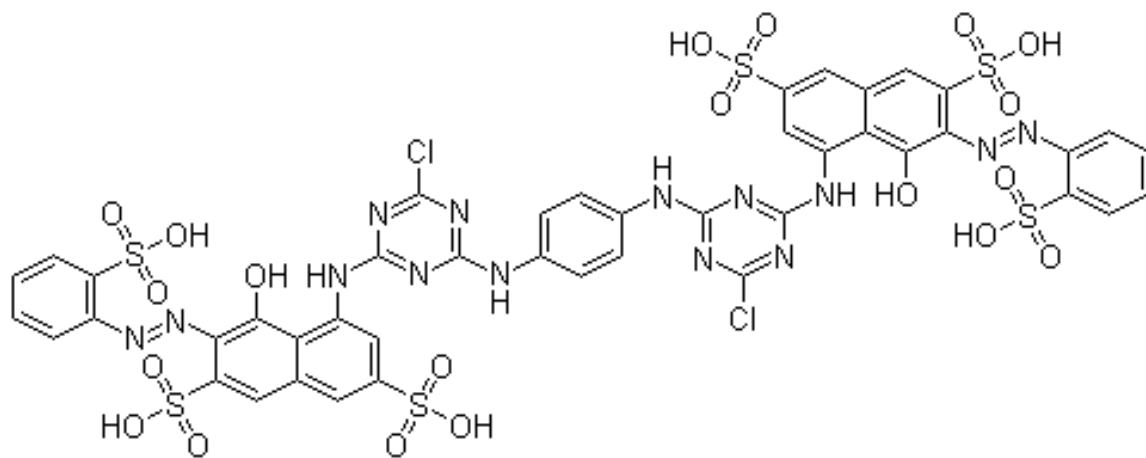


Figure 4.3. Reactive red 120 (Red HE3B).

4.4. Standard Curve

A standard curve was developed and plotted by measuring the optical density of the dye concentrations as shown in Figure 4.4. Table 4.2 represents the values of the optical density obtained from the different concentrations.

4.5. Experimental Design

Experiments were carried out to investigate the degradation efficiency of the oxidants UV, H₂O₂ and TiO₂ in different combinations of UV, UV/ H₂O₂ and UV/TiO₂. Different concentrations of the dye solution (50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mg/L) were tested with the different combinations of the oxidants under 12 different retention times. Figure 4.5 shows the experimental layout. The dye solution retention time inside the reactor is based on the flow rate set on the peristaltic pump as shown in the Table 4.3.

The retention time of the dye inside the reactor is based on the flow rate set on the peristaltic pump. The flow rate is calculated using the following formula.

$$\frac{\text{Volume of the reactor}}{\text{Retention time required}} = \text{Flow rate} \quad (4.1)$$

4.6. Experimental Protocol

The first set of experiments was carried out using UV alone. The desired amount of dye was mixed in water and the pH was adjusted, the optical density of the raw feed was determined using spectrophotometer at 253 nm (DR/2500 Illuminator Model, HACH Company, Love land, Colorado, U.S.A). Then, the raw dye was fed into the reactor at a flow rate of 5.2 ml/min. The OD of the samples collected at the other end after reacting steady state was determined. The same procedure was repeated with other flow rates.

The second experiment was carried out by using TiO₂ and UV to treat the dye. TiO₂ was coated on the coil using the procedure described by Verma and Ghaly (2008). 17.2 ml of Tetrabutylorthotitanate and 4.8 ml of diethanolamine were dissolved in 67.28 ml of

Table 4.2. Concentrations and the corresponding optical density at 535 nm.

Concentration (mg/L)	OD
50	0.042
100	0.091
150	0.143
200	0.193
250	0.244
300	0.295
350	0.346
400	0.398
450	0.445
500	0.488

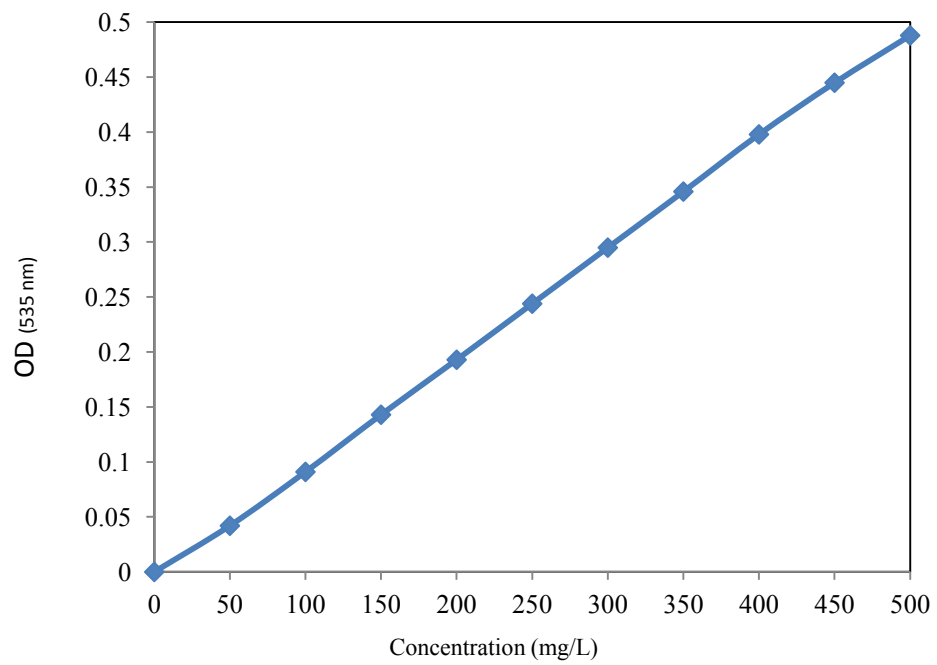


Figure 4.4. Standard graph.

Table 4.3. Flow rate and the corresponding retention time.

Flow rate (ml/min)	Retention Time (min)
160	05.25
84	10.00
56	15.00
42	20.00
33	25.45
28	30.00
24	35.00
21	40.00
18	46.66
17	49.41
15	56.00
14	60.00

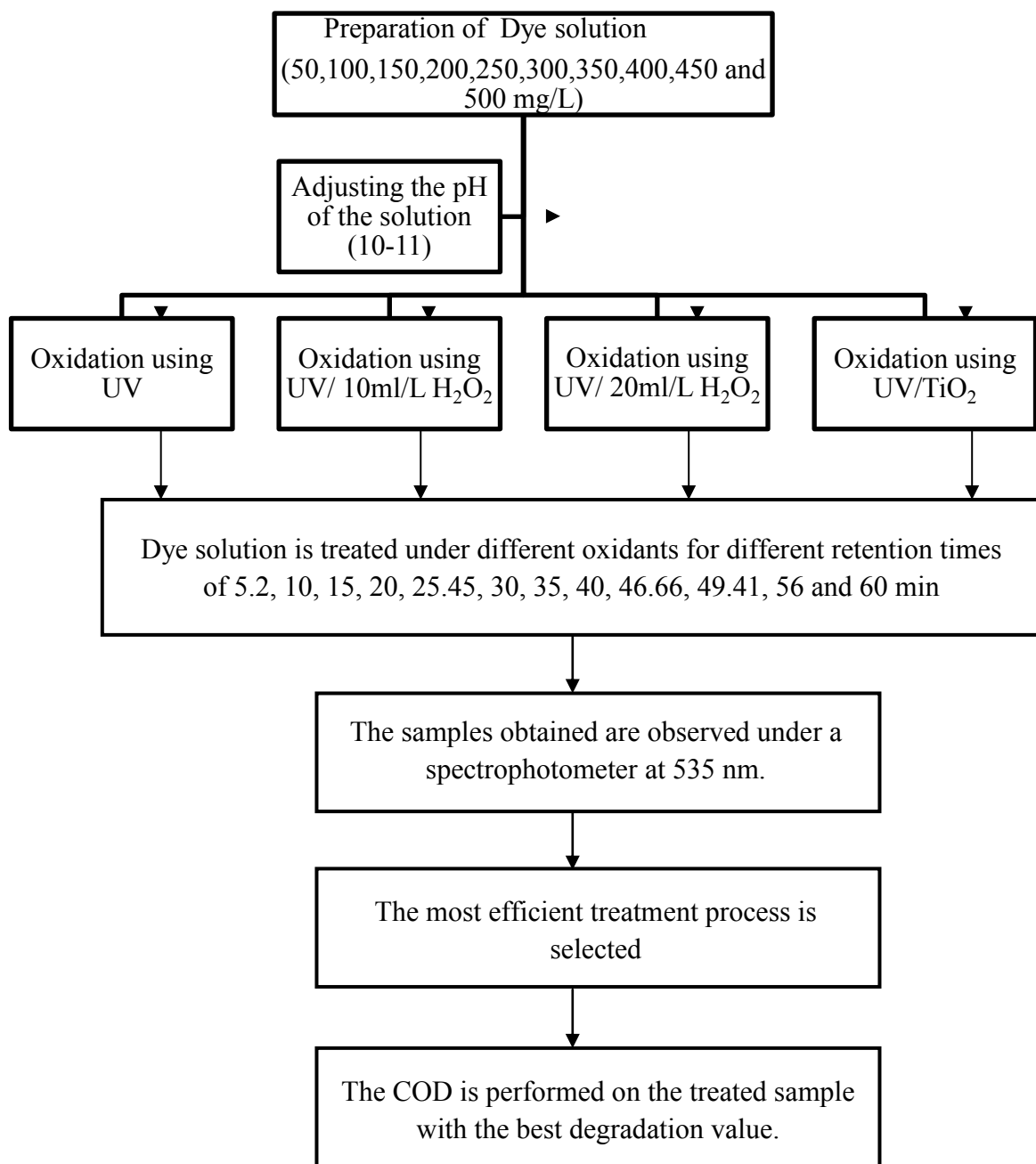


Figure 4.5. Experimental procedure.

