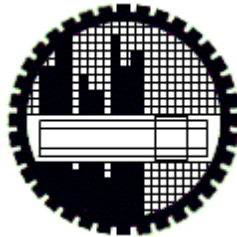# EFFECTIVENESS OF FENTON'S REAGENT IN THE TREATMENT OF TEXTILE EFFLUENT

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MASTER OF SCIENCE IN CIVIL ENGINEERING (ENVIRONMENTAL)

JUNE 2014

DEPARTMENT OF CIVIL ENGINEERING

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

DHAKA

EFFECTIVENESS OF FENTON'S REAGENT IN THE TREATMENT OF TEXTILE EFFLUENT

By

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A thesis submitted to the department of Civil engineering of BUET, Dhaka in partial fulfillment of the requirements for the degree of

M. Sc. in civil Engineering (Environmental)

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JUNE 2014

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It is hereby declared that except for the contents where specific references have been made to the work of others, the studies contained in this thesis are the result of investigation carried out by author. No part of this thesis has been submitted for any other degree or other qualification except for publication.

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Nusrat Rezwana Binte Razzak

Dedicated To

To my Loving Parents,

A. N. M. Abdur Razzaque And Razia Sultana

ACKNOWLEDGEMENT

ABSTRACT

Textile industry is one of the largest consumers of water and consequently, one of the largest producers of wastewater among all industries in Bangladesh. Dyeing and finishing are two important steps involved of man-made or natural fibers to the desired permanent colors and processing of the fibers into final commercial products. Textile wastewater from dyeing and finishing processes has been a serious environmental threat for years. This wastewater, with high Chemical Oxygen Demand (COD) and a strong dark color, is classified as a high strength wastewater. Moreover, textile wastewater exhibit low BOD to COD ratios indicating their non-biodegradable nature. The discharge of this type of wastewater without any type of treatment brings about considerable adverse impacts on the receiving water bodies and thus demands for an efficient treatment process. Textile wastewater is usually treated by conventional methods such as chemical coagulation, biological oxidation and activated carbon adsorption. However, these conventional methods suffer from a few limitations or drawbacks related to cost, efficiency and sludge generation. The limitations of conventional methods can be overcome by using Fenton's reagent.

In present study, textile effluents were collected from two different sections like cotton dyeing and finishing; then its characterization was done. The aim of the work was mainly to investigate the efficiency of the Fenton's processes for the removal of COD, color and Turbidity from a real textile wastewater. The Fenton's process employs ferrous ions and hydrogen peroxide H_2O_2 under acidic pH conditions. The experimental variables studied include doses of iron salts and hydrogen peroxide, oxidation time, pH for oxidation and coagulation. The COD, color and turbidity removal reached a maximum of 97.2%, 96.8% and 84.8% respectively at a reaction time of 20 minutes under low doses of H_2O_2 and Fe^{2+} for cotton dyeing effluent. At optimized conditions 85.7% reduction in color, 99.8% reduction in turbidity and 99.9% reduction in COD is obtained for finishing effluent. Optimum dose of hydrogen peroxide was 2.0 ml/500 ml and 1.5 ml/500 ml for cotton dyeing and finishing effluent, respectively. Optimum dose of ferrous sulphate was 1.0 gm/500 ml and 0.5 gm/500ml for cotton dyeing and finishing effluent, respectively. Maximum removal occurred in the 20 minutes reaction time for cotton dyeing effluent and 30 minutes reaction for finishing effluent. The tested parameters after Fenton's process met the standard of

Bangladesh environmental conservation rules for disposing of treated effluent into sewerage system. In this study optimum pH was found to be 4.0 and 6.0 respectively for oxidation and coagulation for both samples. It is observed that at an extremely low and high pH, removal efficiency decreased. COD was removed primarily by Fenton's coagulation, rather than by Fenton's oxidation. In this study Fenton process is found technically effective for the treatment of finishing effluent as compared to dyeing effluent.

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LIST OF ABBREVIATIONS

AOP   Advanced oxidation process

APHA   American public health association

BOD   Biochemical oxygen demand

BOD_5 5 days Biochemical oxygen demand

BPT   Best practical control tech.

COD   Chemical oxygen demand

CCM   Computer Color Matching

DO   Dissolved Oxygen

DoE   Department of Environment

EPA   Environmental protection agency

ETP   Effluent Treatment plant

EWA   European Water Association

GAC   Granular activated Carbon

NTU   Nephelometric Turbidity Unit

PAC   Powdered activated carbon

Ppm   Parts per million

SBR   Sequencing Batch Reactor

TDS   Total Dissolved Solid

TOC   Total organic carbon

TSS   Total Suspended Solid

TS   Total Solid

UASB   Up flow Anaerobic sludge blanket

WHO   World Health Organization

w/w   Weight by weight

CHAPTER ONE

INTRODUCTION

1.1   General

Textile is one of the important sectors in Bangladesh and has a long history of many centuries. Bangladesh, being a labor-abundant country, started the process of industrialization by concentrating on labor-intensive products such as textiles and clothing. Textile industry in Bangladesh first came in existence in July 1972. Bangladesh has substantially liberalized its trade regime; moving away from costly protectionist policy toward a more export-friendly trade regime. The industrial policy (1999) and Export Policy (1997-2002) have identified the textile and clothing sector as one of the "thrust" sectors in Bangladesh. This sector alone accounts for 75% of the national export earnings of Bangladesh.

Textile is a flexible woven material consisting of a network of natural or artificial fibers often referred to as thread or yarn. Yarn is produced by spinning raw fibers of wool, flax, cotton, or other material to produce long strands. Colored designs in textiles can be created by weaving together fibers of different colors, adding colored stitches to finished fabric. Three synergic and intrinsic factors that triggered the textile boom in Bangladesh are resources, opportunities and policy decision. The resources include abundant labor forces, low cost energy and natural gas. In that branch of industry there are different production processes which produce excessive wastewater. Wastewater amount, pollutant types and concentrations show different data's (Olmez et al. 2003).

The textile industry consumes a substantial amount of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. Textile dyeing is a process in which clothing material is imparted the desired colors or shades by applying dyes and host of organic or inorganic chemicals in aqueous media often at elevated temperatures and pressures in stages. In the textile dyeing process in addition to dyes large quantity of other organic or inorganic chemicals like electrolytes, carriers, leveling agents, promoting agents, chelating agents, emulsifying oils, softening agents etc. are also added. About 10 to 20 % of

the dye remains in the dye bath and is discharged along with other residual chemicals as exhausted dye bath waste. The exhausted dye bath wastes still contain significant quantities of coloring matter and impart color to the receiving water bodies. In addition to imparting color dye baths also contribute to organic and inorganic load of the receiving streams. Dye bath wastes are typically characterized by residual color, alkaline pH (mostly), excess TDS content, high COD but relatively low BOD values.

The textile wastewater is rated as the most polluting among all industrial sectors considering both volume and composition of effluent (Vanndevivera et al., 1998). It is a complex and highly variable mixture of many polluting substances ranging from inorganic compounds and elements to polymers and organic products (Banat et al., 1996). It induces persistent color coupled with organic load leading to disruption of the total ecological/symbiotic balance of the receiving water stream. Dyes with striking visibility in recipients may significantly affect photosynthetic activity in aquatic environment due to reduced light penetration and may also be toxic to some aquatic lives due to metals, chlorides, etc., associated with dyes or the dyeing process. It is difficult to remove dyes from effluents since dyes are stable to light, heat and oxidizing agents and are non-biodegradable (Robinson et al. 2001).

1.2   Background of the Study

Textile industry includes a wide number of sub-sectors, from the production of raw material to the finished product, and water management is part of the whole environmental policy for emission minimization. Textile industry can be classified into three categories viz., cotton, woolen, and synthetic fibers depending upon the used raw materials. The textile industry uses vegetable fibers such as cotton; animal fibers such as wool and silk; and a wide range of synthetic materials such as nylon, polyester and acrylics. The production of natural fibers is approximately equal in amount to the production of synthetic fibers. The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, such as complex components, many aerosols, high chromium, high COD and BOD concentration as well as much more hard-degradation materials. The toxic effects of dyestuffs and other organic compounds, as well as

acidic and alkaline contaminants, from industrial establishments on the general public are widely accepted. At present, the dyes are mainly aromatic and heterocyclic compounds, with color-display groups and polar groups. The structure is more complicated and stable, resulting in greater difficulty to degrade the printing and dyeing wastewater (Shaolan et al. 2010). Sandyha and Swami Nathan 2006 listed some important pollutants in textile wastewater which are organics and color, toxic materials, inhibitor compounds, active substances, chlorine compounds, pH, salt and dying substance.The two major processes responsible for textile wastewater pollution are dying and finishing processes because they involve the use of wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure.

Textile industry involves wide range of raw materials, machineries and processes to engineer the required shape and properties of the final product. Dyeing and finishing are two important steps involve the dyeing of man-made or natural fibers to the desired permanent colors and processing of the fibers into final commercial products. Waste stream generated in this industry is essentially based on water-based effluent generated in the various activities of wet processing of textiles. The main cause of generation of this effluent is the use of huge volume of water either in the actual chemical processing or during re-processing in preparatory, dyeing, printing and finishing. Our biosphere is under constant threat from continuing environmental pollution. Impact on atmosphere, hydrosphere and lithosphere by anthropogenic activities cannot be ignored. The characteristics of textile wastewater are high chemical oxygen demand (COD), high biological oxygen demand (BOD), high temperature, high pH, solid materials, phenol, sulphur and the colors caused by different dyes (Demir et al. 2000). Because of these characteristics, treatment of textile wastewater is an essential requirement before it is being disposed to natural water system (Kabir et al. 2002).

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. The importance of the pollution control and treatment is undoubtedly the key factor in the human future. If a textile mill discharges the wastewater into the local environment without any treatment, it will have a serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD_5, presence of particulate matter and sediments, and oil and grease in the effluent causes depletion of

dissolved oxygen, which has an adverse effect on the aquatic ecological system. Effluent from textile mills contains chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat (Joseph 2007).

The textile industry consumes considerable amounts of water. Dyes pollutants from the textile industry are a major source of environmental contamination. Due to the large degree of aromatics present in these molecules and the stability of dyes, most conventional treatment methods are ineffective for decolonization and degradation (Aleboyeh et al., 2005). Color removal from textile wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain but also because of their coloring effect on natural waters (Aleboyed et al. 2003; Muruganandham and Swami Nathan, 2004).

Many physical, biological, and chemical processes are used in wastewater treatment. But some contaminants found in wastewater are recalcitrant to some degree to commonly applied processes. Chemical oxidation processes are transformation processes that may augment current treatment schemes. Oxidation processes may destroy certain compounds and constituents through oxidation and reduction reactions.

Currently, there are no economically attractive technologies to achieve color removal. Existing physic-chemical technologies such as membrane filtration or activated carbon adsorption are expensive and commercially unattractive. Furthermore, these processes just transfer pollutants from one phase to another rather than eliminating them from the water matrix (Alaton et al. 2002). Advanced Oxidation Processes (AOPs) have been successfully applied to the treatment of the various water pollutants (Aleboyeh et al., 2005). In the textile industries there is growing interest for the process water. Since the purified wastewater in the textile industry is required to satisfy strict quality standards before reuse becomes possible, advanced purification techniques must be available which are efficient and reliable. Advanced oxidation is a chemical oxidation process predominantly involve the generation of very powerful, short-lived and non-selective oxidizing species, the hydroxyl radicals ($\bullet$OH) for

the destruction of refractory and hazardous pollutants observed in industrial wastewaters, surface waters and groundwater (Schrank et al. 2004). Hydroxyl radicals may be produced in systems using Fenton's reagent (ferrous iron and hydrogen peroxide) which is found to be effect in removal of excessive, color, COD, turbidity from textile wastewater.

1.3   Objectives of the Study

The objective of this study was to determine the effectiveness of Fenton's process in the treatment of textile wastewater. The specific objectives are as follows:

- Assess the characteristics of raw effluent collected from textile industry.
- Explore optimum pH and effective reaction time for Fenton's oxidation and coagulation.
- Determine optimum doses of Fenton's reagent for effective removal of Color, Turbidity and COD.
- Investigate the effectiveness of Fenton's reagent in removing COD, color and Turbidity

1.4   Methodology of the study

The Fenton's reagent is used to remove COD, strong Color and Turbidity of textile effluent characterized by its extremely high value of COD and a low value of BOD. For the experimental purposes wastewater samples was collected from cotton dyeing section and finishing section of Polmol Textile mills, Mauna, Sreepur, Gazipur. Combined effluent containing waste water of all processes was collected from a textile industry located in Sikalbaha, Chittagong.

At first the characteristics of raw wastewater samples were assessed. In Fenton's process wastewater is treated by means of oxidation and coagulation. Optimum pH for the Fenton's process was found out. The optimum dose of H_2O_2 with varying doses of $FeSO_4$ and optimum dose of $FeSO_4$ with varying doses of H_2O_2 were tested.

1.5   Outline of the Thesis

Outcome of this thesis comprises five distinct chapters. This is the introductory chapter of this thesis includes the objectives and brief description of methodology. Apart from this chapter, the

remainder of the thesis has been divided into four chapters.

Chapter two includes compilation of the relevant literature that has been reviewed for the study including the details chemistry of Fenton's reagents. Chapter three presents Methodology of the research. It also explains the procedures follows in the laboratory tests. Chapter four provides results and discussion on the research findings. In chapter five attempts are made to bring the findings of the study together in the form of conclusions and outline the recommendations for actions and studies to be required in future.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Rapid industrial development and growth of cities throughout the world especially in the developing world have led to the recognition and increasing understanding of the relationship between pollution, public health and the environment at large. The treatment of textile effluents is a growing concern due to their toxic and esthetic impacts on receiving waters. The increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to dye wastewater becoming one of the substantial sources of severe pollution problems in current times (Sen and Demirer. 2003 and Ogugbue and Sawidis 2011). One of the most difficult tasks confronted by the wastewater treatment plants of textile industries is the removal of the color of these compounds, mainly because dyes and pigments are designed to resist biodegradation, such that they remain in the environment for a long period of time. As regulations become more stringent, the effectiveness and cost of treatment processes becomes more significant. So, there is a need for advanced treatment process to remove excessive color and COD from wastewater.

2.2 Textile wastewater –A Global Scenario

The textile industry consumes large amounts of potable and industrial water as processing water (90-94%) and a relatively low percentage as cooling water (6-10%). The recycling of treated wastewater has been recommended due to the high levels of contamination in dyeing and finishing processes (i.e. dyes and their breakdown products, pigments, dye intermediates, auxiliary chemicals and heavy metals, etc.) (Adapted from Bertea and Bertea, 2008; Bisschops and Spanjers, 2003; Correia et al., 1994; Orhon et al., 2001). In Europe, environmental legislation has necessitated increasingly green textile processing. This has, and is being achieved, through recycling of chemicals and water, production and use of biodegradable textile chemicals and dyes, as well as efficient effluent treatment (Mohr, 1992*).* According to U.S

E.P.A, an average dying facility generates 1 to 2 million gallons of wastewater per day. About 10,000 different dyes and pigments are produced annually worldwide.

As the wastewater is harmful to the environment and people, there are strict requirements for the emission of the wastewater. However, due to the difference in the raw materials, products, dyes, technology and equipment, the standards of the wastewater emission have too much items. It is developed by the national environmental protection department according to the local conditions and environmental protection requirements which is not fixed. The textile industry standards for water pollutants in China, Germany, and U.S have been stated below.

Table 2.1: Textile effluent discharge standards (Dyeing and Finishing) for water pollutants in China. (Zongping et al. 2011)

Serial Number	Parameters	The limits of Discharged Concentration	The limits of Discharged Concentration for New Factory	The Special limits of Discharged Concentration
1	COD	100 mg/L	80 mg/L	60 mg/L
2	BOD	25 mg/L	20 mg/L	15 mg/L
3	pH	6-9	6-9	6-9
4	SS	70 mg/L	60 mg/L	20 mg/L
5	Chrominance	80	60	40
6	TN	20 mg/L	15 mg/L	12 mg/L
7	NH_3-N	15 mg/L	12 mg/L	10 mg/L
8	TP	1.0 mg/L	0.5 mg/L	0.5 mg/L
9	S	1.0 mg/L	Cannot be detected	Cannot be detected
10	CLO_2	0.5 mg/L	0.5 mg/L	0.5 mg/L
11	Cr^{6+}	0.5 mg/L	Cannot be detected	Cannot be detected
12	Aniline	1.0 mg/L	Cannot be detected	Cannot be detected

The emission standards for different indictors in textile industry standards for water pollutants in Germany have been shown in table 2.2

Table 2.2: Discharge standard of water pollutants for dyeing and finishing of textile industry (Zongping et al. 2011)

Serial No.	Parameters	The limits of Discharged Concentration
1	COD	160 mg/L
2	BOD	25 mg/L
3	TP	2.0 mg/L
4	TN	20 mg/L
5	NH3-N	10 mg/L
6	Nitrite	1.0 mg/L

The requirements using BPT (best practical control tech.) which is published by EPA has shown in Table 2.3.

Table 2.3: Emission standards for gross printing and dyeing wastewater in USA (Zongping et al. 2011)

Serial No.	Parameters	BPT	
		(kg/t) fabric	
		Maximum	Average of 30 days
1	BOD_5	22.4	11.2
2	COD	163.0	81.5
3	TSS	35.2	17.6
4	S	0.28	0.14
5	Phenol	0.14	0.07
6	Cr	0.14	0.07
7	pH	6.0-9.0	6.0-9.0

2.3 Textile Wastewater Characteristics

One of the main sources with severe pollution problems worldwide is the textile industry and its dye-containing wastewaters; 10,000 different textile dyes with an estimated annual production of 7.10^5 metric tonnes are commercially available worldwide; 30% of these dyes are used in excess of 1,000 tonnes per annum, and 90% of the textile products are used at the level of 100 tonnes per annum or less. (Robinson et al., 2001). 10-25% of textile dyes are lost during the dyeing process, and 2-20% are directly discharged as aqueous effluents in different environmental components. In the textile industry, up to 200,000 tons of dyes are lost to effluents every year during the dyeing and finishing operations, due to the inefficiency of the dyeing process

(Ogugbue and Sawidis 2011). Unfortunately, most of these dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration (Couto 2009). The most common textile processing technology consists of desizing, scouring, bleaching, mercerizing and dyeing processes (EPA, 1997).