anhydrous ethyl alcohol and mixed vigorously for 2 hour. During mixing, 2.7 ml of water and 10 ml of ethanol was mixed together and added to the mixing solution drop wise within the 2 hours of mixing. The resulting solution was left to stand for 2 hours in order for the hydrolysis to take place. The stainless steel coils were coated with TiO₂ by immersing the coils into the solution and letting it stand for 15 min. The coils were withdrawn at a rate of 6 mm/sec. The resulting TiO₂ coated coils was calcinated in a furnace (186 A, Fisher Scientific, Montreal, Quebec, Canada) at 100°C for an hour and then at 900°C for 2 hours. The resulting coil was fitted into the UV reactor. The solution was prepared by dissolving the required amount of dye in water. The solution was fed to the reactor at a rate of 5.2 ml/min. The OD of the raw dye and the samples taken at the other end were measured.

The third set of experiments was carried out using both UV and H₂O₂. The reactive dye was weighed and mixed in water. Then, H₂O₂ (10 ml/L) was mixed along with the dye in the desiered amount of water and stirred. The optical density of the raw dye was measured. The pH was adjusted and the resulting solution was fed to the reactor at a flow rate of 5.2 ml/L. The optical density of the sample at the other end was measured. The same procedure was repeated with other flow rates.

The fourth set of experiments was similar to the second set except that the amount of H₂O₂ added to the dye solution was 20 ml/L. The sample procedure was followed till all flow rates have been tested. The Chemical Oxygen Demand analysis was performed on the effluent according to the procedure described by APHA (1980).

The percentage reduction of dye after the treatment was calculated as follows.

$$\text{Reduction} = \frac{\text{Initial-Final}}{\text{Initial}} * 100 \quad (4.2)$$

Chapter 5. RESULTS

5.1. Decolourization of Reactive Red 120 Dye with UV

The dye degradation percentages for different concentrations as a result of exposure to UV are shown in Table 5.1 and Figure 5.1. When the dye solution was treated with a low pressure UV lamp (380 nm), only 27.1% of the least concentration of dye (50 mg/L) used under the maximum retention time (60 min) was degraded. Increasing the dye concentration and/or reducing the exposure time reduced the removal efficiency. Only 1.14% of the dye was removed when the lowest concentration of 50 mg/L when exposed to UV for 5.2 minutes and 0.33% of the dye was removed when the highest concentration of 500 mg/L was exposed to UV for 60 min.

Analysis of variance was performed on the data using Minitab (Quality Plaza, PA, USA) as shown in Table 5.2. Tukey's grouping was also performed on the data to test the differences among the levels of each factor as shown in Table 5.3. The analysis of variance showed that the effects of dye concentration and exposure time were significant at the 0.001 level. The interaction between the dye concentration and exposure time was also significant at the 0.001 level. The results of Tukey's grouping indicated that most of the concentrations were significantly different from one another at the 0.05 level except for the concentration 300 and 250 and 200 and 150 mg/L which were each significantly different from the other concentrations but not significantly different from each other at the 0.05 level. Similarly, most of the exposure times were significantly different from one another at the 0.05 level except for the exposure times 10 and 5.2 min which were significantly different from other exposure times but were not significantly different from each other at the 0.05 level.

5.2. Decolourization of Reactive Red 120 Dye with UV and TiO₂

The dye degradation percentages for different concentrations as a result of exposure to UV and TiO₂ are shown in Table 5.4 and Figure 5.2. A degradation efficiency of 46.70%

Table 5.1. Degradation percentage of reactive red 120 Under UV.

Time (min)	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm	500 ppm
5.2	1.14	0	0	0	0	0	0	0	0	0
10.0	3.44	0	0	0	0	0	0	0	0	0
15.0	9.77	1.09	0.57	0	0	0	0	0	0	0
20.0	11.49	4.37	2.29	1.05	0	0	0	0	0	0
25.4	14.94	5.73	2.48	2.07	0.63	0	0	0	0	0
30.0	16.66	9.01	4.01	2.20	1.74	0.83	0	0	0	0
35.0	18.39	11.47	4.58	4.51	3.01	1.91	0	0	0	0
40.0	21.83	14.75	5.73	5.41	4.44	2.50	0	0	0	0
46.6	22.41	17.48	6.88	6.57	6.19	3.34	0.19	0	0	0
49.4	24.71	18.57	7.45	7.08	6.98	5.49	1.07	0.98	0	0
56.0	25.28	19.12	8.98	7.85	8.25	6.33	1.86	1.31	0.83	0
60.0	27.01	23.49	11.28	8.23	9.36	7.40	2.94	2.51	2.01	0.33

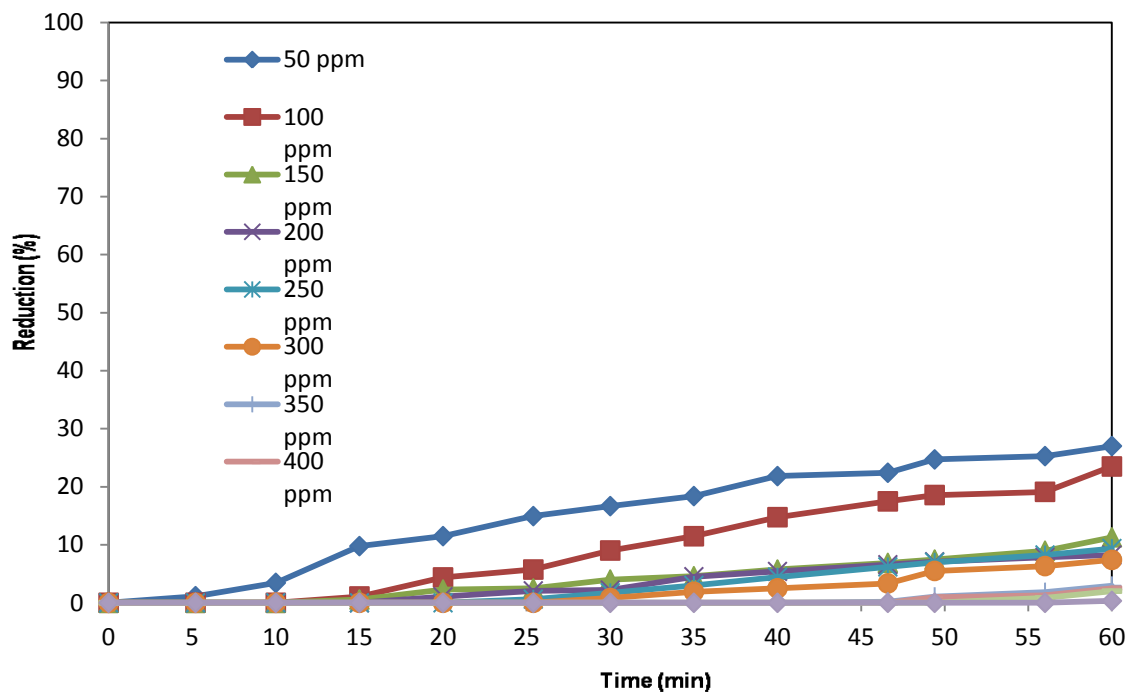


Figure 5.1.. Degradation efficiency of reactive red 120 against time when treated with UV.

Table 5.2. Analysis of variance for treatment with UV.