Table 2.4: Wet processes producing textile wastewater (Naveed et al. 2006)

Process	Textile Effluent
Singering, Desizing	High BOD, high TS, neutral pH
Scouring	High BOD, high TS, high alkalinity, high temperature
Bleaching, Mercerizing	High BOD, high TS, alkaline wastewater
Heat-setting	Low BOD, low solids, alkaline wastewater
Dyeing, Printing & Finishing	Wasted dyes, high BOD, COD, solids, neutral to alkaline

Seizing is the first preparation step, in which seizing agents such as starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose are added to provide strength to the fibres and minimize breakage. Deseizing is used to remove sizing materials prior to weaving. Scouring removes impurities from the fibres by using alkali solution (commonly sodium hydroxide) to breakdown natural oils, fats, waxes and surfactants, as well as to emulsify and suspend impurities in the scouring bath. Bleaching is the step used to remove unwanted color from the fibers by using chemicals such as sodium hypochlorite and hydrogen peroxide. Mercerising is a continuous chemical process used to increase dye-ability, lustre and fibre appearance. In this step a concentrated alkaline solution is applied and an acid solution washes the fibres before the dyeing step. Dyeing is the process of adding colour to the fibres, which normally requires large volumes of water not only in the dye bath, but also during the rinsing step. Depending on the dyeing process, many chemicals like metals, salts, surfactants, organic processing aids, sulphide and formaldehyde, may be added to improve dye adsorption onto the fibres.

Table 2.5: water consumption and organic load in different steps of textile (EWA, 2005)

Process	Water consumption (% from total consumption of the textile plant)			Organic load (% from total organic load of the textile plant)		
	Minimum	Medium	Maximum	Minimum	Medium	Maximum
General	6	14	33	0.1	2	8
Dyeing	4	29	53	4	23	47
Printing	42	55	38	42	59	75
Finishing	0.3	2	4	0.1	3	7

Table 2.6: Wastewater characteristics in the textile Industry (Economopoulos, 1993)

Process and Unit (U)	Waste volume m^3/U	BOD, Kg/U	TSS, Kg/U	Other pollutants, Kg/U	
Wool processing (metric ton of wool)					
Average un-scoured stock	544	314	196	oil	191
Average scoured stock	537	87	43	Cr	1.33
Process specific				Phenol	0.17
Scouring	17	227	153	Cr	1.33
Dyeing	25	27		Phenol	0.17
washing	362	63			
Carbonizing	138	2	44	oil	191
bleaching	12.5	1.4		Cr	1.33
				Phenol	0.17
Process and Unit (U)	Waste volume m^3/U	BOD, Kg/U	TSS, Kg/U	Other pollutants, Kg/U	
Process specific					
Yarn sizing	4.2	2.8			

Continued Table 2.6: Wastewater characteristics in the textile Industry

Desizing	22	58	30	
Kiering	100	53	22	
Bleaching	100	8	5	
Mercerizing	35	8	2.5	
Dyeing	50	60	25	
Printing	14	54	12	
Other fabric (metric ton of product)				
Rayon processing	42	30	55	
Acetate processing	75	45	40	
Nylon processing	125	45	30	
Acrylic processing	210	125	87	
Polyester processing	100	185	95	

The textile industry uses a large quantity of chemicals. Detergents and caustic, which are used to remove dirt, grit, oils, and waxes. Bleaching is used to improve whiteness and brightness.

Table 2.7: principal pollutants of textile wastewater (EWA, 2005)

Type of finished textile product	Dyes, g/kg textile product	Auxiliaries, g/kg textile product	Basic chemical compounds, g/kg textile product
Polyester fibers	18	129	126
Fabrics from synthetic fibers	52	113	280
Fabrics from cotton	18	100	570

Table 2.8: Principal characteristics of a cotton wet processing wastewater (Copper, 1995)

Process	COD, g O$_2$/L	BOD, g O$_2$/L	TS, g/L	TDS, g/L	pH	Color (ADMI)	Water Usage L/kg Product
Desizing	4.6-5.9	1.7-5.2	16.0-32.0	-	-	-	3-9
Scouring	8.0	0.1-2.9	7.6-17.4	-	10-13	694	26-43
Bleaching	6.7-13.5	0.1-1.7	2.3-14.4	4.8-19.5	8.5-9.6	153	3-124
Mercerizing	1.6	0.05-0.1	0.6-1.9	4.3-4.6	5.5-9.5	-	232-308
Dyeing	1.1-4.6	0.01-1.8	0.5-14.1	0.05	5-10	1450-4750	8-300

Many of these chemicals become part of the final product whereas the rest are removed from the fabric, and are purged in the textile effluent. The annual estimated load with pollutants of a textile wastewater is of: 200,000-250,000 t salts; 50,000-100,000 t impurities of natural fibres (including biocids) and associated materials (lignin, sericine, etc.); 80,000-100,000 t blinding agents (especially starch and its derivatives, but also polyacrylates, polyvinyl alcohol, carboxymethyl cellulose); 25,000- 30,000 t preparation agents (in principal, mineral oils); 20,000-25,000 t tensides (dispersing agents, emulsifiers, detergents and wetting agents); 15,000-20,000 tonnes carboxylic acids (especially acetic acid); 10,000-15,000 t binders; 5,000-10,000 t urea; 5,000-10,000 t ligands, and < 5,000 t auxiliaries (EWA, 2005). The environmental authorities have begun to target the textile industry to clean up the wastewater that is discharged. The principal quality indicators that regulators are looking for polluting effect or toxicity are the high salt content, high Total Solids (TS), high Total Dissolved Solids (TDS), high Total Suspended Solids (TSS), Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), heavy metals, colour of the textile effluent and other potential hazardous or dangerous organic compounds included into each textile processingtechnological steps (Carmen and Daniela, 2012)

The wastewater composition is depending on the different organic-based compounds, inorganic chemicals and dyes used in the industrial dry and wet-processing steps. Textile effluents from the dyeing and rinsing steps represent the most Colored fraction of textile wastewaters, and are characterized by extreme fluctuations in many quality indicators such as COD, BOD, pH, color,

salinity and temperature. The color of textile wastewater is mainly due to the presence of textile dyes, pigments and other Colored compounds. A single dyeing operation can use a number of dyes from different chemical classes resulting in a complex wastewater (Correia et al. 1994). Moreover, the textile dyes have complex structures, synthetic origin and recalcitrant nature, which makes them obligatory to remove from industrial effluents before being disposed into hydrological systems (Anjaneyulu et al. 2005).

2.4 Dye: Classification and Characteristics

Dyeing is an ancient art which predates written records. It was practiced during the Bronze age in Europe. Primitive dyeing techniques included sticking plants to fabric or rubbing crushed pigments into cloth. The methods became more sophisticated with time and techniques. Today, dyeingis a complex, specialized science. Nearly all Dyestuffs are now produced from synthetic compounds. The textile dyes represent a category of organic compounds, generally considered as pollutants, presented into wastewaters resulting mainly from processes of chemical textile finishing.

2.4.1 Definition of Dye

Dyes are used to impart color to textiles, paper, leather, and other materials such that the coloring is not readily altered by washing, heat, light, or other factors to which the material is likely to be exposed. Most dyes are organic compounds.The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Dye may be defined as substances that, when applied to a substrate provides color by a process that alters, at least temporarily, any crystal structure of the colored substances (Bafana et al. 2011). Such substances with considerable coloring capacity are widely employed in the textile, pharmaceutical, food, cosmetics, plastics, photographic and paper industries (Zollinger, 1987 and Carneiro et al. 2007). The dyes can adhere to compatible surfaces by solution, by forming covalent bond or complexes with salts or metals, by physical adsorption or by mechanical retention (Bafana et al. 2011).

The nature and origin are firstly considered as criteria for the general classification in natural and synthetic textile dyes.

2.4.1.1 Natural dyes

Archaeologists have found evidence of textile dyeing dating back to the Neolithic period. In China, dyeing with plants, barks and insects has been traced back more than 5,000 years.The essential process of dyeing changed little over time. Typically, the dye material is put in a pot of water and then the textiles to be dyed are added to the pot, which is heated and stirred until the color is transferred. Textile fiber may be dyed before spinning "dyed in the wool", but most textiles are "yarn-dyed" or "piece-dyed" after weaving. Until the 1850s virtually all dyes were obtained from natural sources, most commonly from vegetables, such as plants, trees, and lichens, with a few from insects.

Natural fibers come mainly from two distinct origins, animal origin or vegetable origin. Natural dyes have a strong affinity to fibers of animal origin, especially wool, silk and mohair and the results with these fibers are usually good. Fibers of plant origin include cotton, flax or linen, ramie, jute, hemp and many others. Many natural dyes require the use of chemicals called mordants to bind the dye to the textile fibers; tannin from oak galls, salt, natural alum, vinegar, and ammonia from stale urine were used by early dyers. Natural dyes cannot be applied directly to cotton, in contrast to wool and silk, although cotton can be dyed by vatting or by pretreatment with inorganic salts known as mordants (from Latin *mordere*, meaning ―to bite"). A mordant is a substance used to set dyes on fabrics by forming an insoluble compound with the dye. These are adsorbed on the fiber and react with the dye to produce a less soluble form that is held to the fabric. Alum, $KAl(SO_4)_2 \times H_2O$, as well as iron, copper, and tin salts were common ancient mordants.

Until 1857 the dye industry utilized natural dyes almost exclusively; however, by 1900 nearly 90 percent of industrial dyes were synthetic. Several factors contributed to the commercial decline of natural dyes. By 1850 the industrial revolution in Europe led to a burgeoning textile industry, which created increased demand for readily available, inexpensive, and easily applied dyes and revealed the important economic limitations of natural dyes. Since most dyes were imported from distant sources, transportation delays were likely to slow the production of dyed materials. Dye quality was affected by the whims of nature and the dye maker's skills. In addition, inefficient processes were often required for optimum results. (Encyclopedia Britannica)

2.4.1.2 Synthetic Dyes

In 1856 the first commercially successful synthetic dye, mauve, was serendipitously discovered by British chemist William H. Perkin, who recognized and quickly exploited its commercial significance. The introduction of mauve in 1857 triggered the decline in the dominance of natural dyes in world markets. Mauve had a short commercial lifetime (lasting about seven years), but its success catalyzed activities that quickly led to the discovery of better dyes.

The synthetic dye industry arose directly from studies of coal tar. By 1850 coal tar was an industrial nuisance because only a fraction was utilized as wood preservative, road binder, and a source of the solvent naphtha. The success of mauve led to demands by English textile manufacturers for other new dyes. By trial and error, reactions of coal tar compounds were found to yield useful dyes. However, Hofmann became disenchanted with this purely empirical approach, insisting that it was more important to understand the chemistry than to proceed blindly. In 1865 he returned to Germany, and by 1875 most of his students had been lured to German industrial positions. By 1900 more than 50 compounds had been isolated from coal tar, many of which were used in the developing German chemical industry. By 1914 the synthetic dye industry was firmly established in Germany, where 90 percent of the world's dyes were produced. Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials.

The synthetic dyes can be named according to the chemical structure of their particular chromophoric group. For example, diphenylmethane derivatives, triphenylmethane compounds oxazine compounds, xanthene compounds, Azo dyes are one of the most popular varieties of synthetic dyes. Today it is being used up to 90% in the dyeing units, as they are versatile and simple to synthesize. Most of the synthetic dyes with a few exception are aromatic organic compounds which can be divided into groups like non-ionic (oil soluble), cationic, and anionic.

2.4.2 Dye Classification

Dyes are classified in two different ways, according to their application characteristics (i.e. CI Generic Name such as acid, basic, direct, disperse, mordant, reactive, sulphur dye, pigment, vat,

azo insoluble) and based on its chemical structure (CI Constitution Number suchas nitro, azo, carotenoid, diphenylmethane, xanthene, acridine, quinoline, indamine, sulphur, amino- and hydroxy ketone, anthraquinone, indigoid, phthalocyanine, inorganic pigment, etc.) and are composed of a group of atoms known as chromophores, responsible for the dye color. These chromophore-containing centers are based on diverse functional groups, such as azo, anthraquinone, methine, nitro, arilmethane, carbonyl and others. In addition, electrons withdrawing or donating substituents so as to generate or intensify the color of the chromophores are denominated as auxochromes. The most common auxochromes are amine, carboxyl, sulfonate and hydroxyl (Christie 2001; Prasad and Bhaskara 2010).

Considering only the general structure, the textile dyes are also classified in anionic, nonionic and cationic dyes. The major anionic dyes are the direct, acid and reactive dyes (Robinson et al., 2001), and the most problematic ones are the brightly Colored, water soluble reactive and acid dyes (they cannot be removed through conventional treatment systems). The major nonionic dyes are disperse dyes that does not ionized in the aqueous environment, and the major cationic dyes are the azo basic, anthraquinone disperse and reactive dyes, etc. The most problematic dyes are those which are made from known carcinogens such as benzidine and other aromatic compounds (i.e. anthraquinone-based dyes are resistant to degradation due to their fused aromatic ring structure). The organic dyes used in the textile dyeing process must have a high chemical and photolytic stability and the conventional textile effluent treatment in aerobic conditions does not degrade these textile dyes, and are presented in high quantities into the natural water resources in absence of some tertiary treatments. Classification of all the commercial textile dyes by their generic name and chemical constitution has been done by the Color Index (C.I.), a journal published by the Society of Dyers and Colorists (United Kingdom) in association with the American Association of Textile Chemists and Colorists (AATC). Textile dyestuffs can be grouped into the following categories taking general dye chemistry as one of the basis for classification:

- Acid Dyes
- Azoic Dyes

- Sulphur Dyes
- Oxidation Dyes

- Basic Dyes
- Direct Dyes
- Disperse Dyes
- Reactive Dyes

- Mordant Dyes (Chrome Dyes)
- Optical / Fluorescent Brightener
- Solvent Dyes
- Vat Dyes

Table 2.9: Distribution of each chemical class between major applications ranges (Cooper, 1995)

Chemical class	Distribution between application ranges, %								
	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Unmetallized azo	20	5	30	12	12	6	10	5	-
Metal complex	65	-	10	-	-	-	12	13	-
Thiazole	-	5	95	-	-	-	-	-	-
Stilbene		2	98	-	-	-	-	-	-
Anthraquinone	15	2	-	25	3	4	6	9	36
Indigoid	2	-	-	-	-	17	-	-	81
Quinophthalene	30	20	-	40	-	-	10	-	-
Aminoketone	11	-	-	40	8	-	3	8	20
Phtalocyanine	14	4	8	-	4	9	43	15	3
Chemical class	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Formazan	70	-	-	-	-	-	30	-	-
Methine	-	71	-	23	-	1	-	5	-
Nitro, Nitroso	31	2	-	48	2	5	-	12	-
Triarylmethane	35	22	1	1	24	25	-	12	-
Xanthene	33	16	-	-	9	2	2	38	-
Chemical class	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Acridine	-	92	-	4	-	-	-	4	-
Oxazine	-	22	17	2	40	9	10	-	-
Thiazine	-	55	-	-	10	-	-	10	25

2.4.3 General features of dyes and dyeing

In dyeing operations, the dye must become closely and evenly associated with a specific material to give even coloring with some measure of resistance to moisture, heat, and light—i.e., fastness. These factors involve both chemical and physical interactions between the dye and the fabric. The dyeing process must place dye molecules within the microstructure of the fiber. The dye molecules can be anchored securely through the formation of covalent bonds that result from chemical reactions between substituents on the molecules of the dye and the fiber. These are the reactive dyes which introduced in 1956. Many dye-fiber interactions, however, do not involve covalent bond formation. While some dyeing methods have several steps, many dyes can be successfully applied simply by immersing the fabric in an aqueous solution of the dye; these are called direct dyes. In other cases, auxiliary compounds and additional steps are required to obtain the desired fastness.

Fiber molecules are polymeric chains of repeating units of five major chemical types. Wool, silk, and leather are proteins, which are polymers of α-amino acids, $RCH(NH_2)COOH$ (where R is an organic group). Each chain consists of a series of amide linkages ($-CO-NH-$) separated by one carbon to which the R group, characteristic of each amino acid, is bonded. These groups may contain basic or acidic substituents, which can serve as sites for electrostatic interactions with dyes having, respectively, acidic or basic groups.

Polyamides (nylons) are synthetic analogs of proteins having the amide groups separated by hydrocarbon chains, $(CH_2)n$, and can be made with an excess of either terminal amino ($-NH_2$) or terminal carboxyl groups ($-COOH$). These and the amide groups are sites for polar interactions with dyes. Polyester polyethylene terephthalate), or PET, is the main synthetic fiber, accounting for more than 50 percent of worldwide production of synthetic fibers. The terminal hydroxyl groups ($-OH$) can serve as dyeing sites, but PET is difficult to dye because the individual chains pack tightly. Acrylics have hydrocarbon chains bearing polar groups, mainly nitriles, made by copolymerization of acrylonitrile (at least 85 percent) with small amounts (10–15 percent) of components such as acrylamide and vinyl acetate to produce a fiber with improved dye ability. Fibers with 35–85 percent acrylonitrile are termed modacrylics.

2.4.3.1 Fiber porosity

Fibers are made by various spinning techniques that produce bundles of up to several hundred roughly aligned strands of polymer chains with length-to-diameter ratios in the thousands. For the dyeing process, an important characteristic of fibers is their porosity. There are a huge number of submicroscopic pores aligned mainly on the longitudinal axis of the fibers such that there are roughly 10 million pores in a cross-section of a normal fiber. The internal surface area therefore is enormous about 45,000 square meters per kilogram (5 acres per pound) for cotton and wool some thousand times greater than the outer surface area. To produce deep coloration, a layer of 1,000–10,000 dye molecules in thickness is needed. Upon immersion in a dye bath, the fabric absorbs the aqueous dye solution, and the dye molecules can move into pores that are sufficiently large to accommodate them. Although many pores may be too small, there are an ample number of adequate sizes to give satisfactory depths of color.

2.4.3.2 Dye retention

Various attractive forces play a role in the retention of particular dyes on specific fibers. These include polar or ionic attractions, hydrogen bonding, Van der Waals forces, and solubility's. The affinity of a dye for a given substrate through such interactions is termed it's substantively.

Attractive ionic interactions are operative in the case of anionic (acid) and cationic (basic) dyes, which have negatively and positively charged groups, respectively. These charged groups are attracted to sites of opposite polarity on the fiber. Mordant dyes are a related type. In the mordanting process, the fabric is pretreated with metallic salts, which complex with polar groups of the fiber to form more highly polarized sites for better subsequent interaction with the dye molecules.Nonionic groups can also be involved in attractive interactions. Since the electro-negativities of oxygen, nitrogen, and sulfur are greater than those of carbon and hydrogen, when these elements are part of a compound, the electron densities at their atomic sites are enhanced and those at neighboring atoms are decreased. An O−H bond is therefore polar, and an attractive interaction between the hydrogen of one bond and the oxygen of a neighboring bond can occur. Hydrogen bonding may be exhibited by any weakly acidic hydrogen. Although there is no

chemical bond, strong attractive forces are involved. Phenolic hydroxyl groups are more highly polarized and, in dyes, can act as auxochromes and as good hydrogen-bonding sites.

Attractive forces are operative between other closely spaced polarized groups. These are the Van der Waals interactions, which are effective for dye adsorption if the separation between molecules is small. Such interactions are particularly important for cellulosics, which tend to have relatively large planar areas to which dye molecules are favorably attracted.

2.4.3.3 Dye fixation on textile fibers

All the dyes are not fixed to the fiber during the process of dyeing. The fixation efficiency varies with the class of azo dye used, which is around 98% for basic dyes and 50% for reactive dyes (Bertea and Bertea 2008; O'Neill et al., 1999). Large amounts of salts such as sodium nitrate, sodium sulphate and sodium chloride are used in the dye bath, as well as sodium hydroxide that are widely applied to increase the pH to the alkaline range. It is estimated that during the mercerizing process the weight of these salts can make up 20% of the fiber weight (EPA, 1997).

Table 2.10: Fixation degree of different dye classes on textile support (EWA, 2005)

Dye class	Fiber type	Fixation degree, %	Loss in effluent, %
Acid	polyamide	80-95	5-20
Basic	Acrilic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal Complex	Wool	90-98	2-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Dye-stuff	Cellulose	80-95	5-20

The problem of high Colored effluent or dye-containing effluent has become identified particularly with the dyeing of cellulose fibers (cotton – 50% of the total consumed fibers in the textile industry worldwide), and in particular with the use of reactive dyes (10-50% loss in

effluent), direct dyes (5-30% loss in effluent), vat dyes (5-20% loss in effluent), and sulphur dyes (10-40% loss in effluent). After the textile dyeing and finishing processes, a predicted environmental concentration of a dye in the receiving water can be estimated based on the following factors:

      (i)   daily dye usage;

      (ii)   dye fixation degree on the substrate (i.e. textile fibers or fabrics);

      (iii)   dye removal degree into the effluent treatment process, and

      (iv)   Dilution factor in the receiving water.

Some scenario analyses were mentioned the values of dye concentration in some receiving rivers of 5-10 mg/L (average value, 50 days each year) or 1300-1555 mg/L (the worst case, 2 days each year) for batch wise dyeing of cotton with reactive dyes, and of 1.2-3 mg/L (average value, 25 days each year) or 300-364 mg/L (the worst case, 2 days each year) for batch wise dyeing of wool yarn with acid dyes (Cooper, 1995).

2.4.4 Textile dyeing process

Dyeing process is the process of giving of color at textile material equally. In principle mechanism of dying process consists of 3 steps:

1. Migration dyestuff towards fiber

2. Adsorption molecule dye stuff at surface of fiber.

3. Diffusion dyestuff from surface of fiber to fiber interior

To get good dyeing result hence 6 important things must be taken care of:

1. Hardness of water

2. Chemicals balance (dyes, auxiliaries, salt, alkali)

3. Liquor Ratio (comparison of water with fabric weight)

4. pH dye solution (beginning of process and phase process of fixation)

5. Dyeing temperature

6. Dyeing time

In principle process of dyeing 100% cotton knitted fabric with reactive dye is with circulation material textile with dye solution and some auxiliaries, with certain concentration, certain time and certain temperature applies of dyeing machine. Materials that are used in textile dyeing process include water, fiber, yarn or cloth. Further, these include a host of process chemicals like:

- Acids, e.g. acetic, formic.
- Alkalis- NaOH, potassium hydroxide, sodium carbonate.
- Bleaches- Hydrogen peroxide, sodium hypo chlorite, sodium chlorite etc.
- Dyes, for example direct, disperse, pigment, vat.
- Salts, e.g. NaCl.
- Size, e.g. PVA, starch.
- Stabilizers from sodium silicate, sodium nitrate also organic stabilizers.
- Surfactants
- Auxiliary finishes, like fire retardant, softener

2.5 Environmental pollution for Textile Industries

Textile dyeing processes include pre-treatment, dyeing and printing, finishing. The main pollutants are organic matters which come from the pre-treatment process of pulp, cotton gum, cellulose, hemicellulose and alkali, as well as additives and dyes using in dyeing and printing processes. Pre-treatment wastewater accounts for about 45% of the total, and dyeing/printing process wastewater accounts for about 50% - 55%, while finishing process produces little. In China, chemical fiber accounts for about 69% of total in which polyester fibers accounts for more than 80%. Cotton accounts for 80% of the natural fiber production. Therefore, the dyeing wastewater analysis of production and pollution is based on these two fibers. Pre-treatment of cotton includes desizing and scouring. The main pollutants are the impurities in the cotton, cotton gum, hemicellulose and the slurry, alkali in weaving process. The current average COD concentration in the pre-treatment is 3000 mg/L. The main pollutants in dyeing/printing are auxiliaries and the residual dyes. The average concentration of COD is 1000 mg/L and the total average concentration is 2000 mg/L after mixing. Pre-treatment of polyester fibers mainly involves in the reduction with alkali. The so-called reduction is treating the polyester fabric with

8% of sodium hydroxide at 90°C for about 45 minutes. Some polyester fabrics will peel off and decompose into terephthalic acid and ethylene glycol so that a thin polyester fabric will have the feel of silk. This process can be divided into continuous and batch type. Taking the batch type as an example, the concentration of COD is up to 20000 mg/L-60000 mg/L. The wastewater from reduction process may account for only 5% of the volume of wastewater, while COD accounts for 60% or more in the conventional dyeing and finishing business. The Chroma is one pollutant of the wastewater which causes a lot of concerns. In the dyeing process, the average dyeing rate is more than 90%. It means that the residual dyeing rate in finishing wastewater is about 10%, which is the main reason of contamination. According to the different dyes and process, the Chroma is 200 to 500 times higher than before. pH is another factor of the dyeing wastewater. Before the printing and the dyeing process, pH is another factor, the pH of dyeing wastewater remains between 10 and 11 when treated by alkali at high temperature around 90°C in the process of desizing, scouring and mercerization. Polyester base reduction process mainly uses sodium hydroxide, and the total pH is also 10 to 11. Therefore, most dyeing water is alkaline and the first process is to adjust the pH value of the textile dyeing wastewater. The total nitrogen and ammonia nitrogen come from dyes and raw materials, which is not very high, about 10 mg/L. But the urea is needed while using batik techniques. Its total nitrogen is 300 mg/L, which is hard to treat. The phosphorus in the wastewater comes from the phosphor detergents. Considering the serious eutrophication of surface water, it needs to be controlled. Some enterprises use trisodium phosphate so that the concentration of phosphorus will reach 10 mg/L. So, this phosphorus must be removed in the pre-treatment. In the production process, suspended substance comes from fiber scrap and un dissolved raw materials. It will be removed through the grille, grid, etc. The suspended solids (SS) in the outflow mainly come from the secondary sedimentation tank, whose sludge has not been separated completely which will reach 10-100 mg/L as usual. Sulfide mainly comes from the sulfur, which is a kind of cheap and qualified dye. Due to its toxicity, it has been forbidden in developed countries. However, in China, some enterprises are still using it, so it has been included in the wastewater standards. The sulfide in the wastewater is about 10 mg/L. There are two main sources of hexavalent chromium. Cylinder engraving makes the wastewater containing hexavalent chromium. However, this technology has not been used. Another possible source is the use of potassium dichromate additive in hair dyeing process. Aniline mainly comes

from the dyes. The color of the dye comes from the chromophore. Some dyes have a benzene ring, amino, etc., which will be decomposed in the wastewater treatment process.

2.6 Textile wastewater treatment processes

The textile dyeing wastewater has a large amount of complex components with high concentrations of organic, high-color and changing greatly characteristics. Owing to their high BOD/COD, their coloration and their salt load, the wastewater resulting from dyeing cotton with reactive dyes are seriously polluted. As aquatic organisms need light in order to develop, any deficit in this respect caused by colored water leads to an imbalance of the ecosystem. Moreover, the water of rivers that are used for drinking water must not be colored, as otherwise the treatment costs will be increased. Obviously, when legal limits exist (not in all the countries) these should be taken as justification. Studies concerning the feasibility of treating dyeing wastewater are very important (Allegre et al. 2006).

In the past several decades, many techniques have been developed to find an economic and efficient way to treat the textile dyeing wastewater, including physicochemical, biochemical, combined treatment processes and other technologies. These technologies are usually highly efficient for the textile dyeing wastewater.

Some selected treatment processes for dyes and color removal of industrial wastewater applied over the time into different textile units are summarized in table 2.16 (Carmen and Daniela 2012)

Table 2.11: treatment processes for dyes and color removal (Carmen and Daniela 2012)

Treatment methodology	Treatment stage	Advantages	Limitations
Physico-chemical treatments			
Precipitation, Coagulation-flocculation	Pre/main treatment	Short detention time and low capital costs. Relatively good removal efficiencies	Agglomerates separation and treatment. Selected operating condition.

Continued Table 2.11: treatment processes for dyes and color removal (Carmen and Daniela 2012)

Treatment methodology	Treatment stage	Advantages	Limitations
Electro kinetic coagulation	Pre/main treatment	Economically feasible	High sludge production
Fenton process	Pre/main treatment	Effective for both soluble and insoluble colored contaminants. No alternation in volume.	Sludge generation; problem with sludge disposal. Prohibitively expensive.
Ozonation	Main treatment	Effective for azo dye removal. Applied in gaseous state: no alteration of volume	Not suitable for dispersed dyes. Releases aromatic dyes. Short half-life of ozone (20 min)
Oxidation with NaOCl	Post treatment	Low temperature requirement. Initiates and accelerates azo-bond cleavage.	Cost intensive process. Release of aromatic amines
Adsorption with solid adsorbents such as:			
Activated carbon	Pre/post treatment	Economically attractive. Good removal efficiency of wide variety of dyes.	Very expensive; cost intensive regeneration process

Continued Table 2.11: treatment processes for dyes and color removal (Carmen and Daniela 2012)

Treatment methodology	Treatment stage	Advantages	Limitations
Peat	Pre treatment	Effective adsorbent due to cellular structure. No activation required.	Surface area is lower than activated carbon
Coal ashes	Pre treatment	Economically attractive. Good removal efficiency.	Larger contact times and huge quantities are required. Specific surface area for adsorption is lower than activated carbon.
Wood chips/wood sawdust	Pre treatment	Effective adsorbent due to cellular structure. Economically attractive. Good Adsorption capacity for acid dyes	Long retention times and huge quantities are required.
Silica gels	Pre treatment	Effective for basic dyes	Side reactions prevent commercial application
Irradiation	Post treatment	Effective oxidation at lab scale	Requires a lot of dissolved oxygen
Photochemical process	Post treatment	No sludge production	Formation of by-products

Continued Table 2.11: treatment processes for dyes and color removal (Carmen and Daniela 2012)

Treatment methodology	Treatment stage	Advantages	Limitations
Electrochemical oxidation	Pre treatment	No additional chemical required and the end products are non-dangerous/hazardous	Cost intensive process; mainly high cost of electricity.
Ion exchange	Main treatment	Regeneration with low loss of adsorbents	Specific application; not effective for all dyes.
Biological Treatments			
Aerobic process	Post treatment	Partial or complete decolorization for all classes of dyes	Expensive treatment
Anaerobic process	Main treatment	Resistant to wide variety of complex colored compounds. Bio gas produced is used for stream generation.	Longer acclimatization phase.
Single cell (Fungal, Algal & Bacterial)	Post treatment	Good removal efficiency for low volumes and concentrations. Very effective for specific color removal.	Culture maintenance is cost intensive. Cannot cope up with large volumes of WW.
Emerging treatments			

Continued Table 2.11: treatment processes for dyes and color removal (Carmen and Daniela 2012)

Treatment methodology	Treatment stage	Advantages	Limitations
Other advanced oxidation process	Main treatment	Complete mineralization ensured. Growing number of commercial applications.	Cost intensive process
Membrane filtration	Main treatment	Removes all dye types; recovery and reuse of chemicals and water	High running cost. Concentrated sludge production. Dissolved solids are not separated in this process.
Photo catalysis	Post treatment	Process carried out at ambient conditions. Inputs are no toxic and inexpensive. Complete mineralization with shorter detention times.	Effective for small amount of colored compounds. Expensive process.
Sonication	Pre treatment	Simplicity in use. Very effective in integrated systems.	Relatively new method and awaiting full scale application.
Enzymatic treatment	Post treatment	Effective for specifically selected compounds.	Enzyme isolation and purification is tedious.

The various methods of treatment of textile wastewater are as follows:

- Physical treatment
- Chemical treatment
- Biological treatment
- Advanced oxidation processes

2.6.1 Physical Treatment

Physical processes such as sedimentation, equalization, segregation, filtration (e.g., sand filter) are capable of removing the suspended solids, however the removal of organic load is found to be negligible. Physical processes followed by physico-chemical or biological process show good results.

2.6.1.1 Adsorption

One of the most effective and proven treatment with potential application in textile wastewater treatment is adsorption. This process consists in the transfer of soluble organic dyes (solutes) from wastewater to the surface of solid, highly porous, particles (the adsorbent). The adsorbent has a finite capacity for each compound to be removed, and when is ‗spent' must be replaced by fresh material (the ‗spent' adsorbent must be either regenerated or incinerated). The principal influencing factors in dye adsorption are dye/adsorbent interaction, adsorbent surface area, particle size, temperature, pH, and contact time. Adsorbents which contain amino nitrogen tend to have a significantly larger adsorption capacity in acid dyes. Commonly used adsorbents are activated carbon, silicon polymers and kaolin. Different adsorbents have selective adsorption of dyes. Adsorption is an economically feasible process for dyes removal or decolorization of textile effluents being the result of two mechanisms adsorption and ion exchange.

- **Adsorption with activated carbon**

Activated carbon has been engineered for optimal adsorption of the contaminants found in dyehouse effluents: large, negatively charged or polar molecules of dyes. Powdered or granularactivated carbon (specific surface area of 500-1500 m^2/g; pore volume of 0.3-1 cm^3/g; bulk density of 300-550 g/L) has a reasonably good color removal capacity when is introduced in

a separate filtration step. The activated carbon is used as granulate (GAC) in columns or as powder (PAC) in batch wise treatment into a specific treatment tank or basin. High removal rates are obtained for cationic mordant and acid dyes (Anjaneyulu et al., 2005), and a slightly lesser extent (moderate) for dispersed, direct, vat, pigment and reactive dyes (Cooper, 1995; Nigam et al., 2000) with consumable doses of 0.5-1.0 kg adsorbent/m^3 wastewater (i.e. dye removal of 60-90%). Activated carbon has selection to adsorb dyes, it can effectively remove the water-soluble dyes in wastewater, such as reactive dyes, basic dyes and azo dyes, but it can't adsorb the suspended solids and insoluble dyesThe adsorption on activated carbon without pretreatment is impossible because the suspended solids rapidly clog the filter, and may be feasible in combination with flocculation-sedimentation treatment or a biological treatment (Matsui et al. 2005; Ramesh et al. 2007).

2.6.1.2 Irradiation

The irradiation treatment is a simple and efficient procedure for eliminating a wide variety of organic contaminants, and as well disinfecting harmful microorganism using gamma rays or electron beams (e.g., source for irradiation can be a monochromatic UV lamps working under 253.7 nm). A high quantity of dissolved oxygen is required for an organic dye to be effectively broken down by irradiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. Irradiation treatment of a secondary effluent from sewage treatment plant reduced COD, TOC and color up to 64%, 34% and 88% respectively, at a dose of 15 K Gy gamma-rays (Borrely et al. 1998). The efficiency of irradiation treatment increases when used catalyst as titanium dioxide (Krapfenbauer et al. 1999).

2.6.1.3 Membrane separation process

- **Reverse osmosis**

Reverse osmosis membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate. Decolorization and elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step by reverse osmosis. Reverse osmosis permits the removal of all mineral salts, hydrolyzed reactive dyes, and chemical auxiliaries. It must be noted that higher the concentration of dissolved salt, the more important

the osmotic pressure becomes; therefore, the greater the energy required for the separation process (Ramesh et al. 2007).

- **Nano filtration**

Nano-Filtration was used for the treatment of Colored effluents from the textile industry; mainly in a combination of adsorption (for decreasing of concentration polarization during the filtration process) and Nano filtration (NF modules are extremely sensitive to fouling by colloidal material and macromolecules). NF membranes are generally made of cellulose acetate and aromatic polyamides, and retain low-molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzed reactive dyes, and dyeing auxiliaries. Inorganic materials, such as ceramics, carbon based membranes, zirconia, are also used in manufacturing NF and RO membranes. Typical NF flux rates are 5 to 30 GFD (Gross Flow per Day) (Naveed et al. 2006). A performance of above 70% color removal for a NF plant was reported working at 8 bar/18°C, with four polyether-sulphonate membranes with molecular weight cut offs of 40, 10, 5 and 3 kda for three different effluents coming from dyeing cycle of textile industry (Alves and Pinho, 2000). Values of color removal higher than 90% were reported for single NF process, and also combination MF and NF, in the case of different effluents from textile fabrics processing. An important problem is the accumulation of dissolved solids, which makes discharge of treated effluents in watercourses almost impossible. NF treatment can be an alternative fairly satisfactory for textile effluent decolorization.

- **Ultrafiltration**

Ultra-filtration is used to separate macromolecules and particles, but the elimination of polluting substances such as dyes is never complete (only 31-76% dyes removal). The quality of treated wastewater does not permit its reuse for sensitive processes, such as textile dyeing (Ramesh et al. 2007) but permit recycling of 40% treated wastewater in stages in which salinity is not a problem, such as rinsing, washing, etc. Ultrafiltration can only be used as a pretreatment for reverse osmosis (Ciardelli and Ranieri, 2001) or in combination with a biological reactor (Mignani et al., 1999) or to remove metal hydroxides (reducing the heavy metal content to 1 ppm or less) (Naveed et al., 2006). UF membranes are made of polymeric materials (i.e. polysulfone,

polypropylene, nylon-6, poly tetra fluoro ethylene (PTFE), polyvinyl chlorides (PVC), acrylic copolymer etc.