Source	DF	SS	MS	F	P
Total	239	180460.6			
Model					
Conc	9	21626.3	2402.9	366043.43	0.001
Time	11	63757.5	5796.1	882939.98	0.001
Conc*Time	99	95076.0	960.4	146294.73	0.001
Error	120	0.8	0.0		

DF: Degree of Freedom

SS: Sum of Square

MS: Mean of Square

$R^2 = 100\%$

Table 5.3. Results of Turkey's grouping for treatment with UV.

Factor	Level	N	Mean Reduction (%)	Grouping
Concentration (ml/L)	500	24	7.28	A
	450	24	8.92	B
	400	24	13.37	C
	350	24	14.95	D
	300	24	20.63	E
	250	24	20.73	E
	200	24	26.80	F
	150	24	27.74	F
	100	24	31.93	G
	50	24	37.53	H
Time (min)	60.0	20	54.54	A
	56.0	20	44.39	B
	49.4	20	35.57	C
	46.6	20	27.65	D
	40.0	20	20.31	E
	35.0	20	20.01	E
	30.0	20	19.71	E
	25.4	20	13.85	F
	20.0	20	8.93	G
	15.0	20	5.23	H
	10.0	20	0.86	I
	5.2	20	0.84	I

Table 5.4. Degradation percentage of reactive red 120 under UV and TiO₂.

Time (min)	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm	500 ppm
5.2	1.64	0	0	0	0	0	0	0	0	0
10.0	5.49	0.81	0	0	0	0	0	0	0	0
15.0	9.89	1.91	0.64	0.52	0	0	0	0	0	0
20.0	11.53	4.91	2.42	1.19	0	0	0	0	0	0
25.4	15.38	10.38	4.04	2.24	1.47	0	0	0	0	0
30.0	17.58	12.29	4.69	3.04	2.95	0.26	0	0	0	0
35.0	19.23	13.11	7.11	4.49	3.93	1.34	0	0	0	0
40.0	23.07	13.66	8.41	5.68	5.08	2.41	0.34	0	0	0
46.6	24.72	16.39	10.35	7.80	7.37	3.62	1.53	0	0	0
49.4	32.41	19.94	11.48	8.73	8.36	4.56	2.90	1.63	0.48	0
56.0	35.71	22.95	13.75	10.05	9.67	6.85	5.29	2.83	1.77	0.89
60.0	46.70	24.59	15.85	10.84	10.32	8.06	7.52	4.17	3.70	2.84

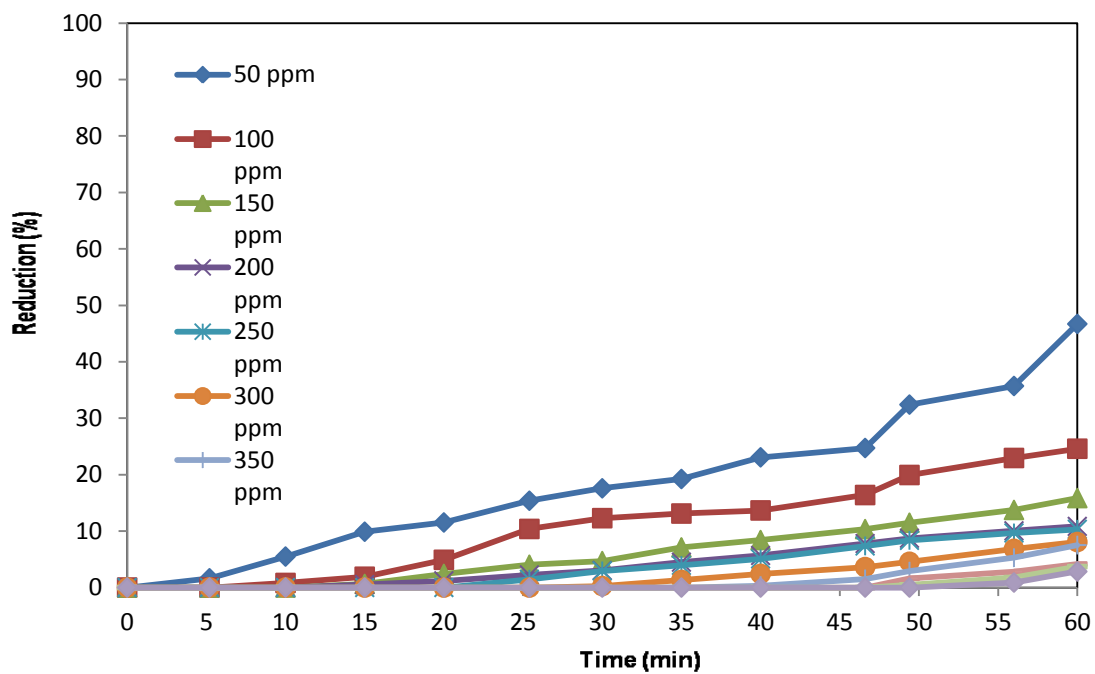


Figure 5.2. Degradation efficiency of reactive red 120 against time when treated with UV and TiO₂.

was observed for the minimum dye concentration (50 mg/L) when exposed to UV and TiO₂ for the maximum exposure time of 60 min. When the highest dye concentration (500 mg/L) was exposed to UV and TiO₂ for time 60 min, only 2.84% reduction in the dye concentration was detected in the samples. Also a degradation efficiency of 1.64% was achieved with the dye concentration of 50 mg/L when exposed to UV and TiO₂ for the minimum time of 5.2 min, while 0% reduction was observed for the dye concentration of 500 mg/L when exposed to UV and TiO₂ for the same time limit (5.2 min).

An analysis of variance was performed on the data using Minitab (Quality Plaza, PA, USA) as shown in Table 5.5. Tukey's grouping was also performed on the levels of each parameter as shown in Table 5.6. The effects of exposure time and dye concentration were significant at the 0.001 level. The interaction between the dye concentration and exposure time was significant at the 0.001 level. The results of Tukey's grouping (Table 5.6) showed that all the concentration levels were significantly different from each other at the 0.05 level. Similarly, all the exposure times were also significantly different from each other at the 0.05 level.

5.3. Decolourization of Reactive Red 120 Dye with UV and 10 ml H₂O₂.

The dye degradation results obtained with UV and 10 ml H₂O₂ are shown in Table 5.7 and Figure 5.3. The dye degradation percentage obtained in this set of experiment was found to be higher than the degradation percentage obtained using only UV and UV/TiO₂. For the least dye concentration (50 mg/L), a degradation efficiency of 93.62% was observed when the dye was exposed to UV and 10 ml H₂O₂ for the minimum time of 5.2 min and a maximum degradation of 99.83% was obtained at 25.4 min. For the highest dye concentration (500 mg/L), a degradation efficiency of 20.46% was observed after 5.2 min and a maximum degradation efficiency of 99.70% was obtained after 60 min.

The results of the analysis of variance performed on data using Minitab (Quality Plaza, PA, USA) is shown in Table 5.8. The Analysis of variance showed that the effects of dye concentration and exposure time were significant at the 0.001 level. The interaction

Table 5.5. Analysis of variance for treatment with UV and TiO₂.

Source	DF	SS	MS	F	P
Total	239	282177.4			
Model					
Conc	9	23339.6	2593.3	587381.02	0.001
Time	11	92381.1	8398.3	1902215.19	0.001
Conc*Time	99	166456.2	1681.4	380832.50	0.001
Error	120	0.5	0.0		

DF: Degree of Freedom

SS: Sequential Sum of Square

MS: Adjusted Mean of Square

R² = 100%

Table 5.6. Results of Turkey's grouping for treatment with UV and TiO₂.

Factors	Level	N	Mean Reduction (%)	Grouping
Concentration (ml/L)	500	24	41.77	A
	450	24	38.21	B
	400	24	31.81	B
	350	24	29.80	C
	300	24	24.45	D
	250	24	23.75	E
	200	24	22.80	F
	150	24	20.44	G
	100	24	14.64	H
	50	24	7.26	I
Time (min)	60.0	20	65.03	A
	56.0	20	63.96	B
	49.4	20	40.15	C
	46.6	20	22.35	D
	40.0	20	22.02	D
	35.0	20	21.75	D
	30.0	20	21.30	D
	25.4	20	15.07	E
	20.0	20	12.84	F
	15.0	20	9.46	G
	10.0	20	9.31	G
	5.2	20	2.68	H

Table 5.7. Degradation percentage of reactive red 120 Under UV and 10ml H₂O₂.