- **Microfiltration**

Micro-filtration is mainly used for treatment of dye baths containing pigment dyes as well as for subsequent rinsing baths (Ramesh et al. 2007). Chemicals that cannot be filtrated by microfiltration will remain in the dye bath. Microfiltration can be used as a pretreatment for Nano filtration or reverse osmosis (Ghayeni et al. 1998), and also to separate suspended solids, colloids from effluents or macromolecules with pores of 0.1 to 1 micron. MF performance is typically of >90% for turbidity or silt density index. Microfiltration membranes are made of specific polymers such as Poly (Ether Sulfone), Poly (Vinylidiene Fluoride), Poly (Sulfone), Poly (Vinylidene Di fluoride), Polycarbonate, Polypropylene, Poly Tetra fluoroethylene (PTFE), etc.

2.6.1.4 Equalization and homogenization

This phase of the process is simple but very important, as its aim is to make the feeding in the oxidation phase the most constant possible with reference to polluting parameters and flow. In this phase air is used in order to move the whole wastewater as well as to avoid the development of anaerobic fermentation areas inside the accumulation unit, which may produce bad smell. It is necessary to supply air, providing in the meantime the movement of the wastewater. Equipment like mixers and air injectors create a whirling movement and a complete mixture of the wastewater. Feeding in the biological phase is realized by means of a pump system that transfers the water assuring a constant flow of water during the 24 hours to the oxidation unit. Hydraulic retention time is generally about 8 h. It is very important to keep all particulate matters in suspension, i.e., to avoid settling of solids.

2.6.1.5 Floatation

The floatation produces a large number of micro-bubbles in order to form the three-phase substances of water, gas, and solid. Dissolved air under pressure may be added to cause the formation of tiny bubbles which will attach to particles. Under the effect of interfacial tension,

buoyancy of bubble rising, hydrostatic pressure and variety of other forces, the micro-bubble adheres to the tiny fibers. Due to its low density, the mixtures float to the surface so that the oil particles are separated from the water. So, this method can effectively remove the fibers in wastewater.

2.6.2 Chemical Process

2.6.2.1 Coagulation flocculation sedimentation

It is clearly known that the Colored colloid particles from textile effluents cannot be separated by simple gravitational means, and some chemicals (e.g., ferrous sulphate, ferric sulphate, ferric chloride, lime, polyaluminium-chloride, polyaluminium-sulphate, cationic organic polymers, etc.) are added to cause the solids to settle. These chemicals cause destabilization of colloidal and small suspended particles (e.g. dyes, clay, heavy metals, organic solids, oil in wastewater) and emulsions entrapping solids or the agglomeration of these particles to flocs large enough to settle (flocculation) or highly improve further filtration (Zaharia et al.2006; Zaharia et al. 2007). In the case of flocculation, anionic and non-ionic polymers are also used.

Coagulation-flocculation refining methods are generally used in order to eliminate organic materials. Coagulant materials are usually effective on dyeing substance which is not decomposed. They have effects on decomposed dyeing substance. The disadvantages of the system are excessive cost, excessive mud and costfor removing that mud (Gaehr et al. 1994).

Chemical coagulation-flocculation (C-F) and precipitation of textile wastewater reduced the load on the biological treatment, working with polyaluminium chloride along with an organic polymer (Lin & Chen, 1997) or ferrous/ferric chloride and a commercial organic coagulant aid at pH of 6.7-8.3 (color removal> 80%) (Venkat et al. 1999). Other efficient textile treatments mentioned by different textile operators consist in coagulation-flocculation followed by membrane technology especially for recycling textile effluents.

2.6.2.2 Ionic exchange

The ion exchange process has not been widely usedfor treatment of dye-containing effluents, mainly because of the general opinion that ion exchangers cannot accommodate a wide range of

dyes (Slokar and Marechal, 1997). The ionic exchange occurs mainly based on the interaction of ionic species from wastewater with an adsorptive solid material, being distinguished from the conventional adsorption by nature and morphology of adsorptive material or the inorganic structure containing functional groups capable of ionic exchange (Macoveanu et al. 2002). The mechanisms of ionic exchange process are well known, and two principal aspects must be mentioned

(1) Ionic exchange can be modeling as well as adsorption onto activated coal;

(2) The ion exchangers can be regenerated without modifying the equilibrium condition (e.g., by passing of a salt solution containing original active groups under ion exchanger layer).

In the case of wastewater treatment, the effluent is passed over the ion exchanger resin until the available exchange sites are saturated (both cationic and anionic dyes are removed). The ionic exchange is a reversible process, and the regenerated ion exchanger can be reused.The essential characteristic of ionic exchange that makes distinction of adsorption is the fact that the replace of ions takes place in stoichiometric proportion (Macoveanu et al. 2002). The effluent treatment by ionic exchange process contributes to the diminishing of energetic consumption and recovery of valuable components under diverse forms, simultaneously with the wastewater treatment. In practice, the ion exchangers are used in combination with other wastewater treatments. The main advantages of ion exchange are removal of soluble dyes, no loss of adsorbent at regeneration, and reclamation of solvent after use. The important disadvantages of this process are the cost, organic solvents are expensive, and ion exchange treatment is not efficient for dispersedyes (Robinson et al. 2001).

2.6.2.3 Electrocoagulation

An advanced electrochemical treatment for dye and color removal is electrocoagulation (EC) that has as main goal to form flocs of metal hydroxides within the effluent to be cleaned by electro-dissolution of soluble anodes. EC involves important processes as electrolytic reactions at electrodes, formation of coagulants in aqueous effluent and adsorption of soluble or colloidal pollutantson coagulants, and removal by sedimentation and flotation. This treatment isefficient even at high pH for color and COD removals being strongly influenced by the current density

and duration of reaction. The EC treatment was applied with high efficiency for textile Orange II and Acid red 14 dye-containing effluents (i.e. > 98% color removal) (Daneshvar et al. 2003) or Yellow 86 dye-containing wastewater (i.e. turbidity, COD, extractible substances, and dye removal of 87.20%, 49.89%, 94.67%, and 74.20%, after 30 min of operation, current intensity of 1 A, with mono polar electrodes) (Zaharia et al. 2005) when iron is used as sacrificial anode. In general, decolorization performance in EC treatment is between 90-95%, and COD removal between 30-36% under optimal conditions (Ramesh et al. 2007).

2.6.2.4 Chemical oxidation

Chemical oxidation process is based on the transference of the electrons among chemical samples. This process can also be called reduction and raising process. The aim of chemical oxidation is to transform a substance in the water into ambivalent or last product by being oxidized chemically. Oxidation implements like Clorur, sodium hiphoroclit, ozone and hydrogen perocsit have been used as an oxidant (Arici 2000; Copper 1995).

- **Fenton reaction**

Oxidative processes represent a widely used chemical method for the treatment of textile effluent, where decolorization is the main concern. Among the oxidizing agents, the main chemical is hydrogen peroxide (H_2O_2), variously activated to form hydroxyl radicals, which are among the strongest existing oxidizing agents and are able to decolorize a wide range of dyes. A first method to activate hydroxyl radical formation from H_2O_2 is the so called Fenton reaction, where hydrogen peroxide is added toan acidic solution (pH=2-3) containing Fe^{2+} ions. Fenton reaction is mainly used as a pre-treatment for wastewater resistant to biological treatment or toxic to biomass. The reaction is exothermic and should take place at temperature higher than ambient. In large scale plants, however, the reaction is commonly carried out at ambient temperature using a large excess of iron as well as hydrogen peroxide. In such conditions ions do not act as catalyst and the great amount of total COD removed has to be mainly ascribed to the $Fe(OH)_3$ co-precipitation. The main drawbacks of the method are the significant addition of acid and alkali to reach the required pH, the necessity to abate the residual iron concentration, too high for discharge in final effluent, and the related high sludge production (Sheng et al.1997).

- **Ozone oxidation**

Ozone is a powerful oxidizing agent (oxidation potential, $E° = 2.07$ V) capable of cleavage the aromatic rings of some textile dyes and decomposition of other organic pollutants from industrial effluents. The ozone decomposes the organic dyes with conjugated double bonds forming smaller molecules with increased carcinogenic or toxic properties, and so Ozonation may be used alongside a physical method to prevent this (i.e. irradiation, membrane separation, adsorption, etc). Ozone can react directly or indirectly with dye molecules. In the direct pathway, the ozone molecule is itself the electron acceptor, and hydroxide ions (i.e. pH > 7-8) catalyze the auto decomposition of ozone to hydroxyl radicals ($\cdot$OH) in aqueous effluents (very strong and non-selective oxidants) which react with organic and inorganic chemicals. At low pH ozone efficiently reacts with unsaturated chromophoric bonds of a dye molecule via direct reactions (Adams and Gorg, 2002). The main advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. A disadvantage of Ozonation is its short half-life, typically being 20 min, the destabilization bythe presence of salts, pH, and temperature, and the additional costs for the installationof Ozonation plant. The improvement of Ozonationperformance is obtained in combination with irradiation (Surpateanu and Zaharia, 2004; Zaharia et al. 2009) or with a membrane filtration technique (Lopez et al., 1999). Treatment of dye-containing wastewater with ozone followed by chemical coagulation using $Ca(OH)_2$ indicated 62% color removal after Ozonation (Sarasa et al. 1998).

2.6.3 Biological wastewater treatment methods

Biological treatments are considered reproduction, artificially or otherwise, of self-purification phenomena existing in natural environment. There are different biological treatments, performed in aerobic or anaerobic or combined anaerobic/aerobic conditions. The processing, quality, adaptability of microorganisms and the reactor type are decisive parameters for removal efficiency (Bornick and Schmidt, 2006). Biological treatment process for decolorization of industrial effluents is ambiguous, different and divergent (Anjaneyulu et al. 2005). The most currently used biodegradation involve aerobic microorganisms, which utilize molecular oxygen as reducing equivalent acceptor during the respiration process. But biodegradation in anaerobic environment conditions (anoxic and hypoxic environments) also occurs, and survival of

microorganisms is possible by using sulphate, nitrates and carbon dioxide as electron acceptors (Birchet et al. 1989). Research data indicates that certain dyes are susceptible to anoxic/anaerobic decolorization, and also that an anaerobic step followed by an aerobic step may represent asignificant advancement in biological decolorization treatment in future (Ong et al. 2005). The treatment plant that receives dye-containing effluents has high potential to form toxic biodegradation products such as toxic amines, benzidine and its derivate, etc. To avoid that risk, anaerobic or aerobic sequential reactor systems seem to be an efficient procedure (i.e. efficient color removal takes place during the anaerobic treatment, and high reduction of aromatic amines and other organic compounds occurs during the subsequent aerobic treatment). Under aerobic conditions, most of the azo dye metabolites are quickly degraded by oxidation of the substituents or of the side branches. However, some of them are still rather recalcitrant. Successful removal of poorly degradable amines was often achieved by adaptation of microorganisms (i.e. acclimatization of biological sludge to nitroaniline containing wastewaters; after gradual adaptation, the microorganisms are able to eliminate 3- and 4-nitroaniline simultaneously) (Bornick and Schmidt, 2006).

2.6.3.1 Aerobic biological treatment

Biological treatment with _activated sludge' was the most used in large scale textile effluent treatment, and the trickling filter or biological aerated filter (BAF) is an alternative, permitting a 34-44% dye-color removal for different high dyeing loads of industrial effluents. Biological aerated filters involve the growth of an organism on inert media that are held stationary during normal operation and exposed to aeration. In aerobic conditions, the mono- and dioxygenase enzymes catalyze the incorporation of dissolved oxygen into the aromatic ring of organic compounds prior to ring fission. Although azo dyes are aromatic compounds, their nitro and sulfonic groups are quite recalcitrant to aerobic bacterial degradation (Dos et al., 2004). The batch experiments with aerobic activated sludge confirmed the biodegradability of sulphonated azo dyes. Only aerobic degradation of the azo dyes is possible by azo reduction (i.e. high color removal (>90%) of Red RBN azo dye-containing effluents (3000 mg/L) working with Aeromonas hydrophila the specific optimal conditions of pH (5.5-10), temperature (20°-38°C), and time (8 days), and mineralization does not occur. The sub sequential anaerobic and aerobic

bioreactor was able to completely remove the sulphonated azo dye (i.e. MY10) at a maximum loading rate of 210 mg/L per day (Tan et al., 2000). The degradation of azo dyes (i.e. Acid Red 151; Basic Blue 41; Basic Red 46, 16; Basic Yellow 28, 19) in an aerobic biofilm system indicated 80% color removal (Anjaneyulu et al., 2005). The improvement of dye biodegradation performance (i.e. >90% color removal) are made by adding activated carbon (PAC) or bentonite in aeration tank.

2.6.3.2 Activated sludge process

Activated sludge is a kind of flocs which is mainly comprised of many microorganisms, which has strong decomposition and adsorption of the organics, so it is called ―activated sludge". The wastewater can be clarified and purified after the separation of activated sludge. Activated sludge process is based on the activated sludge whose main structure is the aeration tank. Activated sludge Process is an effective method. As long as according to the scientific laws, after getting some experiences, higher removal efficiency can be got. In present treatment, the oxidation ditch and SBR process are the commonly used activated sludge process.

- **Oxidation ditch process**

Oxidation ditch is a kind of biological wastewater treatment technology, which developed by the Netherlands health engineering research institute in the 50's of last century. It is a variant of activated sludge, which is a special form of extended aeration.The secondary sedimentation tank also can be omitted in some processes. It has many characteristics, such as high degree of purification, impact resistance, stable, reliable, simple, easy operation and management, easy maintenance, low investment and energy consumption.Oxidation ditch forms aerobic zone, anoxic zone and the anaerobic zone in space, which has a good function of denitrification.

- **Sequencing Batch Reactor Activated Sludge process**

Sequencing Batch Reactor Activated Sludge Process (SBR Process) is a reform process from activated sludge, which is a new operating mode. Its operation is mainly composed of five processes: 1. inflow; 2. reaction; 3. sedimentation; 4. outflow; 5. standby. SBR treatment process not only has a high removal rate of COD, but also has a high removal efficiency of color.

Compared to the traditional methods, using SBR process has the following advantages (Li-yan et al.2001).

2.6.3.3 Biofilm

The biofilm process is a kind of biological treatment that making the numerous microorganisms to attach to some fixed object surface, while letting the wastewater flow on its surface to purify it by contact. The main types of the biofilm process are biological contact oxidation, rotating biological contactors and biological fluidized bed.

- **Biological contact oxidation**

Biological contact oxidation is widely used inthe dyeing wastewater treatment. The main feature of the process is to set fillers in the aeration tanks, so that it has the characteristics of activated sludge and biofilm. The wastewater inoxidation tank contains a certain amount of activated sludge, while the fillers are covered with a large number of biofilm. When the wastewater contact with the fillers, it can be purified under the function of aerobic microorganisms.

- **Rotating Biological Contactor**

Rotating Biological Contactor is an efficient sewage treatment plant developed on the basis of the original biological filter. It is constituted by a series of closed disks which are fixed on a horizontal axis. Under the catalysis of enzyme, though absorbing the dissolved oxygen in the water film, microorganism can oxidize and decompose the organic matter in the sewage and excrete the metabolite at the same time. In the process of disk rotation, the biofilm on the disk get in touch with the sewage and the air constantly alternating, completing the process of adsorption-oxidation-oxidative decomposition continuously to purify the sewage. The advantages of the Biological Rotating Contactor are power saving, large shock load capability, no sludge return; little sludge generated, little noise, easy maintenance and management and so on. On the contrary, the shortcomings are the large area and needing the maintain buildings.

- **Biological fluidized bed**

Fluidized bed process is also called suspended carrier biofilm process, which is a new efficient sewage treatment process. The substance of this method is that using activated carbon, sand, anthracite or other particles whose diameter is less than 1mm as the carrier and filling in the container. Through pulse water, the carrier is made into fluidization and covered by the biofilm on its surface. Due to the small size of thecarrier, it has a great surface area in unit volume (the carrier surface area can reach 2000-3000 m^2/m^3), and can maintain a high level of microbial biomass. The treatment efficiency is about 10-20 times higher than conventional activated sludge process. It can remove much organic matter in short time, but the land acreage is only about 5% of the common activated sludge process.

2.6.3.4 Anaerobic biological treatment

Anaerobic biodegradation of azo and other water-soluble dyes is mainly reported as an oxidation-reduction reaction with hydrogen, and formation of methane, hydrogen sulphide, carbon dioxide, other gaseous compounds, and releasing electrons. The electrons react with the dye reducing the azo bonds, causing the effluent decolorization. Azo dye is considered an oxidizing agent for the reduced flavin nucleotides of the microbial electron chain, and is reduced and decolorized concurrently with reoxidation of the reduced flavin nucleotides (Robinson et al. 2001). An additional carbon organic source is necessary, such as glucose which is a limiting factor in scale set-up technology application. The azo and nitro- components are reduced in anoxic sediments and in the intestinal environment, with regeneration of toxic amines (Banat et al.,1996). Anaerobic decolorization of textile effluents (e.g., color removal of >99% for an Orange II, Black 2HN under anaerobic condition, more than 72 h) is not yet well established although successful pilot-scale and full-scale plants are very well operating (Tan et al. 2000).

2.6.4 Biochemical and physicochemical combination processes

In recent years, as the application of new technologies in textile and dyeing industry, a large number of difficult biodegradable organic matter such as PVA slurry, surface active agents and new additives enter into the dyeing wastewater, which result in the high concentration of the organic matter, complex and changeable composition and the obvious reduction of the

biodegradability. The COD, Cr, removal rate of the simple aerobic activated sludge process which was used to treat the textile dyeing wastewater has decreased from 70% to 50%, and the effluent cannot meet the discharge standards. More seriously, quite a number of sewage treatment facilities cannot normally operate even stop running. Therefore, the biochemical and physicochemical combination processes has been gradually developed. And its application is increasingly widespread (Sheng et al. 2008). The types of the combination process are various, and the main adoptions currently are as following:

- Hydrolytic acidification-contact oxidation-air floatation process
- Anaerobic-aerobic-biological carbon contacts
- Coagulation-ABR-oxidation ditch process
- UASB-aerobic-physicochemical treatment process

Table 2.12: possible treatments for cotton textile wastes and their associated advantages and disadvantages

Process	Advantage	Disadvantages	References
Biodegradation	Rates of elimination by oxidation substances about 90%	Low biodegradability of dyes	Pala and Tokat, 2002; Ledkowicz et al. 2001.
Coagulation-Flocculation	Elimination of insoluble dyes	Production of sludge blocking filter	Gaehr et al. 1994
Process	Advantage	Disadvantages	References
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon	Arslan et al. 2000.
Ozone treatment	Good decolorization	No reduction of the COD	Adams et al. 1995; scott and Ollis, 1995

Continued Table 2.12: possible treatments for cotton textile wastes and their associated advantages and disadvantages.