Time (min)	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm	500 ppm
5.2	93.62	92.67	51.51	48.51	48.19	45.07	33.33	24.57	23.21	20.46
10.0	96.85	95.37	69.18	65.37	59.62	55.74	52.29	36.15	31.72	30.59
15.0	97.74	97.55	97.48	82.17	79.38	69.70	64.59	48.24	44.32	40.29
20.0	99.59	99.30	98.89	89.29	88.04	83.43	70.81	56.82	50.63	41.68
25.4	99.83	99.72	99.68	89.40	87.87	86.60	76.88	59.29	57.98	47.97
30.0		99.89	99.91	99.51	98.96	98.62	79.25	63.84	62.28	53.51
35.0			99.97	99.74	99.61	99.53	98.6	77.76	75.94	59.06
40.0				99.97	99.86	99.80	99.51	99.28	84.97	64.60
46.6					99.98	99.96	99.78	99.64	99.35	84.75
49.4							99.94	99.76	99.43	89.12
56.0								99.94	99.86	99.44
60.0								99.96	99.92	99.70

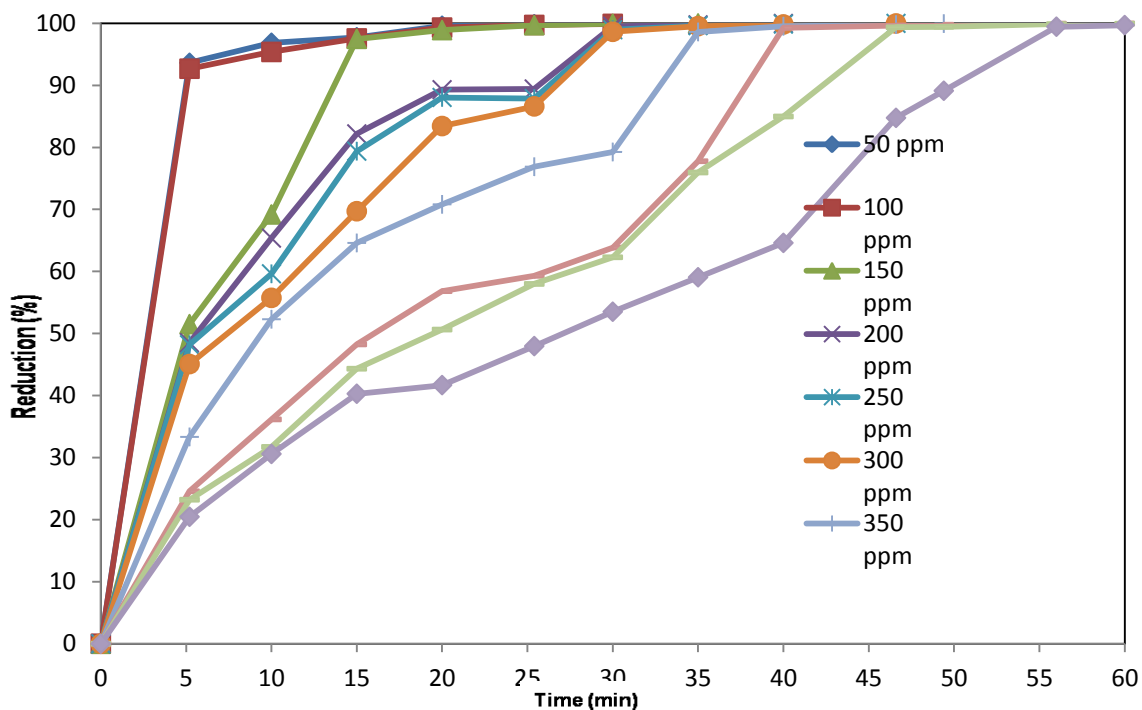


Figure 5.3. Degradation efficiency of reactive red 120 against time when treated with UV and 10 ml H₂O₂.

Table 5.8. Analysis of variance for treatment with UV and 10 ml H₂O₂.

Source	DF	SS	MS	F	P
Total	239	57964.13			
Model					
Conc	9	22648.99	2516.55	5954.46	0.001
Time	11	21014.71	1910.43	4520.30	0.001
Conc*Time	99	14249.71	143.94	340.57	0.001
Error	120	50.72	0.42		

DF: Degree of Freedom

SS: Sequential Sum of Square

MS: Adjusted Mean of Square

R² = 99.91%

between the dye concentration and exposure time was highly significant at the 0.001 level. The results obtained from Tukey's grouping (Table 5.9) showed that most of the concentrations were significantly different from each other at the 0.05 except for the concentrations 500 and 400 mg/L which were not significantly different from each other but were significantly different from other concentrations at the 0.05 level. Also, most of the exposure times were significantly different from each other except the exposure times 15, 10 and 5.2 min which were not significantly different from each other but were significantly different from the other exposure times at the 0.05 level.

5.4. Decolourization of Reactive Red 120 Dye with UV and 20 ml H₂O₂

The results obtained with UV and 20 ml H₂O₂ treatment are shown in Table 5.10 and Figure 5.4. The dye degradation percentages when the dye was treated with UV and 20 ml/L H₂O₂ was higher than that observed when using UV, UV/TiO₂ with 10 ml/L H₂O₂. When the dye with minimum concentration (50 mg/L) was exposed to UV and 20 ml H₂O₂ for the minimum time of 5.2 min., 94.2% of the dye was degraded. A maximum degradation efficiency of 99.96% was obtained after an exposure time of 20 min. For the highest dye concentration (500 mg/L), a degradation efficiency of 23.33% was observed with exposure time of 5.2 min and 99.95% degradation efficiency was obtained after 60 min.

The Analysis of variance was performed on the data using Minitab (Quality Plaza, PA, USA) as shown in Table 5.11. The Analysis of variance results showed that the effects of exposure time and dye concentration were significant at the 0.001 level. The interaction between the dye concentration and exposure time was highly significant at the 0.001 level. The Tukey's grouping results (Table 5.12) showed that all concentrations were significantly different from each other at the 0.05 level. Also, most of the exposure times were significantly different from each other at the 0.05 level except for the exposure times 35, 30, 25.4, 20, 15, 10 and 5.2 min which were not significantly different from each other but were significantly different from other exposure times at the 0.05 level.

Table 5.9. Results of Turkey's grouping for treatment with UV and 10 ml H₂O₂.

Factors	Level	N	Mean Reduction (%)	Grouping
Concentration (ml/L)	500	24	0.03	A
	450	24	0.26	A
	400	24	1.85	B
	350	24	3.32	C
	300	24	4.43	D
	250	24	9.92	E
	200	24	10.14	E
	150	24	17.18	F
	100	24	23.51	G
	50	24	29.32	H
Time (min)	60.0	20	29.32	A
	56.0	20	23.36	B
	49.4	20	18.04	C
	46.6	20	14.43	D
	40.0	20	12.42	E
	35.0	20	9.88	F
	30.0	20	6.41	G
	25.4	20	3.89	H
	20.0	20	1.23	I
	15.0	20	0.88	J
	10.0	20	0.06	J
	5.2	20	0.03	J

Table 5.10. Percentage degradation of reactive red 120 under UV and 20ml H₂O₂.

Time (min)	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm	500 ppm
5.2	94.20	55.66	52.11	51.98	50.72	46.80	40.49	34.90	26.66	23.33
10.0	98.51	88.02	70.42	66.42	62.80	56.59	52.81	47.71	41.89	39.43
15.0	99.62	99.54	99.48	92.62	79.46	70.21	68.48	65.09	55.35	52.39
20.0	99.96	99.94	99.69	99.49	98.85	90.85	87.85	75.84	68.81	62.77
25.4		99.97	99.92	99.82	99.55	99.30	98.83	85.71	81.04	70.12
30.0			99.97	99.91	99.80	99.64	99.14	89.54	87.50	79.34
35.0				99.95	99.94	99.69	99.69	99.55	99.41	99.26
40.0					99.98	99.94	99.90	99.86	99.63	99.62
46.6						99.98	99.96	99.91	99.82	99.77
49.4								99.96	99.91	99.89
56.0								99.97	99.96	99.90
60.0										99.95