Electrochemical process	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge	Lin and peng, 1994; Lin and chen, 1997
Reverse osmosis	Removal of all mineral salts hydrolyzes reactive dyes and chemical auxiliaries	High pressure	Ghayeni et al. 1998
Nano filtration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentration	-	Erswell et al. 1998 Xu et al. 1999; Akbari et al., 2002; Tang and Chen, 2002.
Ultrafiltration-microfiltration	Low pressure	Insufficient quality of the treated wastewater	Waters et al. 1991; Rott and Mike, 1999; Clardelli and Ranieri, 2001; Ghayeni et al., 1998

2.6.5 Advanced Oxidation process (AOP)

Advanced oxidation processes in a broad sense, refers to a set of chemical treatment procedures designed to remove organic and sometimes inorganic materials in water and waste water by oxidation through reactions with hydroxyl radicals (•OH). A wide range of organic compounds is detected in industrial and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in biological treatment systems due to their resistance to biodegradation and toxic effects on microbial

processes. As a result, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. Among them, AOPs have already been used for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals. Moreover, they have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes. The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions comparing to conventional oxidants such as H_2O_2 or $KMnO_4$ (Gogate and Pandit, 2004
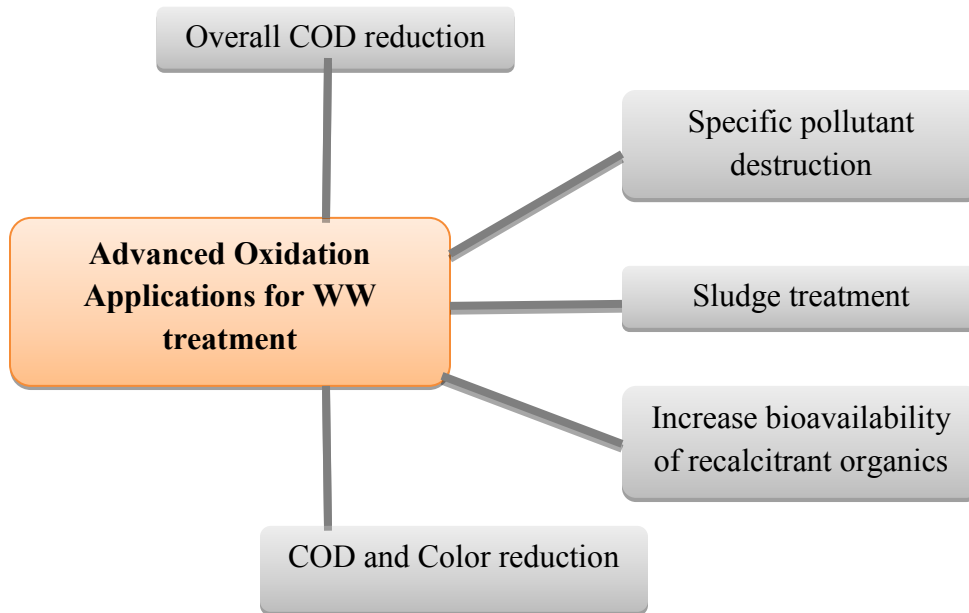
Figure 2.1: Application of AOP'S for wastewater treatment

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Table 2.13: List of typical AOP systems

With Irradiation	Without Irradiation
Homogeneous system	
O_3/ ultraviolet (UV)	O_3/ H_2O_2
H_2O_2 / UV	O_3/ OH^-
Electron beam	H_2O_2 / Fe^{-2} (Conventional Fenton)
Ultrasound (US)	
H_2O_2 / US	
UV / US	
H_2O_2 / Fe^{-2} / UV – Photo-Fenton	
Heterogeneous systems	
Ti O_2 / O_2 / UV	Electro- Fenton
Ti O_2 / H_2O_2 / UV	

AOPs hold several advantages that are unparalleled in the field of water treatment:

- It could effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase.
- Rapid reaction rates
- Due to the remarkable reactivity of -OH, it virtually reacts with almost every aqueous pollutant without much discrimination. AOPs could therefore be applicable in many, if not all, scenarios where many organic contaminants are expected to be removed at the same time.
- Some heavy metals could also be removed in forms of precipitated M(OH)x.
- In some AOPs designs, disinfection could also be achieved, leading AOPs to an integrated solution to some of the water quality problems.
- Since the complete reduction product of -OH is H_2O_2, AOPs theoretically do not introduce any new hazardous substances into the water.

2.7 Kinetic scheme of Fenton's Process

Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic was not applied until the late 1960s. Fenton's reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water.

Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the reaction (Kitis et al.1999, Yoon et al. 2001, Lu et al. 2001)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \qquad\qquad (4)$$

The ferrous iron (Fe^{2+}) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \quad \text{(chain initiation)} \qquad (4)$$

$K_1 = 70\ M^{-1}\ s^{-1}$ (Figg et al. 1954)

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^- \quad \text{(Chain termination)} \qquad (5)$$
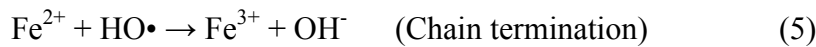
$k_2 = 3.2 \times 10^8\ M^{-1}\ s^{-1}$ (Buxton and Greenstock, 1988)

Moreover, the newly formed ferric ions may catalyze hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in equation 6-10.

$$Fe^{3+} + H_2O_2 <-> \ Fe\text{-}OOH^{2+} + H^+ \qquad\qquad (6)$$
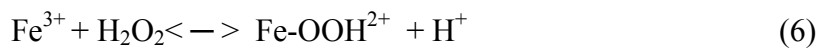
$K_3 = 0.001\text{-}0.01 M^{-1}s^{-1}$ (walling and Goosen, 1973)

$$Fe\text{-}OOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \qquad\qquad (7)$$

The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction (reactions 6 and 7) [wailing and Goosen, 1973; De laat and Gallard, 1999]

$$Fe^{2+} + HO_2 \bullet \rightarrow Fe^{3+} + HO_2^- \tag{8}$$

$K_5 = 1.3 \times 10^6 M^{-1}s^{-1}$ at pH = 3, (Bielski et al. 1985)

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \tag{9}$$

$K_6 = 1.2 \times 10^6 M^{-1}s^{-1}$ at pH = 3, (Bielski et al. 1985)

$$OH \bullet + H_2O_2 \rightarrow H_2O + HO_2 \bullet \tag{10}$$

$K_7 = 3.3 \times 10^7 M^{-1}s^{-1}$ (Buxton and Greenstock, 1988)

As seen in the reaction 10, H_2O_2 can act as an OH• scavenger as well as an initiator (reaction 7)

Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals (R•), which are highly reactive and can be further oxidized (walling and kato, 1971); (Venkatadri and Peters, 1993); (Lin and Lo, 1997)

$$RH + OH \bullet \rightarrow H_2O + R \bullet \rightarrow \text{further oxidation} \tag{11}$$

Since $k_7 = 10^7 M^{-1}s^{-1}$ while $k_2 > 10^8$ (10) can be made unimportant by maintaining a high $[RH]/[H_2O_2]$ ratio.

If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2, water and in the case of substituted organics, inorganic salts if the treatment is continued.

Walling (1975) simplified the overall Fenton chemistry (reaction 7) by accounting for the dissociation water

$$2 Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{12}$$
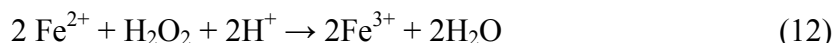
This equation suggests that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidation (Hickey et al. 1995).

In the presence of organic substrate (RH), excess ferrous ion, and at low pH, hydroxyl radicals can add to the aromatic or heterocyclic rings (as well as to the unsaturated bonds of alkenes or alkynes)

They can also abstract a hydrogen atom, initiating a radical chain oxidation (Walling 1975; Lipenzynska et al. 1995)

$$RH + OH\bullet \rightarrow H_2O + R\bullet \text{ (Chain propagation)} \qquad (13)$$

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \qquad (14)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (15)$$

The organic free radicals produced in reaction (13) and then be oxidized by Fe^{3+}, reduces by Fe^{2+}, or dimerised according to the following reactions (Tang and Tassos, 1997)

$$R\bullet + Fe^{3+} \text{ -oxidation} \rightarrow R^+ + Fe^{2+} \qquad (16)$$

$$R\bullet + Fe^{2+} \text{ -reduction} \rightarrow R^- + Fe^{3+} \qquad (17)$$

$$2R\bullet \text{ -dimerization} \rightarrow R\text{-}R \qquad (18)$$
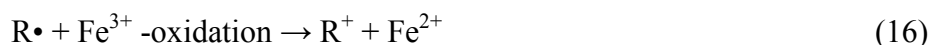
The sequence of reactions (4), (5), (13) and (16) constitute the present accepted scheme for the Fenton's reagent chain.

The ferrous ions generated in the above redox reactions (11) and (12) react with hydroxide ions to form ferric hydroxo complexes according to (walling and kato, 1971), (Lin and Lo, 1997)

$$[Fe(H_2O)_6]^{3+} + H_2O <\text{-}> [Fe(H_2O)_5OH]^{2+} + H_3O^+ \qquad (19)$$

$$[Fe(H_2O)_5OH]^{2+} + H_2O <\text{-}> [Fe(H_2O)_4(OH)_2] + H_3O^+ \qquad (20)$$
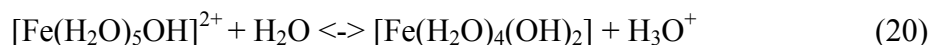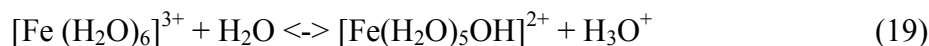
Within pH 3 and 7, the above complexes become

$$2[Fe(H_2O)_5OH]^{2+} <\text{-}> [Fe(H_2O)_8(OH)_2]^{4+} + 2H_2O \qquad (21)$$

$$[Fe(H_2O)_8(OH)_2]^{4+} + H_2O <\text{-}> [Fe_2(H_2O)_7(OH)_3]^{3+} + H_3O^+ \qquad (22)$$

$$[Fe_2(H_2O)_7(OH)_3]^{3+} + [Fe(H_2O)_5OH]^{2+} <\text{-}> [Fe_2(H_2O)_7(OH)_4]^{5+} + 2H_2O \qquad (23)$$
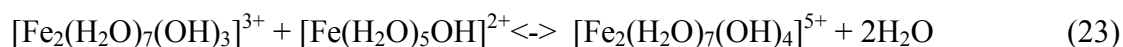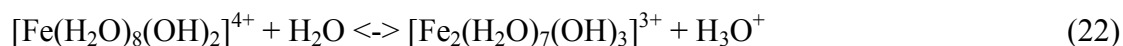
Which accounts for the coagulation capability of Fenton's reagent. Dissolved suspended solids are captured and precipitated. It should be noted that large amounts of small flocs are considerably observed in the Fenton oxidation step. Those flocs take a very long time, sometimes overnight to settle out. Chemical coagulation using polymer is therefore necessary. Fenton's reagent is known to have different treatment functions, as mentioned earlier, depending on the $H_2O_2/FeSO_4$ ratio. When the amount of Fe^{2+} employed exceeds that of H_2O_2, the treatment tends to have the effect of chemical oxidation.

Reaction 16 competes with both the chain termination reaction (reaction 5) and with the propagation reaction (13) of Fenton chemistry. This competition for hydroxyl radical between Fe^{2+}, RH and Fe^{3+} leads to the non-productive decomposition of hydrogen per-oxide and limits the yield of hydroxylated (oxidized) organic compounds. Therefore, the stoichiometric relationship between Fe^{2+}, RH and Fe^{3+} has to be established to maximize the efficiency of the degradation process.

One of the advantages of the Fenton's process with regard to other oxidation techniques is that no energy input is necessary to activate hydrogen peroxide, because the reaction takes place at atmospheric pressure and at room temperature. Furthermore, this method requires relatively short reaction times and uses easy-to-handle reagents.

The main disadvantages are the high cost of hydrogen peroxide and the fact that the homogeneous catalyst, added as iron salt, cannot be retained in the process thus requiring further separation to prevent additional water pollution. In order to avoid the continuous loss of catalyst and the need of removing iron after the treatment, which increases the cost, heterogeneous catalysts, can be used.

2.8 Effects of various parameters on COD, Color and Turbidity removal in Fenton's process

The major parameters affecting Fenton's process are solution's pH, amount of ferrous ions, concentration of H_2O_2, initial concentration of the pollutant and presence of other ions (Gogate and Pandit, 2004). The optimum pH for Fenton's reagent processes ranges from 2 to 4. At pH higher than 4, the Fe^{2+} ions are unstable and they are easily transformed to Fe^{3+} ions, forming

complexes with hydroxyl. Moreover, under alkaline conditions H_2O_2 loses its oxidative power due to its breakdown to oxygen and water (Niaounakis and Halvadakis, 2006).
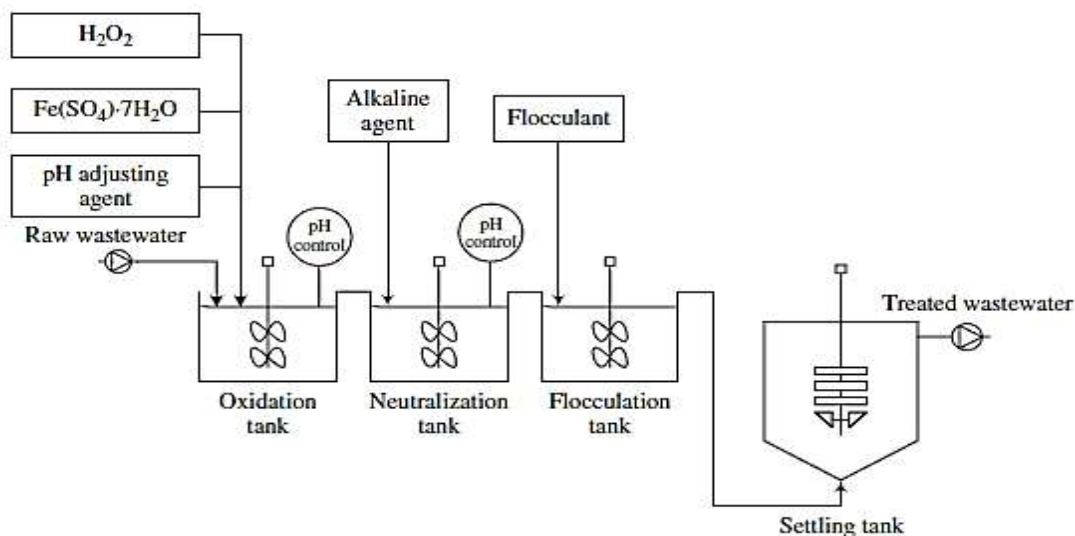
Figure 2.2: Typical scheme of Fenton's treatment

Due to the above, wastewater pH adjustment is usually needed before treatment with Fenton's processes. Increase of ferrous ions and H_2O_2 concentration results to an increase of degradation rate (Lin and Lo, 1997). However, having in mind the toxicity of H_2O_2 to several microorganisms, the use of excess amounts of H_2O_2 could possibly deteriorate overall degradation efficiency for cases that Fenton's process is followed by biological oxidation (Gogate and Pandit, 2004). Fenton oxidation of organic compounds is inhibited by phosphate, sulfate, fluoride, bromide and chloride ions. Inhibition by these species may be due to precipitation of iron, scavenging of HO• or coordination to dissolved Fe(III) to form a less reactive complex (Pignatello et al. 2006).

2.8.1 Effect of Fenton's oxidation reaction time

The time needed to complete a Fenton's reaction will depend on the many variables, most notably catalyst dose and wastewater strength. Decolorization studies reported that much longer oxidation times such as 15 min (Kang and Chang, 1997) and 40–90 min (Kuo, 1992) were

needed to achieve a significant removal. It was also discovered that in the first 10 min of the Fenton's reaction, more than 90% of COD removal can be achieved. Fenton's oxidation process is not only effective for decolorization of dyes but degradation of aromatic Amines is also possible at pH 3 (Tantak, 2006). The change of mean oxidation state of organic carbon is shown in Figure 2.3 (Zhang et al. 2005).
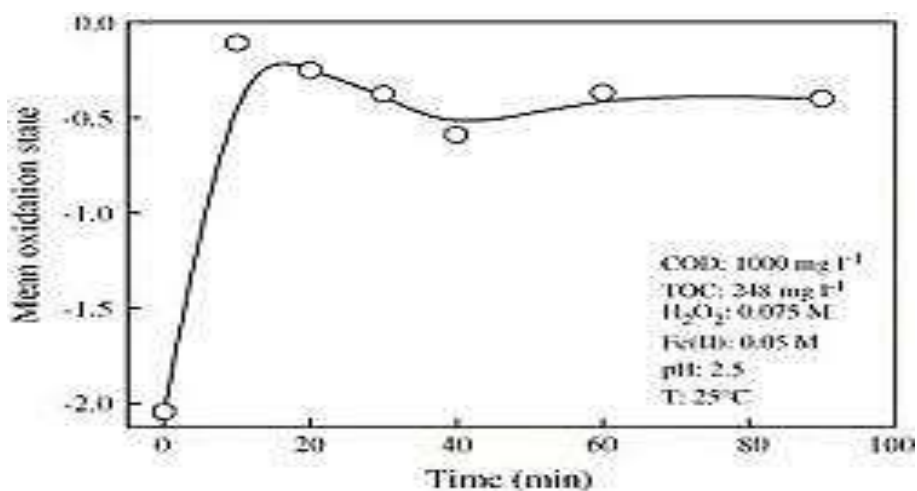
Figure 2.3: Evolution of mean oxidation state with time.

The original organic materials were drastically changed by Fenton's reagent to other more highly oxidized by- products. However, ultimate conversion of organic carbon to inorganic carbon was not completed. It indicated that early oxidation reactions were both partial oxidations (primary degradation and/or acceptable degradation) and ultimate conversion to inorganic carbon with an abundant amount of hydroxyl radicals but further reactions with residual hydroxyl radicals prevailed partial oxidations rather than ultimate conversion. Residual ferrous iron and hydrogen peroxide was measured during Fenton's reaction.

2.8.2 Effect of pH

The pH is the key parameter of the treatment efficiency for Fenton's reagent. The Fenton's process has the highest efficiency when the pH is around 3. At higher pH, the oxidation efficiency of Fenton's reagent may decrease because ferric ions could form $Fe(OH)_3$ (Snoeyink and Jenkins, 1982). $Fe(OH)_3$ has a low activity and will not react with hydrogen peroxide (Lu et

al. 2001). The ferric ions in the solution that can react with hydrogen peroxide are so reduced is the rate-limiting step. When the pH is too low and the concentration of hydrogen ions is too high, it will slow down the formation of $FeOOH^{2+}$ which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well.

Szpyrkowicz, 2001 found Fenton reaction presents its maximum catalytic activity at pH 2.8–3.0, which drastically diminishes with an increase or a reduction of this pH value. At pH higher than 3 Fe^{3+} starts precipitating as $Fe(OH)_3$ and breaks down the H_2O_2 into O_2 and H_2O preferently. Besides, the formation of Fe(II) complexes at high pH values leads to a drop of the Fe^{2+} concentration. (Benitez, 2001) On the other hand, Fe^{2+} regeneration by the reaction of Fe^{3+} with H_2O_2 is inhibited at more acidic pH values (Pignatello JJ, 1992).
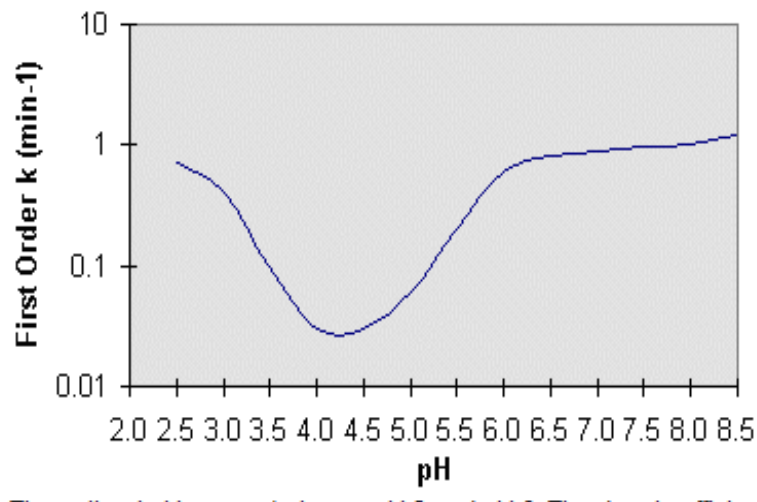
Figure 2.4: Effect of pH on Fenton's reagent

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals.

2.8.3 Effect of doses of Fenton's reagents

Hydrogen peroxide and Ferrous sulphate plays an important role as an oxidizing agent in Fenton's oxidation process. Doses of Fenton's reagent determine, to a large extent, the operating

costs and efficiency of organics removal for the process. Determining optimal doses involves consideration of both levels and their relative ratio. Generally, removal of organics increases with increasing concentration of iron salt. However, the removal increment may be marginal when the concentration of iron salt is high. A similar trend is observed for H_2O_2. Also, excess iron salt contributes to an increase in effluent TDS and electrical conductivity, as well as in the amount of iron sludge flotation, due to O_2 off gassing caused by auto decomposition of excess H_2O_2 (Kim et al. 2001; Lau et al. 2001) and residual H_2O_2 may inhibit downstream biological treatment. When low doses of Fenton's Reagent are used (e.g., < 10-25 mg/L H_2O_2), some research suggests ferrous iron may be preferred.

Haddad et al., 2014 find increase of Fe^{3+} concentration, decreases the mineralization efficiency, this may be due to the increase of a brown turbidity that hinders the absorption of light required for the Fenton process and to scavenging effects of hydroxyl radicals by Fe^{3+} and Fe^{2+} since these parasitic reactions become competitive at higher Fe^{2+} or Fe^{3+} concentrations. The decrease in the decolorization can be explained by the redox reaction since hydroxyls radicals HO• are scavenged by the reaction with another Fenton's reagent Fe^{2+} by the following reactions:

$$Fe^{2+} + HO• \rightarrow HO• + Fe^{3+} \qquad (2)$$
$$H_2O_2 + HO• \rightarrow HO_2• + H_2O \qquad (3)$$
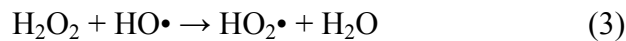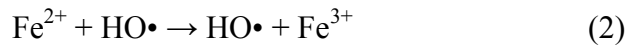
The dose of H_2O_2 and the concentration of Fe^{2+} are two relevant factors affecting the Fenton's process, being both closely related. The H_2O_2 dose has to be fixed according to the initial pollutant concentration. It is frequent to use an amount of H_2O_2 corresponding to the theoretical stoichiometric H_2O_2 to chemical oxygen demand (COD) ratio (Lucking 1998) although it depends on the response of the specific contaminants to oxidation and on the objective pursued in terms of reduction of the contaminant load. In Fenton's reagent, the H_2O_2 doses could be referred to as the stoichiometric weight ratio between the hydrogen peroxide and COD, R = H_2O_2/COD =2.125, which are calculated assuming the complete oxidation of COD:

1 g COD = 1 g O_2 = 0.03125 mol O_2 = 0.0625 mol H_2O_2 = 2.125 H_2O_2 (Marco and Jose, 2009)

2.9 Fenton's Oxidation as wastewater treatment technique

- At a work in 1991 Sedlak and Andren studied Chloro-benzene and found that all the intermediate products disappeared within 2 hr. intermediates have been identified using GC/MS analysis. Product distribution is dependent on the presence or absence of oxygen. Reaction pathway has been also proposed. Optimum pH was in the range of 2-3. Experiment was done with 500 ml capacity Fenton reactor maintained at $25^{o}c$. Operating pH varied in the range 2-7. Addition of Fe^{2+} ions at rate of 5 ml/h or as bulk quantity of 10 ml at the start. Addition of hydrogen peroxide at the rate of 5 mM/h.

- Lin and Lio studied effluent containing poly-vinyl alcohol and two dyes as Blue G and Black B in 1997. At their work they have found that the extent of degradation rapidly decreases above pH of 3. With the increase in the $FeSO_4$ concentration and keeping the H_2O_2 concentration same, the extent of COD removal increases. Hydrogen peroxide may also interfere in the COD measurements and hence amount of the same should be adjusted such that it is completely utilized. Optimum operating temperature was observed to be $30^{0}c$ above which the increase in COD removal is marginal. Chemical coagulation after Fenton oxidation treatment helps in keeping the concentration of soluble iron within the limits. Experiments were done using a Fenton reactor; 2 l beaker equipped with variable mixer and cooling jacket for temperature control. Initial concentration of pollutant was 1500 mg/L, operating pH was in the range of 2-5 and time of treatment was 1 hr.

- In 1999 Lin and his co-workers analyzed Surfactant wastewater containing alkyl benzene sulfonate and linear alkyl benzene sulfonate. Optimum treatment time was calculated based on the variation of residual concentration of hydrogen peroxide in the stream. After a particular time, the concentration starts leveling off. Optimum pH of 3 has been observed. Optimum concentration of $FeSO_4$ and H_2O_2 were obtained as 90 and 60 mg/L, respectively. Subsequent treatment with chemical coagulation is recommended for improving the settling characteristics. Kinetic analysis has also been presented and reaction is reported to be of first order with respect to concentration of reactants where the rate constant is also dependent on the concentration of $FeSO_4$ and H_2O_2. In the experimental studies simple stirred reactor with capacity of 2 l beaker was used.

FeSO$_4$concentration was varied in the range of 30-180 mg/L whereas hydrogen peroxide concentration was in the range 20-80 mg/L. Time of treatment was 3hr.

- In 1999 Arslan carried out his studies with Dye house effluent. It was observed that the effluent had to be diluted 40 times before measureable degradation occurred. The rate constant for the degradation was estimated at 0.9521 min-1 and it was quite higher as compared to hydrogen peroxide/UV combination technique and lower as compared with the photo-Fenton's oxidation. Additional UV irradiation to the Fenton's oxidation system results in enhanced utilization of hydrogen peroxide (it increased from 39% to 82%) and hence the degradation efficiencies are better. The COD removal was only approximately 25% indicating that Fenton's oxidation system alone is not sufficient.

- In the year 2000 Kang and Hwang examined real effluent with COD of approximately 1500 mg/L. the COD removal efficiency was shown to be the maximum around a reaction pH of 3.5 and it drastically decreased above a pH of 6. COD removal efficiency increased with an increase in the FeSO$_4$ doses (Till a concentration of 500 mg/L beyond which the removal efficiency remains constant) and hydrogen peroxide doses.(2 L capacity Fenton reactor operated at constant temperature of 25°c and mixed with a magnetic stirrer. pH varied in the range 2-9. FeSO$_4$ doses in the range of 250-2250 mg/L and hydrogen peroxide dose in the range of 0-1600 mg/L.

- Benitez (2001) studied p-hydroxy-penyl acetic acid in his study. He observed that percentage degradation increased with an increase in the concentration of ferrous ions and hydrogen peroxide whereas it decreased with an increase in the initial concentration of pollutant. Optimum pH has been obtained again at 3. Type of the buffer solution used for adjustment of the pH also plays a crucial role in the degradation efficiency. Acetate, phosphate as well as sulfate buffers were found to retard the degradation. Detailed kinetic analysis has been presented. For the experimental purpose 500 ml capacity Fenton reactor agitated with the help of a mechanical stirrer. Operating pH as 3 and temperature of 20°c with Fe^{2+} and H$_2$O$_2$ concentration varied in the range 0.25-5 mM and 50-200μM, respectively.

- Benitez investigated different chloro-phenols (2001). Fenton oxidation was found to be not effective in degradation of chloro-phenols studied in the work (only 4 chlorophenol

showed 55% removal in 80 min of treatment time; rest all viz 2,4 –dichlorophenol, 2, 4, 6-trichlorophenol, 2, 3, 4, 5-tetra chlorophenol and tetra-cholrophenol showed less than 10% degradation). Kinetic analysis has been presented for 4- chlorophenol and a first order fit is observed. Reactor filled with 350 ml of effluent with initial concentration as 0.3 mM was used in the laboratory. operating temperature was fixed at 25°c. Initial concentration of ferrous ions and hydrogen peroxide was kept at 0.01mM and 0.5 mM, respectively.

- Chamarro analyzed different organic compounds viz formic acid, acetic acid, 4-chlorophenol, 2, 4-dichlorophenol and nitrobenzene in 2001. Hydrogen peroxide doses were found to be sufficient at molar ration of 3 with respect in the organic compound. Extent of mineralization increased with an increase in the concentration of ferrous ions possibly due to enhanced formation of hydroxyl radicals. Optimum molar ratio of Fe to hydrogen peroxide was estimated at 0.1:10. It has been shown that complete mineralization using Fenton's oxidation alone requires considerable time as well as very high doses of the oxidants and hence is recommended only for improving the biodegradability. Fenton's reactor used was 30ml capacity vials and operated at room temperature. The ferrous ion dose was varied in the range 0.01-1 per unit compound whereas H_2O_2/compound molar ratio was varied in the range 0.1-50.

- Rivas observed ρ- hydroxy-benzoic acid in 2001 and showed that increase in the concentration of both ferrous ions as well as hydrogen peroxide led to an increase in the removal of the pollutant, however, an optimum concentration of ferrous ion was observed at 5mM. Hydrogen peroxide is observed to be completely utilized in the reaction and is the limiting reactant in deciding the overall rate. Increase in pH from 3 to 7 decreased the rates, appreciably, an increase in the operating temperature from 10 to 40°c showed no change on the extent of degradation. Intermediate products have been identified and mechanism for the destruction of pollutant has been presented along with a detailed kinetic model for the process. In the experiment Fenton reactor was operated at a constant capacity of 1 l. ferrous ion concentration was varied in the range of 0-0.01 M whereas hydrogen peroxide concentration was varied in the range of 0-4 M. operating temperature of 20°c and pH of 3.2 concentration of pollutant is fixed at 0.01M.

- In 2001 Arslan and Balcioglu analyzed the wastewater of simulated dye bath. Only hydrogen peroxide gave no degradation indicating that the generation of hydroxyl radical is a must. Fenton oxidation system gave a TOC removal of 80.8% for an initial TOC loading of 200 mg/l with a pseudo-first order rate constant of 0.12 l/min. the rate constant was found to be 100% more as compared to photo catalytic oxidation using near UV light (pH of 4) but slightly less than that of Ozonation (pH of 12 and ozone loading of 2340 mg/l). Use of Fe^{3+} ions instead of Fe^{2+} ions reduced the rate constant by approximately 30%. (Fenton reactor used has a capacity of 1000 ml made up of borosilicate glass and operated in batch mode for 1 h. the concentration of Fe^{3+} and H_2O_2 was fixed at 0.5 mM and 5mM, respectively, with operating pH of 3.

- In 2001 Chang et al. examined phenanthrene; variation of the residual concentration of the pollutant with time indicated that chemical reaction in the initial period was rapid and reached equilibrium degradation within 20 min (up to 70% removal depending on the ferrous ion concentrations). The optimum conditions as obtained in the work can be given as ferrous solution concentration of 7.2 mM, hydrogen peroxide concentration of 103 mM and mixing speed of 150 rpm. With respect to the pollutant concentration the optimum conditions can be given as molar ratio of phenanthrene ferrous: hydrogen peroxide = 1:7:97

CHAPTER THREE

METHODOLOGY

3.1 Introduction

The textile processing industries produce wastewater which is one of the main sources of pollution of the rivers, canals and require proper management. The stages of textile production are fiber production, fiber processing and spinning, yarn preparation, fabric production, bleaching, dyeing and printing and finishing. Textile wastewater treatment for industrial reuse or disposal remains as a complicated problem due to higher levels of chemical oxygen demand (COD), biological oxygen demand (BOD) and total dissolved solids (TDS) content and Non-biodegradable nature of organic dye stuffs present in the effluent.

3.2 Sample Collection

3.2.1 Sampling Location

The wastewater used in this study was raw effluent from Polmol Textile Industry, a Textile Manufacturing Company located in Mauna, Sreepur, Gazipur. The company manufactures various cotton fabrics which involved some complicated processes like dyeing and finishing. The production plant drains into the treatment plant. The plant treats and discharges water into the local water body.

The impact and contribution to pollution by industries depend on process technology, size, nature of products, characteristic and complexity of waste discharged. Textile wastewater from dyeing and finishing processes has been a serious environmental threat for years (Can et al. 2006). Wastewater from dyeing may contain residual of reactive dyes and chemicals used as fixer, binder, thickener, etc. For the experimental process the Raw samples were taken from outlets of the dyeing process and finishing section.

Combined effluent before discharging into natural drains was collected from Deep bore well of a Textile industry which is located in Sikalbaha, Chittagong. In case of combined effluent a sample

directly after Fenton's treatment and another sample which was filtered after Fenton's Process were analyzed.

3.2.2 Sampling program

The objective of sampling was to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes while still accurately representing the material being sampled. Samples met the requirements of the sampling program and handled so that it does not deteriorate or become contaminated or compromised before it is analyzed. Plastic bottles were used for collecting the samples. Air bubbles were removed and the containers were capped immediately. Amount of each sample was 10 liters. Samplings were carried out on the 28th November, 2012 to 27th December, 2012 and 22nd July, 2013.

Figure 3.1 shows the brief description of research methodology.
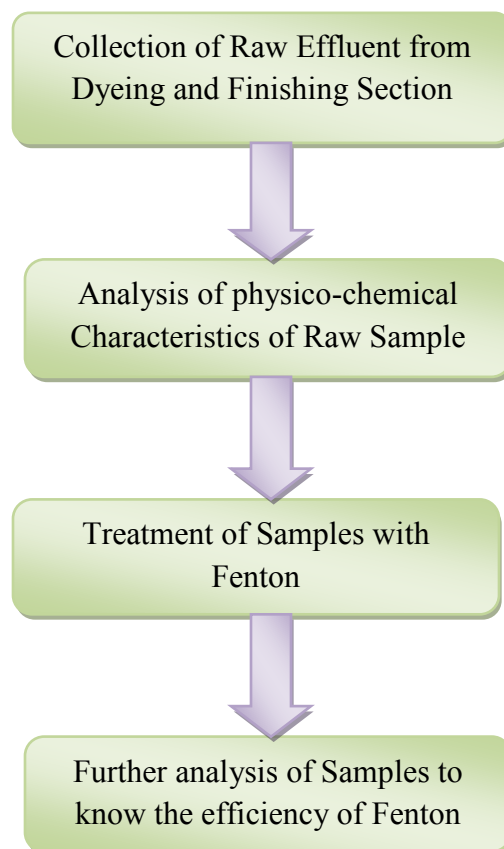
Figure 3.1: Flowchart showing different stages of experimental study

Proper standard collection of samples for analysis is of great importance. Representative combined samples were tested in the laboratory for the assessment of the existing pollutants and treatment options. The collected samples were transported to laboratory quickly and then samples were preserved in refrigerator in accordance with the standard methods. All possible efforts were made to minimize the time lag between collection and analysis so that no significant change may occur in the quality of the samples. Prior to the experiments, large particles and debris were removed to minimize particulate effects in oxidation reactions.

3.3 Analysis of Effluent Quality

Characteristics of the samples were determined through extensive laboratory analysis. Important parameters that are tested in the laboratory are given below:

- pH
- Chloride (Cl^-)
- Turbidity
- Color
- Alkalinity
- Biochemical oxygen demand (BOD_5)
- Total Dissolved Solid (TDS)
- Total Suspended Solid (TSS)
- Total Solid (TS)
- Chemical Oxygen Demand (COD)
- EC

- NH_3-N (T)
- NO_3-N
- SO_4
- S^{-2}
- NO_2-N
- Cu
- Cd
- Cr
- Pb
- Zn

Parameters were analyzed by method given in APHA (1995) standard methods. The pH is a logarithmic scale generally used to express the acidic, alkaline or neutral nature of a solution.The pH is an essential factor to be estimated in each and every phase of water and wastewater treatment. Digital pH meter was used for the determination of pH of the sample. In case of wastewater the biological treatment involves decomposition of organic matter available in wastewater by different species of aerobic bacteria. The growth and activity of these depend on the pH level in wastewater. Generation and emission of malodorous gases are also controlled by pH variations. In chemical treatment of wastewater, the coagulation of

wastewater, dewatering of sludge and oxidation of certain substances such as cyanide are also pH dependent processes.

EC is an important parameter to assess the wastewater quality. It is a measure of ionic concentration. It is an indicator of salinity also and measured in $\mu S/cm$. It can be measured accurately in the field using a portable conductivity probe and meter. The most accurate way to determine water's turbidity is with an electronic turbidimeter. The turbidimeter has a light source and a photoelectric cell that accurately measures the light scattered by suspended particles in a water sample. In this study 2100P Turbidimeter was used. The concentrations of dissolved species were determined by DR-4000U Spectrophotometer. UV-visible at the following wavelengths:

- NO_3-N was determined at $\lambda = 400$ nm (cadmium reduction method, using Nitra ver 5 Nitrate reagent)
- Ammonia nitrogen at $\lambda = 425$ nm (Nessler reagent, using Nessler reagent, Mineral stabilizer and polyvinyl Alchohol Dispersing Agent 8038).