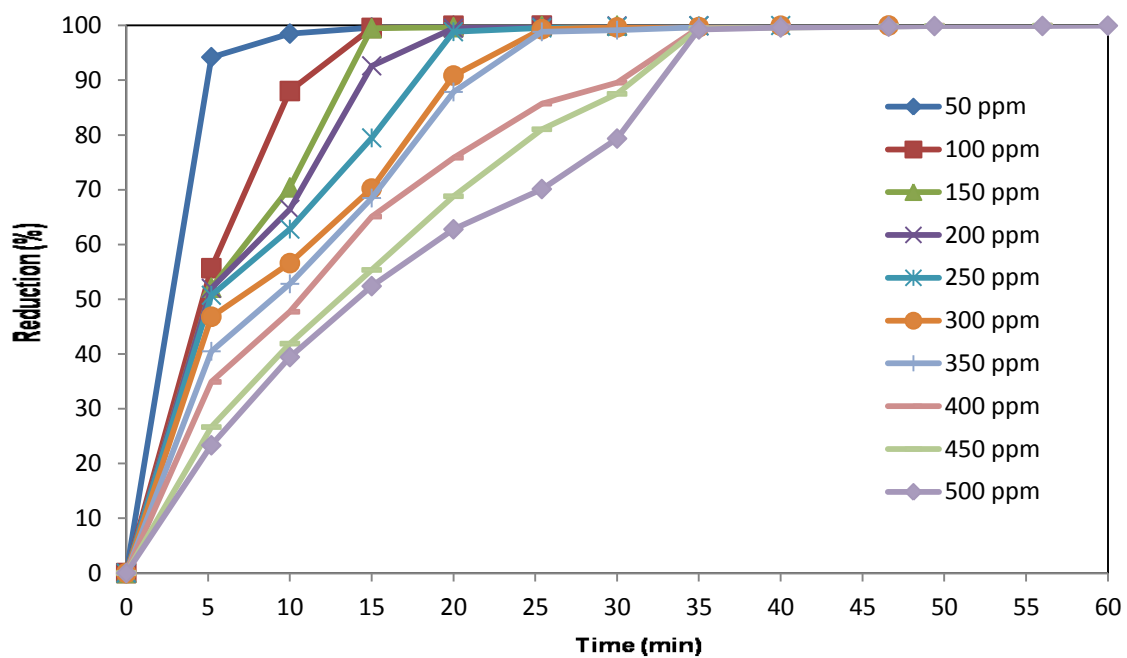


Figure 5.4. Degradation efficiency of reactive red 120 against time when treated with UV and 20 ml H₂O₂.

Table 5.11. Analysis of variance for treatment with UV and 20 ml H₂O₂.

Source	DF	SS	MS	F	P
Total	239	95269.85			
Model					
Conc	9	21359.52	2373.28	1347194.82	0.001
Time	11	43893.47	3990.32	2265106.32	0.001
Conc*Time	99	30016.65	303.20	172110.90	0.001
Error	120	0.21	0.00		

DF: Degree of Freedom

SS: Sequential Sum of Square

MS: Adjusted Mean of Square

R² = 100%

Table 5.12. Results of Turkey's grouping for treatment with UV and 20 ml H₂O₂.

Factors	Level	N	Mean Reduction (%)	Grouping
Concentration (ml/L)	500	24	0.05	A
	450	24	1.05	B
	400	24	1.86	C
	350	24	2.90	D
	300	24	5.65	E
	250	24	8.05	F
	200	24	11.81	G
	150	24	17.16	H
	100	24	21.85	I
	50	24	29.41	J
Time (min)	60.0	20	40.73	A
	56.0	20	32.59	B
	49.4	20	20.72	C
	46.6	20	12.45	D
	40.0	20	7.57	E
	35.0	20	5.21	F
	30.0	20	0.24	G
	25.4	20	0.12	G
	20.0	20	0.06	G
	15.0	20	0.03	G
	10.0	20	0.02	G
	5.2	20	0.01	G

Table 5.13. Maximum removal efficiency for various treatments.

Treatment	Dye Concentration (mg/L)	Time (min)	Maximum Removal Efficiency (%)
UV	50	60	27.01
	500	60	0.33
UV/TiO ₂	50	60	46.70
	500	60	2.84
UV/10 ml H ₂ O ₂	50	25	99.83
	500	60	99.70
UV/20 ml H ₂ O ₂	50	20	99.96

5.5. Comparative Analysis

Table 5.13 shows us the comparative analysis of the percentage of maximal removal efficiency under each oxidation mechanism from which it could be seen that UV used with 20 ml H₂O₂ provides the maximum decolourisation for the inspected time limit.

5.6. Analysis of Chemical Oxygen Demand

It appears from the results that the UV with 20 ml of H₂O₂ provided the best decolourisation. However, the amount of chemicals in the treated water was determined by performing the Chemical Oxygen Demand (COD) in order to evaluate the level of pollution in wastewater before disposal in the environment. The results obtained from COD analysis are listed in Table 5.14. Figure 5.5 shows the COD pattern in the treated water over time. The results showed that the highest COD concentration (704-1184 mg/L depending on the dye concentration) was observed at 5 minutes from the start and the COD decreased (256-416 mg/L depending on the dye concentration and exposure time) as the contact time increased. Hence, it could be concluded that a complete degradation of chemicals could be achieved if the treated samples were exposed to UV and 20 ml H₂O₂ for longer time periods.

Analysis of variance was performed on the COD data using Minitab (Quality Plaza, PA, USA) as shown in Table 5.15. Tukey's grouping was also performed on the data to test the differences among the levels of each factor as shown in Table 5.16. The results of the analysis of variance showed that the effect of dye concentration and time of exposure were significant at the 0.001 level. The interaction between the dye concentration and exposure time was also found to be significant at the 0.001 level. The results of Tukey's grouping indicated that all the dye concentrations were significantly different from each other at the 0.05 level. Similarly, all the exposure times were significantly different from each other at the 0.05 level.

Table 5.14. Chemical oxygen demand (mg/L) after treatment with UV and 20 ml H₂O₂.

Time (min)	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm	500 ppm
5.2	704	832	864	864	928	1024	1088	1152	1152	1184
10.0	608	672	736	800	832	896	928	1056	1088	1120
15.0	512	512	608	704	672	736	800	832	1024	1056
20.0	416	384	448	544	576	672	704	800	800	864
24.4		288	384	416	480	608	640	736	704	768
30.0			224	352	416	512	544	640	672	704
35.0				256	320	448	416	512	576	640
40.0					224	288	320	448	480	544
46.6						192	224	384	416	448
49.4								288	352	416
56.0								256	224	320
60.0										256

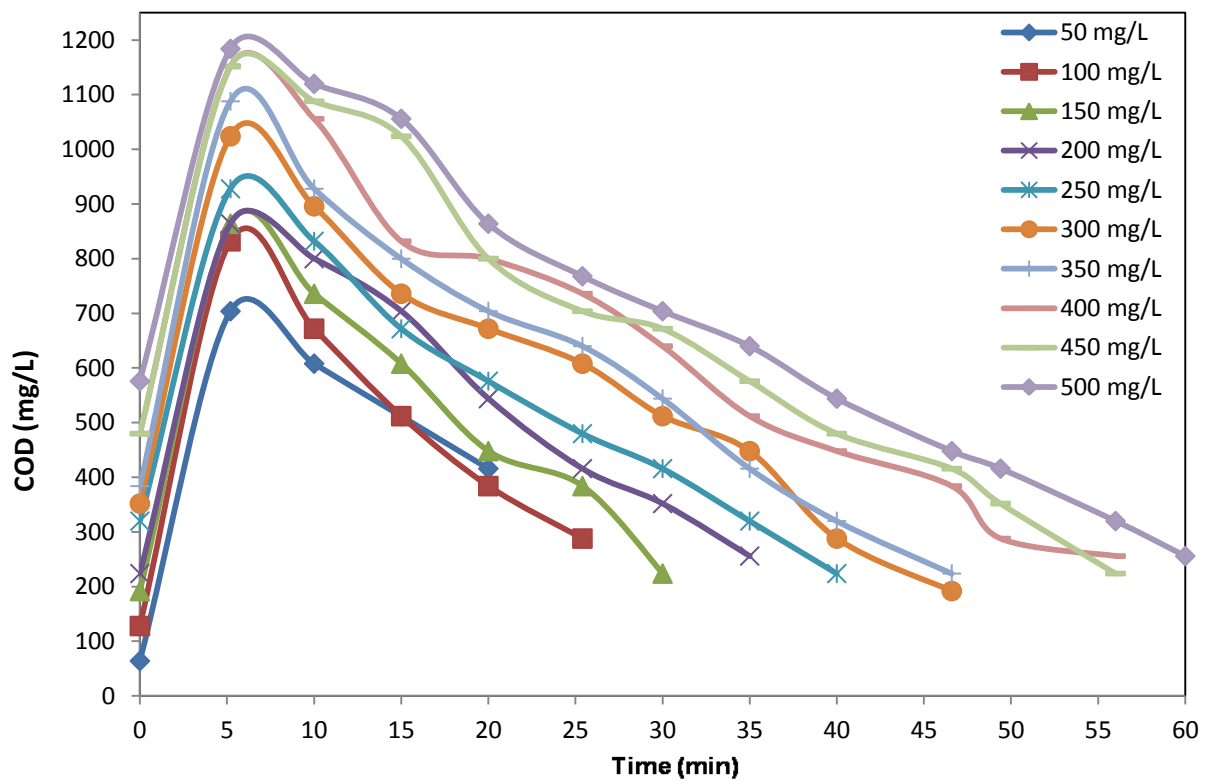


Figure 5.5. The chemical oxygen demand after treatment with UV/20 ml/L H₂O₂.