Total alkalinity was measured by titration with 0.02N H_2SO_4. BOD_5 is the difference of the dissolved oxygen concentration of the sample and measured by incubation in the dark at $20^{o}c$ for 5 days. Suspended and dissolved solids were dried to a constant weight at $105^{o}c$. In summary, testing for dissolved solids involves weighing a clean beaker to the nearest mg. Fill the beaker with test water and evaporate off the water. Weigh the beaker again with the resulting residue. Then subtract the two results to determine the amount of milligrams of residue per liter of water.

Chloride (Cl^-) was determined by Mohr method. The COD is considered mainly the representation of pollution level of domestic and industrial wastewater or contamination level of surface, ground and potable water. The COD values include the oxygen demand created by biodegradable as well as non-biodegradable organic substances because it involves oxidation of organic matter withstrong oxidizing chemicals. As a result, COD values are greater than BOD and may be much greater when significant amounts of biologically resistant organic matter is present. COD digester (Hatch DR/ 2010) was used for the digestion of samples in the process of COD determination.

The water samples were analyzed for metals by atomic absorption method and spectrometer AAS 6800 was used.

3.4 Fenton's treatment

Several attempts were made to minimize the chemical doses and the sludge production from each process. Additionally, the operation mode was adjusted to enhance the COD and color removal rates. Overall COD and color removal efficiencies under various operating conditions were investigated. Specifically absolute doses of Fenton's reagents, oxidation reaction time, and initial pH, pH during Fenton coagulation are described in this work.

In the experiment, a beaker equipped with a glass bar was used as a reactor; work was carried out by taking sample water into the beaker. Initial pH of sample water was adjusted to the desired value with concentrated sulfuric acid (H_2SO_4) such as for Fenton's oxidation to get the pH value below 5.0. The next step involves the addition of a definite amount of solid ferrous sulfate ($FeSO_4 \cdot 7H_2O$). To start up the Fenton's reaction, 30% (w/w) hydrogen peroxide (H_2O_2) solution was added. Figure 3.2 shows the schematic of batch experimental apparatus for the Fenton's process.
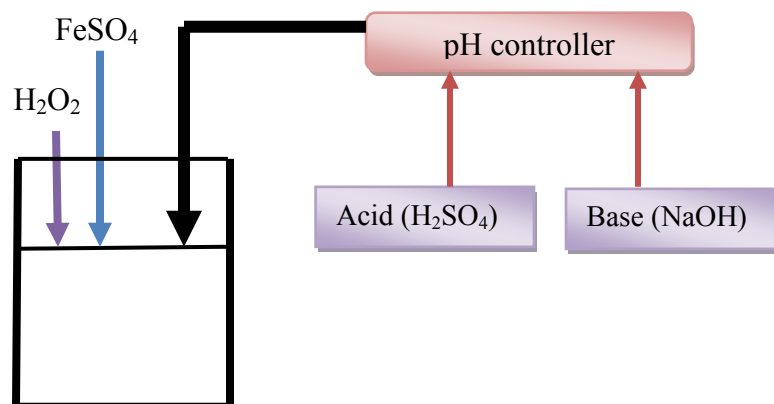
Figure 3.2: Schematic diagram of Fenton's reactor

The samples were mixed using glass rod for oxidation process to take place and left for different reaction time. After the reaction, rapid mixing at 45 rpm for 1 min, slow mixing at 25 rpm for 14 min was done. For Fenton Coagulation pH greater than 6.0 was maintained. The pH was