Table 5.15. Analysis of variance for COD of the effluent from the treatment with UV and 20 ml H₂O₂.

Source	DF	SS	MS	F	P
Total	239	31077356			
Model					
Conc	9	6605020	733891	292095.98	0.001
Time	11	23027503	2093409	833197.74	0.001
Conc*Time	99	1444532	14591	5807.46	0.001
Error	120	302	3		

DF: Degree of Freedom

SS: Sequential Sum of Square

MS: Adjusted Mean of Square

R² = 100%

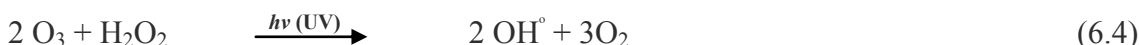
Table 5.16. Results of Tukey's grouping for the COD of effluent from the treatment with UV and 20 ml H₂O₂.

Factors	Level	N	Mean Reduction (%)	Grouping
Concentration (ml/L)	500	24	693.29	A
	450	24	623.88	B
	400	24	591.71	C
	350	24	472.71	D
	300	24	447.46	E
	250	24	370.67	F
	200	24	327.67	G
	150	24	271.83	H
	100	24	223.75	I
	50	24	186.50	J
Time (min)	60.0	20	979.10	A
	56.0	20	873.20	B
	49.4	20	745.10	C
	46.6	20	620.55	D
	40.0	20	501.85	E
	35.0	20	406.25	F
	30.0	20	316.65	G
	25.4	20	230.20	H
	20.0	20	167.35	I
	15.0	20	105.60	J
	10.0	20	79.90	K
	5.2	20	25.60	L

Chapter 6. DISCUSSION

6.1. Advanced oxidation using UV

The decomposition of textile effluent when exposed to UV could be explained by the following reactions (SET, 2012, EPA US, 2012).



Equation 6.1 shows the production of atomic oxygen radicals, which in turn reacts with other oxygen molecules resulting in the production of ozone as shown in Equation 6.2. Equation 6.3 shows the reaction between ozone and water that results in the production of hydrogen peroxide. Equation 6.4 shows the production of hydroxyl radicals which helps in the destruction of dye molecules. Kesselman et al, (1996) stated that the ozone and the hydrogen peroxide produced in Equations 6.2 and 6.3 are found to be very minimal and short lived, hence they are not that effective in degradation of the dye (Kesselman et al, 1996)

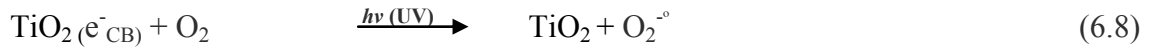
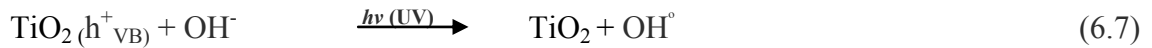
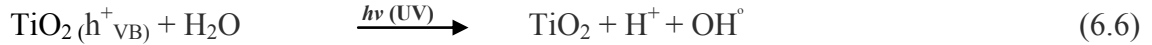
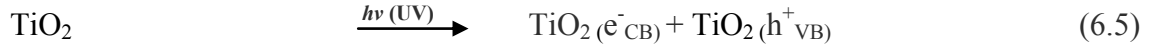
The maximum degradation achieved when 50 mg/L dye was exposed 60 min of UV was 27.01%, while the maximum degradation achieved when 500 mg/L was exposed to UV for 60 min was 0.33%. The results showed that as the dye concentration increased the dye removal efficiency decreased. No reduction in the dye concentration was witnessed after 56 min when 500 mg/L was exposed to the UV. The very low removal efficiency is due to the low quantity of hydroxyl radicals produced and/or the very short life span of ozone and hydrogen peroxide produced as reported by Kesselman et al. (1996).

Georgiou et al. (2002) observed no colour reduction when the dye effluent was treated with just UV. Ince and Gonenc (1997) reported that when an azo dye concentration of 40

mg/L was exposed to UV in the photo reactor no significant decomposition was observed. Malik and Sanyal (2004) noted that the degradation rates of the dye when using just UV even under a lower pH was much slower when compared to using UV in a combination with other oxidants. Galindo et al (1999) stated that the disappearance of dye molecules when used with UV (in the absence of oxidants) was negligible. Ozkan et al (2004) tested the effects of UV on the degradation of azo dyes and noted that when UV was used alone it did not give any colour reduction in at pHs 7 and 11, while when used in a combination with other oxidants it resulted in a 92% decomposition rate. Mahmoud et al. (2007) reported that two UV reactors fed remazol dye solution at 25° C and 100° C achieved a maximum degradation of 12.3%, proving that the temperature had no effect on degradation of dye.

6.2. Oxidation using UV and TiO₂

Tang and An (1995) and Tang et al (2010) proposed a mechanism for the degradation of textile dyes with UV and TiO₂.



Where:

TiO₂(h⁺_{VB}) - Valence-band holes

TiO₂(e⁻_{CB}) - Conduction-band Electrons

Upon irradiation by UV, the electrons on the surface of the semiconductor gets excited to the conduction band forming positive holes in the valance band (Equation 6.5). The valance band holes thus formed are good oxidizers; they have the potential to oxidise

water or OH ions in to OH radicals as shown in Equations 6.6 and 6.7. The conduction band electrons on the other hand act as reducers (Equation 6.8). Chain termination would occur as shown in Equations 6.9, 6.10, 6.11 and 6.12. Ehrampoush Et al (2010) registered that there was no significant reduction in COD values when the dye solutions were exposed to TiO₂/UV.

A maximum degradation of 46.7% was observed when 50 mg/L dye concentration was treated with UV/TiO₂ for 60 min. When the 500 mg/L dye concentration was treated with UV/TiO₂, the maximum reduction observed after 60 min was 2.84%. Kusvuran et al, (2004) reported that a 40% degradation of 40 mg/L reactive red 120 dye was observed when the textile effluent was exposed to UV/TiO₂ for 30 min and 90% degradation was achieved when the pH of the solution was reduced to 3. Kavitha and Palanisamy (2010) stated that only a slight degradation was observed when azo dyes were exposed to UV/TiO₂ for 30 min and that may be due to the absorption of dye molecules onto the surface of TiO₂. They also noted that an azo dye degradation of 84% could be obtained when the dye was exposed for 120 min. Verma and Ghaly. (2008) reported only a 12.5% remazol dye removal after exposing the effluent to the combination of UV/TiO₂ for 84 min. Sohrabi and Ghavami (2008) noted that 83.58% of direct dyes was degraded when the solution was exposed for 140 min.

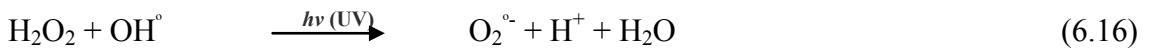
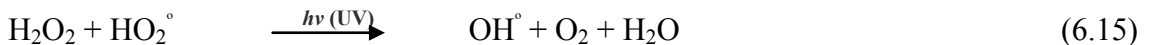
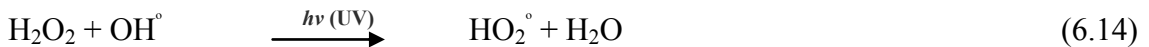
6.3. Oxidation using UV and H₂O₂

El-Dein et al (2003) and Daneshvar et al (2005) proposed a mechanism for the decolourization of reactive dyes with the H₂O₂/UV process

Initiation



Hydroxyl radical propagation and termination





Equation 6.13 shows the initiation reaction between UV and H₂O₂ leading to the production of hydroxyl radicals. Equations 6.14, 6.15, 6.16 and 6.17 shows the propagation of the reaction involving the production of hydroxyl radicals and its reactions on H₂O₂ leading to the further production of hydroxyl radicals which helps in the reduction of dye molecules. Equations 6.18, 6.19 and 6.20 show the termination of the reactions which result in the formation of End Product.

When reactive red 120 dye solution was treated with UV and 10/L ml H₂O₂, a complete degradation was observed for all the concentrations. The time required for complete degradation depended on the initial dye concentration. From the results, 99.83% degradation was achieved for the 50 mg/L dye concentration after 25.4 min when treated with UV/10 ml/L H₂O₂. When UV/20 ml/L H₂O₂ was used for the same dye concentration, 99.96% degradation was achieved after 20 min. When the 500 mg/L dye concentration was treated with to UV/10 ml/L H₂O₂, a degradation of 99.70% was obtained after 60 min. 99.95% degradation was achieved when the same dye concentration was treated with UV/20 ml/L H₂O₂ for 60 min.

Crittenden et al. (1999) stated that when H₂O₂ is exposed to UV, it splits to form two hydroxyl radicals which in turn react with the organics in the solution. Kdasi et al. (2004) stated that oxidation with UV/H₂O₂ was more effective than with H₂O₂ alone. Kurbus et al. (2003) noted that the decolourisation time required for H₂O₂/UV process was lesser than the time required for H₂O₂/O₃. Galindo and Kalt (1999) noted that the action of UV alone or H₂O₂ alone on the azo dyes were found to be ineffective (as more than 99% of dye remained in the system after treatment for 120 min) but when the same sample was treated with a combination of UV/H₂O₂, a dramatic increase in the degradation of the dye was observed.

Georgiou et al. (2002) reported that more than 50% degradation was obtained within 20 min for 100 mg/L reactive dyes. Percowski and Kos (2003) reported that 99% degradation of the effluents from a dye house was achieved after 2 hours. Fang et al. (1999) reported that the amount of colour removal was found to be advantageous as the reaction time increased. Yang et al. (1998) reported that a 95% colour removal was achieved on some reactive, acid, direct and basic dyes when used with H₂O₂/UV. Verma and Ghaly (2008) reported a 99.9% degradation of 300 mg/L ramazol dye when treated with UV/H₂O₂ at a residence time of 42 min, which was a much greater degradation than those obtained with just UV or just H₂O₂. Shu and Chang (2005) compared the decolourization effects of six different azo dyes and determined that more than 95% degradation was achieved when treated with UV/H₂O₂ in less than 11.5 min, which was higher than the degradation rate achieved with UV/O₃ for the same time period.

From the results obtained it was witnessed that the degradation percentage of reactive red 120 under UV and 20 ml/L H₂O₂ was found to be slightly higher than the degradation efficiency of UV and 10 ml H₂O₂. Georgiou et al. (2002) noted that even a small amount of H₂O₂ (0.1 ml/L) was found to completely destruct colour in less than an hour and if the peroxide amount was increased the destruction time was found to decrease. Modirshala et al. (2006) reported that the improvement in decolourisation was not found to be significant above certain amount of H₂O₂ due to the recombination of hydroxyl radicals in the solution or the reaction between hydroxyl radicals and H₂O₂ creating hydroxyl radical scavenging capacity.

6.4. Comparative analysis

The treatments with UV/TiO₂ gave higher degradation rates compared to the treatments with UV alone. The maximum degradation obtained for the 50 mg/L concentration after 60 min (46.7%) was almost twice the degradation obtained with UV alone (27.01%). The maximum degradation for the 500 mg/L concentration exposed to UV without TiO₂ for 60 min was 0.33% which increased to 2.84% when exposed to UV and TiO₂ for 60 min (8.6 fold).

Treatment of the 50 mg/L dye concentration with UV/ 10 ml/L H₂O₂ provided higher degradation (99.83% after 25.4 min) than the treatments with UV (27.01% after 60 min) and UV/TiO₂ (46.70% after 60 min). When the 500 mg/L dye concentration was treated with UV/ 10 ml/L H₂O₂, it also provided higher degradation (99.70% after 60 min) than UV (0.33% after 60 min) and UV/TiO₂ (2.84% after 60 min)

When the H₂O₂ was increased to 20 ml/L (UV/ 20 ml/L H₂O₂), the dye degradation was much better (99.96% after 20 min for 50 mg/L dye concentration and 99.95% after 60 min for 500 mg/L dye concentration). Since the UV/20 ml/L H₂O₂ was the most efficient treatment for the dye at all concentrations, the Chemical Oxygen Demand (COD) analysis was performed on the samples to determine the amount of chemicals present in the solution after treatment. From the COD results it was evident that the longer the exposure time, the more the reduction in COD values (416 mg/L for 50 mg/L dye concentration after 20 min and 256 mg/L for 500 mg/L dye concentration after 60 min). Hence textile effluents could be exposed to UV/ 20 ml/L H₂O₂ for more than 60 min to lower the COD to the disposal limit of 80 mg/L (CCME, 2012).

Soutsas et al. (2010) stated that, the COD reduction was a function of the dye concentration, the higher the dye concentration, the lower the reduction. They attained complete dye degradation when a dye concentration of 100 mg/L was exposed to UV/H₂O₂, while only an 86% reduction was found when the solution was exposed to UV without H₂O₂. Azbar et al. (2004) reported COD reduction of 90% when polyester and acetate dyes were treated with UV/H₂O₂ for a retention time of 90 min, but they attained a higher COD and colour removal when they performed the experiments under an acidic condition (a pH of 3). Kurbus et al (2003) reported a higher COD reduction with H₂O₂/UV compared to H₂O₂/Fe²⁺. Shu and Hsieh (2006) experimented with azo, acid and reactive dyes and noted 41.2% COD reduction after being exposed to UV alone for 180 min, 20% COD reduction after being exposed to H₂O₂ alone for 72 hours and 99.5% COD reduction after being exposed to a combination of UV and H₂O₂ for 120 min. Bedoul et al. (2008) reported that the COD reduction rate was increased as the amount of H₂O₂ was increased from 1.8 ml/L to 2.75 ml/L. White (2011) stated that excess amount

of H₂O₂ added to the effluent for treatment might not cause an environmental hazard due to its capacity to degrade under sunlight as shown in Equation 6.19.



6.5. Effect of pH

Several researchers indicated that photo oxidation is more efficient under acidic conditions than alkaline conditions. Galindo and Kalt (1998) reported that H₂O₂/UV oxidation was far more efficient when used under an acidic pH. They stated that when H₂O₂ is used with UV under an alkaline condition, it undergoes decomposition forming dioxygen and water which is believed to be the reason for the less initial concentration of OH[•]. Ganesan and Thanasekaran (2011) reported that the effect of UV/H₂O₂ degradation decreases as the pH increases. They have also noted that the decolourisation efficiency increased as the concentration of H₂O₂ was increased due to the additional production of hydroxyl radicals. Kavitha and Palanisamy (2011) stated that the photocatalytic activity was maximum under acidic condition and was found to decrease when the pH range was increased above 6. Neamtu et al. (2003) examined colour removal at different pH levels (2, 3, 6.5 and 9.7) and found the best colour removal efficiency (99%) of reactive red 120 to be achieved at pH of 2 within 15 min. Azbar et al. (2004) reported that the best reduction in COD and colour was obtained when treatment was performed in an acidic pH rather than an alkaline pH.

In this study, the pH was adjusted to 10-11 which is the range of pH for textile effluent. After treatments, the pH was found to decrease and the final pH of the treated effluent was, however, within the pH discharge limits of 6-9.

Although low pH was reported to achieve better dye removal, the effluent was treated at the discharge pH (10-11) in order to eliminate the acidification step and minimize the impact on the environment. However, the 50 mg/L and 500 mg/L dye concentrations were treated at a low pH of 3 using the most efficient treatment (UV with 20 ml/L H₂O₂) in order to investigate the effect of pH on removal efficiency. The decolourisation of reactive red 120 dye was found to be faster when treated under acidic pH (99.97%

degradation after 15 min for 50 mg/L dye concentration and 99.95% degradation after at 46.6 min for 500 mg/L dye concentration) compared to that achieved under alkaline condition (99.96% after 20 min for 50 mg/L dye concentration and 99.95% after 60 min for 500 mg/L dye concentration). However, the pH after treatment was reduced further to 2.8 after 15 min exposure time for 50 mg/L dye concentration and to 2.5 after 46.6 min exposure time for 500 mg/L dye concentration.

Although, treatment in acidic pH provided faster decolourisation (16-25%) than alkaline conditions, the difference in decolourization time does not justify the disposal problems associated with lower pH and the cost of chemical addition to the effluent to bring the pH to 3 first and then to the neutral value. Also, the increase in COD under acidic condition (618 mg/L for 50 mg/L concentration and to 454 mg/L for 500 mg/L) compared to that under alkaline condition (416 mg/L for 50 mg/L concentration and 256 mg/L for 500 mg/L) will require additional costly treatment.

Chapter 7. CONCLUSION

A photo reactor consisting of a low pressure UV lamp, emitting a UV light at an intensity of 380 nm was used to study the degradation efficiency of reactive red 120 dye. Ten different dye concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/L) and 12 different resident times (5.2, 10, 15, 20, 25.4, 30, 35, 40, 46.6, 49.4, 56 and 60 min) were investigated. The effects of UV radiation, TiO₂ coating with UV radiation, UV/ 10 ml H₂O₂ and UV/ 20 ml H₂O₂ were evaluated and the results were compared to select the best oxidation method. The following conclusions are made from the study

1. The maximum degradation obtained after 60 min exposure to UV alone was 27.01% and 0.33% for 50 mg/L dye concentration and 500 mg/L dye concentration, respectively.
2. The maximum degradation obtained after 60 min exposure to UV/TiO₂ was 46.70% and 2.84% for the 50 mg/L dye solution and 500 mg/L dye concentration, respectively.
3. Using UV/TiO₂ resulted in a better degradation than using UV alone (almost two times higher).
4. The degradation obtained after exposure to UV/10 ml/L H₂O₂ was 99.83% after 25.4 min for the 50 mg/L concentration and 99.70% after 60 min for the 500 mg/L concentration.
5. Almost complete degradation of the effluent was achieved with UV/10 ml/L H₂O₂ in a much shorter time making the treatment superior to UV/TiO₂ and UV treatments.

6. Exposure to UV/ 20 ml/L H₂O₂ resulted in the degradation of 99.96% after 20 min for the 50 mg/L dye concentration and 99.95% degradation after 60 min for the 500 mg/L dye concentration.
7. Increasing the H₂O₂ from 10 ml/L to 20 ml/L (UV/20 ml/L H₂O₂) improved the oxidation efficiency and reduced the treatment time.
8. The Chemical Oxygen Demand (COD) analysis performed on UV/20 ml/L H₂O₂ treated samples showed the COD of the effluent (after treatment) was 416 mg/L after 20 min for the 50 mg/L dye concentration and 256 mg/L after 60 min for the 500 mg/L dye concentrations which are higher than the COD discharge limit of 80 mg/L.
9. The COD discharge limit of 80 mg/L could be achieved with UV/ 20 ml/L treatment by increasing the exposure time (longer than 60 min).
10. The pH of the treated effluent is within the discharge accepted limit of 6-9.
11. Treatment of the dye effluent under acidic condition was faster but does not justify the cost of chemicals addition to adjust the pH and the further treatment to remove the chemicals before disposal.
12. The temperature after treatment was always found to be increased from 22°C to 41°C after 60 min of exposure to UV.

Chapter 8. RECOMMENDATIONS

1. A longer exposure time of the effluent containing 20 ml/L H_2O_2 to UV was found to reduce COD further. Hence, a longer exposure time, even after complete decolourization, is recommended in order to reduce the COD to the acceptable limit of 80 mg/L.
2. Excess of H_2O_2 , if present, was found to stay in the system even after treatment with UV. However, H_2O_2 can be degraded under sunlight. Hence, exposing the effluent to sunlight after treatment is highly recommended to remove the remaining H_2O_2 in the effluent.
3. The textile effluent from the industry has a temperature of 35-45° C and treatment with UV would increase it even further. Hence, a storage unit should be used to allow the effluent to cool down before discharge into the environment in order to avoid thermal pollution.

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APPENDIX A

Dye Degradation under Alkaline Condition

Table A 1. Dye degradation after treatment with UV

Time	50	100	150	200	250	300	350	400	450	500
(min)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
5.2	8.60	0	0	0	0	0	0	0	0	0
10	8.40	0	0	0	0	0	0	0	0	0
15	7.85	18.10	26.00	0	0	0	0	0	0	0
20	7.70	17.50	25.55	38.55	0	0	0	0	0	0
25.4	7.40	17.25	25.50	38.15	50.08	0	0	0	0	0
30	7.25	16.65	25.10	38.10	49.52	66.40	0	0	0	0
35	7.10	16.20	24.95	37.35	48.88	65.68	0	0	0	0
40	6.80	15.60	24.65	36.85	48.16	65.28	0	0	0	0
46.66	6.75	15.10	24.35	36.40	47.28	64.72	81.44	0	0	0
49.41	6.55	14.90	24.20	36.20	46.88	63.28	80.72	90.50	0	0
56	6.50	14.80	23.80	35.60	46.24	62.72	80.08	90.20	83.60	0
60	6.35	14.00	23.20	35.35	45.92	62.00	79.20	89.10	82.60	106.92

Table A 2. Dye degradation after treatment with UV/TiO₂.

Time	50	100	150	200	250	300	350	400	450	500
(min)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
5.2	8.95	0	0	0	0	0	0	0	0	0
10	8.60	18.15	0	0	0	0	0	0	0	0
15	8.20	17.95	30.70	37.55	0	0	0	0	0	0
20	8.05	17.40	30.15	37.35	0	0	0	0	0	0
25.4	7.70	16.05	29.65	36.95	60.1	0	0	0	0	0
30	7.50	16.40	29.45	36.65	59.2	74.20	0	0	0	0
35	7.35	15.90	28.70	36.10	58.6	73.40	0	0	0	0
40	7.00	15.60	28.30	35.65	57.9	72.60	87.45	0	0	0
46.66	6.85	15.30	27.70	34.85	56.5	71.70	86.40	0	0	0
49.41	6.15	14.65	27.35	34.50	55.9	71.00	85.20	99.00	123.40	0
56	5.85	14.10	26.65	34.00	55.1	69.30	83.10	97.80	121.80	132.40
60	4.85	13.80	26.00	33.70	54.7	38.40	81.15	96.45	119.40	129.80

Table A 3. Dye degradation after treatment with UV/ 10ml H₂O₂.

Time	50	100	150	200	250	300	350	400	450	500
(min)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
5.2	0.311	1.43	12.84	18.08	20.93	38.72	36.00	46.40	58.48	59.68
10	0.039	0.903	8.160	7.6	16.31	31.20	25.76	39.28	52.00	52.08
15	0.028	0.477	0.667	6.26	8.33	21.36	19.12	31.84	42.40	44.80
20	0.005	0.135	0.293	3.74	4.83	11.68	15.76	26.56	37.60	43.76
25.4	0.002	0.053	0.084	3.72	2.10	0.118	12.48	25.04	32.00	39.04
30		0.021	0.023	0.172	0.420	0.968	11.20	22.24	28.72	34.88
35			0.006	0.088	0.154	0.330	0.751	13.68	18.32	30.72
40				0.01	0.055	0.141	0.263	0.441	11.44	26.56
46.66					0.005	0.027	0.116	0.218	0.492	11.44
49.41							0.032	0.143	0.433	8.16
56								0.034	0.106	0.415
60								0.021	0.058	0.225

Table A 4. Dye degradation after treatment with UV/20 ml H₂O₂.

Time	50	100	150	200	250	300	350	400	450	500
(min)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
5.2	0.452	9.000	13.60	13.3	19.95	37.50	50.7	66.30	80.10	98.55
10	0.116	3.400	8.400	9.300	13.95	30.60	51.60	53.25	63.45	77.85
15	0.029	0.128	0.146	0.573	8.500	21.00	26.85	35.55	48.75	61.20
20	0.003	0.012	0.088	0.211	0.711	6.45	10.35	24.60	34.05	47.85
25.4		0.005	0.022	0.074	0.279	0.491	0.994	14.55	20.70	38.40
30			0.008	0.035	0.121	0.247	0.727	10.65	13.65	26.55
35					0.036	0.214	0.258	0.455	0.636	0.941
40					0.008	0.042	0.08	0.142	0.394	0.485
46.66						0.012	0.028	0.089	0.194	0.283
49.41								0.036	0.088	0.134
56								0.028	0.042	0.118
60										0.058

APPENDIX – B

COD Analysis

Table B 1. COD of the effluent treated with UV/ 20 ml/L H₂O₂.

Time	50	100	150	200	250	300	350	400	450	500
(min)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
5.2	704	832	864	864	928	1024	1088	1152	1152	1184
10	608	672	736	800	832	896	928	1056	1088	1120
15	512	512	608	704	672	736	800	832	1024	1056
20	416	384	448	544	576	672	704	800	800	864
25.4		288	384	416	480	608	640	736	704	768
30			224	352	416	512	544	640	672	704
35				256	320	448	416	512	576	640
40					224	288	320	448	480	544
46.66						192	224	384	416	448
49.41								288	352	416
56								256	224	320
60										256

APPENDIX – C

Dye Degradation under Acidic Condition

Table C 1. Percentage degradation of reactive red dye under UV/20 ml H₂O₂ at an acidic pH of 3

Time (min)	50 mg/L	500 mg/L
5.2	95.40	34.55
10	99.68	42.67
15	99.97	59.93
20		77.44
25.4		89.95
30		90.34
35		98.51
40		99.84
46.66		99.95
49.41		
56		
60		

APPENDIX – D

Temperature of the Treated Effluent

Table D 1. Temperature of the treated effluent.

Time (min)	Temperature (°C)
5.2	22
10	23
15	26
20	28
25.4	29
30	31
35	33
40	35
46.66	36
49.41	38
56	40
60	41