controlled with an accuracy of ± 0.02 by adding either sodium hydroxide or sulfuric acid prior to the mixing process, if necessary. Then samples were allowed to sediment for periods of 30 min to settle down the produced sludge. After the precipitation, the upper liquid was separated from the precipitate to find out the efficiency of the Fenton's oxidation-coagulation process. These steps were repeatedly done for several parametric changes to assess the effects on COD, color and Turbidity removal efficiency. A flow diagram is shown in figure 3.3 to express the different process that has been carried out during the Fenton's process.

```
┌──────────┐   ┌──────────┐   ┌──────────┐   ┌──────────┐   ┌──────────┐
│   Raw    │→  │Initial pH│→  │Addition of│→ │ Addition │→  │ Reaction │
│  Sample  │   │Adjustment│   │FeSO₄.7H₂O │   │ of H₂O₂  │   │   Time   │
└──────────┘   └──────────┘   └──────────┘   └──────────┘   └──────────┘
                                                                  │
                                                                  ↓
┌────────────────────┐   ┌─────────────┐   ┌────────┐   ┌──────────┐
│Collection of       │←  │Sedimentation│←  │ Mixing │←  │    pH    │
│supernatant for     │   │             │   │        │   │ Control  │
│analyzing the       │   │             │   │        │   │          │
│treated sample      │   │             │   │        │   │          │
└────────────────────┘   └─────────────┘   └────────┘   └──────────┘
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Figure 3.3: Schematic of the Experimental procedure for Fenton's process

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

Textile industry involves wide range of raw materials, machineries and processes to engineer the required shape and properties of the final product. The main cause of generation of effluent is the use of huge volume of water either in 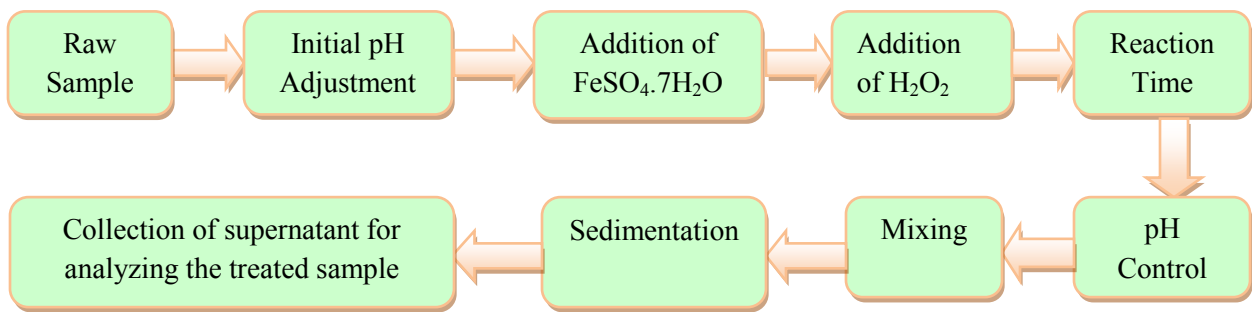the actual chemical processing or during re-processing in preparatory, dyeing, printing and finishing. Due to the nature of various chemical processing of textiles, large volumes of waste water with numerous pollutants aredischarged from textile industries. Since these streams of water affect the aquatic eco-system in number of ways such as depleting the dissolved oxygen content or settlement of suspended substances in anaerobic condition, growth of excessive aquatic by introducing nutrients, it demands a special attention. In the past, biological treatment systemshad been used extensively but they are not efficient for the color removal of the more resistant dyes. Therefore, the treatment of waste stream is done by various methods, which include physical, chemical and biological treatment depending on pollution load.

4.2 Characteristics of Textile Effluents

A detailed physico-chemical status of raw effluent is shown in Table 4.1. The Department of Environment (DoE), as per the Environment Conservation Rules-1997 (ECR-1997), has set the following standards for the effluents to be discharged from composite textile plant and large processing unit.

pH

pH is an important factor to that must be considered to remove or reduce ammonia, BOD, COD and other metals. The test results of pH of raw effluent are presented in table 4.1. The pH was found for cotton dyeing effluent as 9.75 and 7.45 for finishing effluent. pH of the dyeing effluent is higher and not satisfy the standards for releasing into inland surface water.

Table 4.1: Concentration of different parameters of raw effluent

Sl No.	Parameters	Unit	Cotton dyeing	Finishing Section	Bangladesh Standard for releasing into Inland surface water
1	pH	-	9.75	7.45	6-9
2	COD	mg/l	875	23500	200
3	BOD$_5$	mg/l	380	2800	50
4	TDS	mg/l	1275	1005	2100
5	TSS	mg/l	80	7288	150
6	TS	mg/l	1355	8293	-
7	Color	pt-co	251	14 (filtered)	-
8	Turbidity	NTU	44.2	5550	-
9	Cr (Total)	ppm	0.008	0.009	0.5
10	Zn	ppm	0.23	0.12	5.0
11	Cu	ppm	0.93	0.12	0.5
12	Cd	ppm	0.0	0	0.05
13	Pb	ppm	0.05	0.02	0.1
14	Chloride (Cl-)	mg/l	190	20	600
15	Alkalinity as CaCO$_3$	mg/l	271	161	-
16	NO$_3$-N	mg/l	14.8	0.9	10.0
17	NH$_3$-N	mg/l	1.8	1.040	5.0
18	NO$_2$-N	mg/l	0.025	0.0445	-
19	SO$_4$	mg/l	29	11.6	-
20	S^{-2}	mg/l	0.088	4.0	1.0
21	EC	mS/cm	5.98	4.1	-

In case of Fenton treatment process, this higher pH required more acid to get favorable pH range of less than 5.0 for Fenton oxidation. Previous studies show that in most the cases dyeing waste water has pH ranging from 7.0-12.99.

Color

The measurement of color is a key test for aesthetic quality of water. The color of the cotton dyeing effluent was found 251 pt-co units and for filtered finishing effluent was found 14 pt-co units. Color is higher due to higher concentration of total solids in the effluent. Though there is no standard limit of color for discharging treated effluent into inland surface water body but US (EPA) allowable limit for that is 150 pt-co units. Color content should be removed from samples for the aesthetic reason.

Turbidity

The results are reported in units called Nephelometric Turbidity Units or NTUs. The turbidity of effluent was found 44.2 NTU and 5550 NTU for cotton dyeing and finishing section respectively.

Alkalinity

The test results of alkalinity of the different sampling points are presented in table 4.1. The alkalinity was 271 mg/l and 161 mg/l as $CaCO_3$ in the effluents.

Electrical Conductivity (EC)

The electrical conductivity of water often been used as an index of the total dissolved solids (TDS) carried by a stream. Since the current flowing through the water is proportional to the concentration of dissolved ions in the water, the electrical conductivity can be measured. The higher the dissolved salt/ion concentration, the more conductive the sample and hence the higher the conductivity reading. The standard procedure is to measure the conductivity in a cubic-centimeter field at 25^0c and can be express the results in µS/cm (micro Siemens/cm). The electrical conductivity of the water depends on the water temperature, the higher the temperature, the higher the electrical conductivity would be. The electrical conductivity of water increases by

2-3% for an increase of 1 degree Celsius of water temperature. EC in sample water was found as 5.98 µS/cm and 4.1µS/cm. EC depends on the overall ionic con centration in water.

Nitrate and Nitrite

The concentration of NO_3 and NO_2 was 0.025 mg/l and 14.8 mg/l respectively for cotton dyeing effluent. The concentration of NO_3 and NO_2 was 0.9 mg/l and 0.0445 mg/l respectively for finishing effluent. They are considered together because conversion from one form to the other occurs in the environment and the health effects of nitrates are generally as a consequence of its ready conversion to nitrites in the body. Ammonia can also be converted to nitrite (NO_2) and nitrate (NO_3) by bacteria, and then used by plants.

Ammonia Nitrogen

Ammoniacal nitrogen (NH_3-N) is a measure for the amount of ammonia which is a toxic pollutant. The test results of NH_3-N of raw effluent are presented in table 4.1. Ammonia is found in water where dissolved oxygen is lacking. The concentration of NH_3-N was 1.8 mg/l and 1.040 mg/l in effluent. Bangladesh industrial effluent standard (DoE, 1997) for NH_3-N is 5.0 mg/l. The concentration of raw effluent was within range.

Sulphate and Sulphide

The concentration of SO_4 & S^{2-} was 29 mg/l & 0.088 mg/l in cotton dyeing effluent and 11.6 mg/l & 4.0 mg/l in finishing effluent respectively. Bangladesh industrial effluent standard (DoE, 1997) for S^{2-} is 1.0 mg/l. Sulfate is a constituent of TDS.

Heavy Metals

Textile wastewater contains substantial pollution loads in terms of heavy metals. According to WHO the metals of most immediate concern are chromium, zinc, lead. Table 4.1 represents the complete picture obtained from the textile waste water. Heavy metals have inhibitory effects on the biological treatment process at the wastewater treatment plants. All the samples contain heavy metals lower than the standard for releasing effluent into Inland surface water.

Total Dissolved Solids (TDS)

Concentrations of dissolved solids were found 1275 mg/l for cotton dyeing effluent & 1005 mg/l for finishing effluent. Bangladesh standard for releasing into inland surface water is 2100 mg/l. the TDS of effluent is satisfy the standard.

Total Suspended Solids (TSS)

Total suspended solids are differentiated from total dissolved solids (TDS), in that the former cannot pass through a sieve of two micrometers and yet are indefinitely suspended in solution. Bangladesh industrial effluent standards (DoE, 1997) for suspended solids are 150 mg/l.

Total Solids (TS)

The test results of total solids of the samples are presented in table 4.1. Total solids were 1355 mg/l and 8293 mg/l in cotton dyeing and finishing effluent respectively.

Chemical Oxygen Demand (COD)

In environmental chemistry, the chemical oxygen demand test is commonly used to indirectly measure the amount of organic compounds in water. It is expressed in milligrams per liter (mg/l), which indicates the mass of oxygen consumed per liter of solution. Older references may express the units as parts per million (ppm). The basis for the COD test is that nearly all organic compounds can be oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. The amount of oxygen required oxidizing an organic compound to carbon dioxide, ammonia and water is called COD, COD does not include the oxygen demand caused by the oxidation of ammonia into nitrate. The process of ammonia being converted into nitrate is referred to as nitrification. The level of COD is a critically important factor in evaluating the extent of organic pollution in textile waste water.

Although COD is comparable to BOD, it actually measures chemically oxidizable matter. Generally COD is preferred to BOD in process control applications because results are more reproducible and are available in a few minutes or hours rather than five days. In many industrial samples, COD testing may be the only feasible course because of the presence of bacterial inhibitors or chemicals that will interfere with BOD determination. The concentration of COD

was found 875 mg/l and 23500 mg/l. Bangladesh industrial effluent standard (DoE, 1997) for COD is 200 mg/l. for disposing into inland surface water. The COD was found higher than the limit. High values of COD and BOD_5, presence of particulate matter and sediments, and oil and grease in the effluent causes depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system.

Fenton's reagent is a suitable chemical means of treating waste waters which are resistant to biological treatment or is poisonous to live biomass. Chemical separation uses the action of sorption or bonding to remove dissolved dyes from textile effluent and effective in color removal and also COD removal.

Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) is a chemical procedure for determining the uptake rate of dissolved oxygen by the biological organisms in a body of water. It is not a precise quantitative test, although it is widely used as an indication of the quality of water. BOD can be used as a gauge of the effectiveness of wastewater treatment plants. The BOD test is widely used to determine the pollution strength or domestic and industrial waste water in terms of the oxygen that they will require if it is discharged into natural water bodies in which aerobic condition exists. The concentration of BOD_5 was found 380 mg/l and 2800 mg/l for cotton dyeing effluent and finishing effluent respectively.

BOD_5: COD ratio

BOD/COD ratio is the conventional index of biodegradability. As a first approximation it could be said that higher this ratio, better the biodegradability. The ratio of BOD/COD is about; COD is higher than that of BOD; maximum of up to 4 times in medium scale industries; but it varies based on the industrial process and nature of the raw materials used. The ratio of BOD_5: COD for raw effluents were 0.43 and 0.12. The low BOD/COD ratio, 0.12, indicates this organic matter is mostly non-biodegradable.

4.3 Fenton's treatment of raw effluent

In Fenton there are mainly two steps: first the oxidation process and secondly the coagulation process. For both these processes there are optimum pH ranges for maximizing organic content removal.

4.3.1 Effect of initial pH during Fenton oxidation on COD, Color and Turbidity removal

Fenton process has a typically sharp, preferred pH region in which it is optimally operated. pH affects the activity of both the oxidant and the substrate, the speciation of iron and hydrogen peroxide decomposition. (Sedlak and Andren, 1991) explained higher hydroxyl radical product yields in the pH range of 2-4 by a reaction involving the organo metallic complex where either hydrogen peroxide is regenerated or reaction rates are increased. Also, it is better to remove inorganic carbons from waste water because they can scavenge hydroxyl radicals (Buxton et al, 1988). Inorganic carbons can be easily removed by controlling the pH to the acidic condition.

Initial pH significantly influenced importance of oxidation relative to coagulation. Essential characteristics of the Fenton's process is that pH in the acidic range strongly favors oxidation. Figure 4.1 and 4.2 showed the effect of initial pH during oxidation on COD, color and turbidity removal. In this experiment, optimum pH 4.0 has been found most effective for Fenton's reagent to oxidize the organic matter. Fig. 4.1 declares the percentage of removal decreases in pH lower and greater than optimal. A pH below optimal can inhibit oxidation in three ways. First, at extremely low pH values, the $[Fe(H_2O)]^{2+}$ formed reacts relatively slowly with H_2O_2 producing less OH radical. Second, the scavenging effect of H^+ on •OH becomes more important at a lower pH (Tang and Huang, 1996). Third, exceptionally low pH can inhibit reaction between Fe^{3+} and H_2O_2. On the other hand, a pH above optimal, especially in the neutral to alkaline range also hinders Fenton oxidation. First, the absence of H^+ can inhibit the decomposition of H_2O_2 to reduce production of •OH. Second, H_2O_2 itself rapidly decomposes to water and oxygen with increasing pH above 5.0 which inhibit oxidation. Third, the ferrous catalyst is deactivated with the formation of ferric conditions, the primary forms of aqueous carbonate system are CO_3^{2-} and HCO_3^-, both well-known •OH scavengers. Finally, the oxidation potential of OH radical decreases with increasing pH from $E_0 = 2.8V$ at pH = 0 to $E_{14} = 1.95$ V at pH = 14 Preliminary

batch tests were conducted to determine the optimum pH. Parameters were determined after 20 minutes of the Fenton oxidation for cotton dyeing effluent.

It is observed from figure 4.1 and 4.2, at pH higher than 4.0 COD removal decreased. With pH rises the quantity of unreacted H_2O_2 increases (Lin and Chen, 1997), causing an apparent increase of the COD of the solution as a consequence of the following reaction:

$$K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2$$

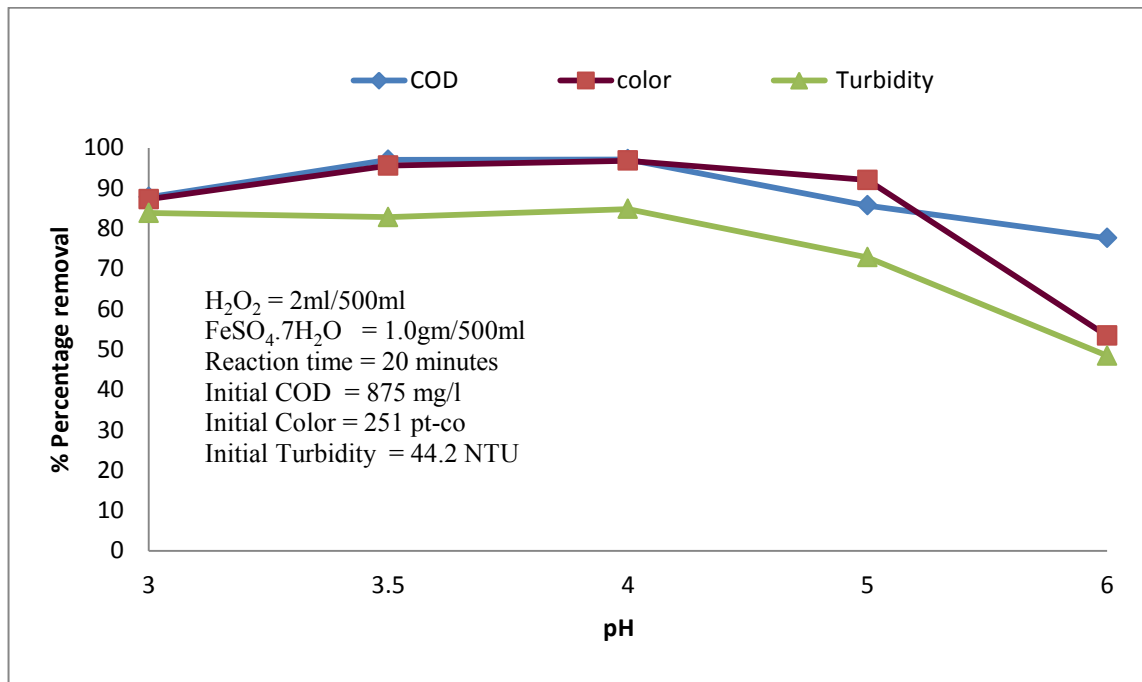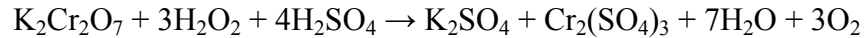Figure 4.1: Effect of initial pH adjustment during Fenton's oxidation on COD, Color and Turbidity removal (Cotton dyeing)

Maximum reduction was achieved in pH 4.0 for finishing effluent. All the test variation has experiences the reduction in the values of tested parameters except for color. In pH 3.0 and 5.0 after Fenton treatment sample has shown a sharp rise in color. It may happen due to the aerial
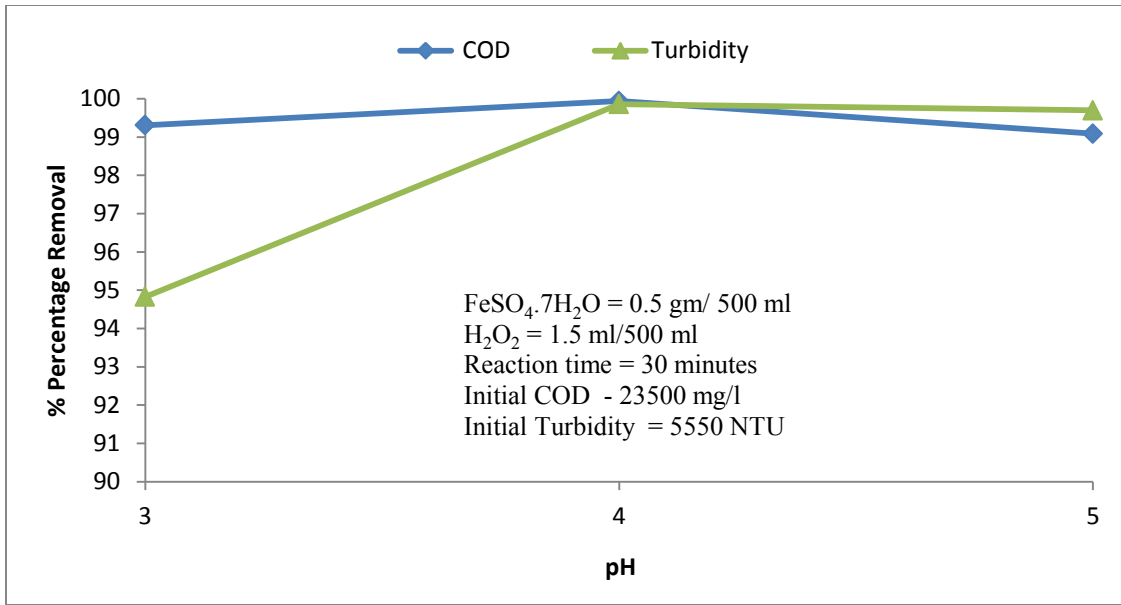
Figure 4.2: Effect of pH during Fenton's oxidation on COD and Turbidity removal (Finishing effluent)

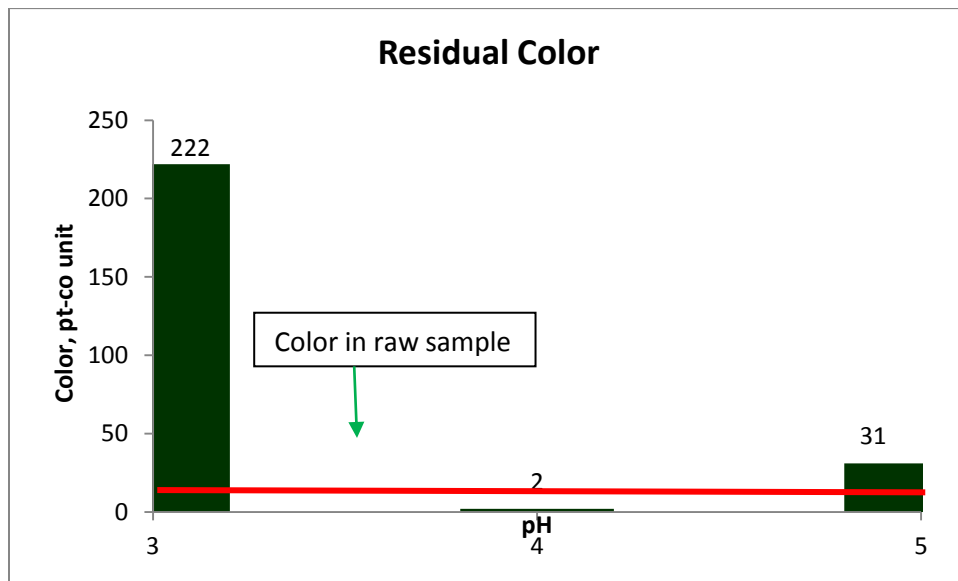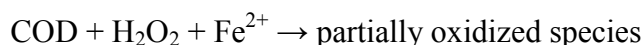Figure 4.3: Residual color after Fenton's process on Finishing effluent.

oxidation of $FeSO_4.7H_2O$ which can be avoided by using Mohr salt and Sulfuric acid. Above pH 4 the decolorization decline because of the decreasing of the free iron species in the solution,

probably due to the formation of Fe^{2+} complex high impeded further reaction of Fe^{2+} and H_2O_2. Moreover it is because of the precipitation of ferric oxy hydroxides. According to the Schulz–Hardy rule, ferric ions have a stronger capability of charge neutralization than ferrous ions. In addition, the solubility product of $Fe(OH)_3$ is much smaller than that of $Fe(OH)_2$. Hence, the ferric salt is applicable as a chemical coagulant than ferrous salt.
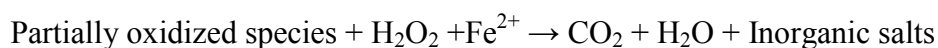
4.3.2 Effect of various doses of H_2O_2 on COD, Color and Turbidity removal

The amount of Fenton's reagent necessary for an effective treatment depends on initial COD strength. This can differ depending on whether the Fenton process has a role of pretreatment or ultimate pretreatment. Experiments were carried out with 500 ml sample. After mixing Fenton reagent with sample, 20 minutes and 30 minutes reaction time was given for samples of cotton dyeing and finishing respectively. Then rapid mixing at 45 rpm for 1 min, slow mixing at 25 for 14 min was performed, followed by sedimentation for periods of 30 minutes was provided to settle down the produced sludge. To find out the optimum doses of Fenton reagents, three to four doses of Fenton reagents were used, the effect of hydrogen peroxide on COD, Turbidity removal and decolonization are evaluated and the results for cotton dyeing effluent are demonstrated in Figures 4.4.

Initial pH of 4.0 and final pH of 6.0 was maintained. In this study a dose of Fe (II) = 1.0 gm/500ml shows that in low dose of peroxide (2.0 ml/500ml) removal of Turbidity is maximum. The extent of oxidation (the degree of direct reduction of COD) depends on the amount of H_2O_2 typically used. In many cases, however, it is not necessary to achieve the complete mineralization of the organic compound in carbon dioxide and water. The partial oxidation in intermediate compounds minimizes the consumption of chemicals reagents and often results in substantial reductions of COD. Generally the reaction of the Fenton system ($H_2O_2 + Fe^{2+}$) to the reduction of COD follows two steps. In first step,

$$COD + H_2O_2 + Fe^{2+} \rightarrow \text{partially oxidized species}$$

And in second Step,

$$\text{Partially oxidized species} + H_2O_2 + Fe^{2+} \rightarrow CO_2 + H_2O + \text{Inorganic salts}$$
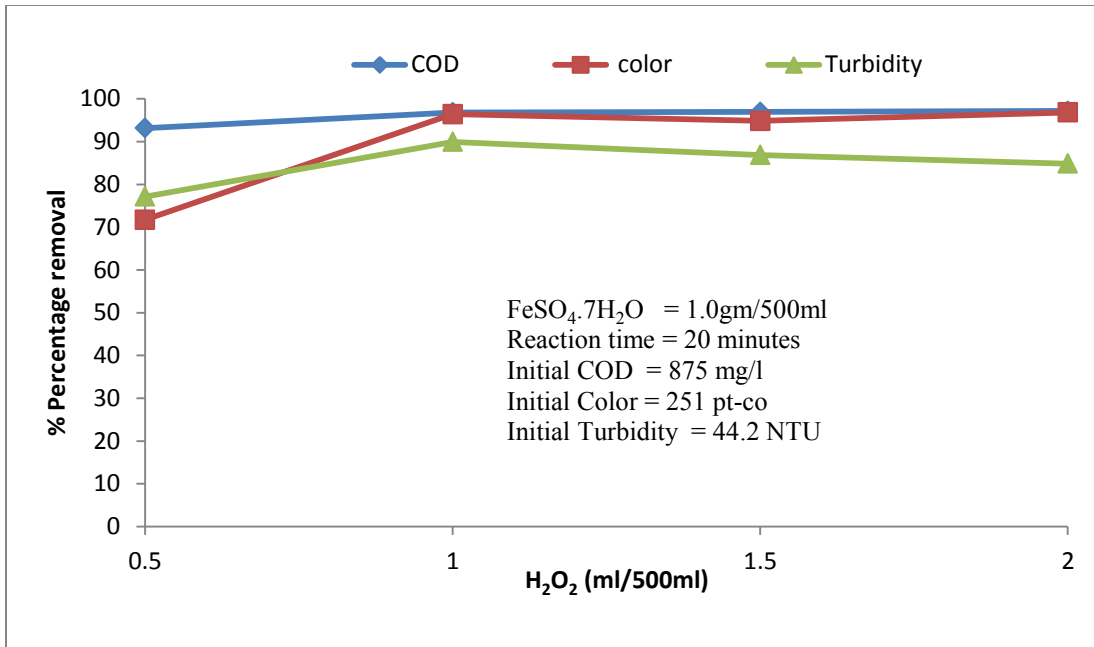
Figure 4.4: Effect of various doses of H_2O_2 on COD, Color and Turbidity removal at pH 4.0 (Fenton's process); (Cotton dyeing)

Fig. 4.5 shows the removal of color, Turbidity and COD for finishing section at different H_2O_2 doses.
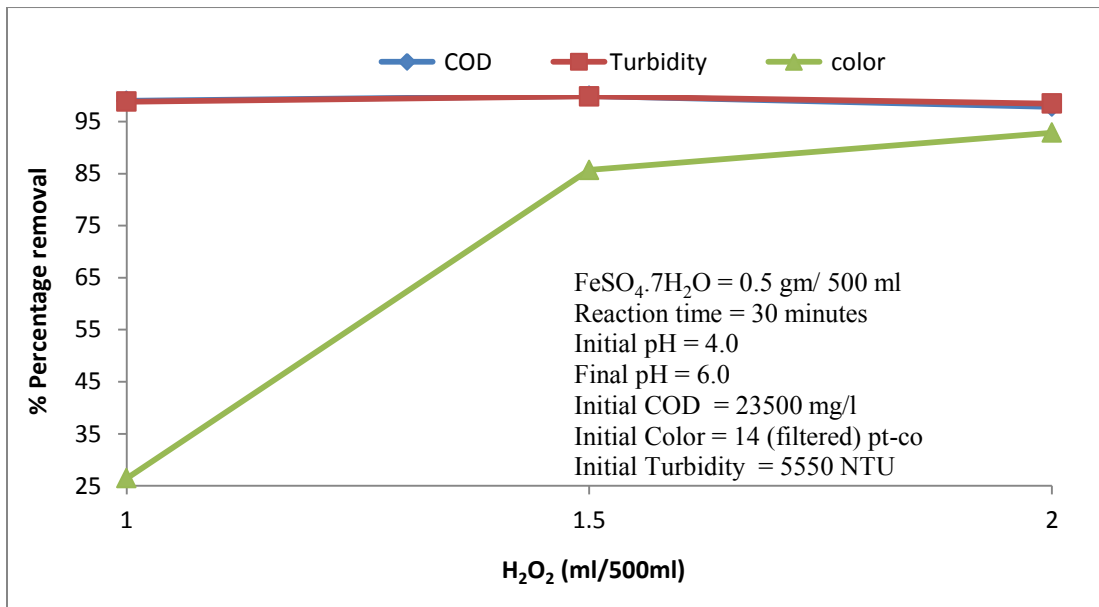

Figure 4.5: Effect of various doses of H_2O_2 on COD and Color removal by Fenton's process(Finishing effluent)

The experiments were performed in the range of 1-2 ml H_2O_2/500ml sample of finishing effluent. As the doses of H_2O_2 changed COD removal efficiency varies from 97.85% to 99.9%. Color and turbidity removal increased from 26.43% to 92.86% and 98.48% to 99.9% respectively. Low dose of $FeSO_4.7H_2O$ is used in the experiments of finishing effluent than dose used in cotton dyeing effluent. As sample from finishing section is more complex or more concentrated, more reaction time is required. The pH was controlled at 4 and the ferrous doses were 0.5 gm/500ml of sample. According to reaction 4 (page 46), the concentration of $OH^\bullet$ is expected to increase with increasing H_2O_2 doses, leading to increased oxidation rates of color and other organic compounds (COD). Maximum COD removal was 99.9% for a dose of H_2O_2= 1.5ml/500ml. In higher doses excess H_2O_2 interferes with the measurement of COD. The residual H_2O_2 in the Fenton process can consume $K_2Cr_2O_7$, leading to the increase of inorganic COD.

4.3.3 Effect of various doses of $FeSO_4.7H_2O$ on COD, Color and Turbidity removal

The removal of color, Turbidity and COD for cotton dyeing effluent under different ferrous doses at constant H_2O_2 doses of 2.0 ml/500ml are shown in Fig. 4.6. At Fe(II) doses of 1gm/500ml, the color and COD removal was maximum 96.8% and 97.2% respectively and Turbidity removal was 84.8%. In Fenton's process ferrous doses significantly affects the COD and Turbidity removal and only slightly increases color removal.

With increasing Fe^{2+} ion concentration in solution it increase the conversion of COD, oxidation rate increases with Fe^{2+} concentration as the result of higher production of hydroxyl radicals according to eq. 4. It is important to minimize the production of Fe^{3+} for color removal which will probably precipitate as $Fe(OH)_3$. A greater concentration of Fe^{2+} can cause the recombination of radical HO•. In this case the Fe^{2+} reacts with the hydroxyl radical functioning as a scavenger.
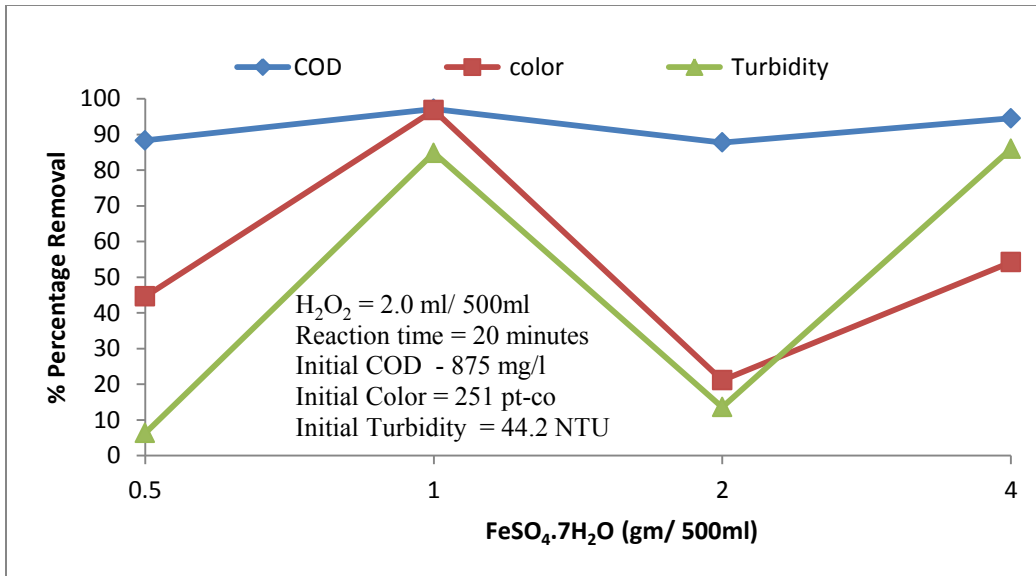
Figure 4.6: Effect of various doses of $FeSO_4.7H_2O$ on COD, Color and Turbidity removal (oxidation) at pH= 4.0 (Cotton dyeing)
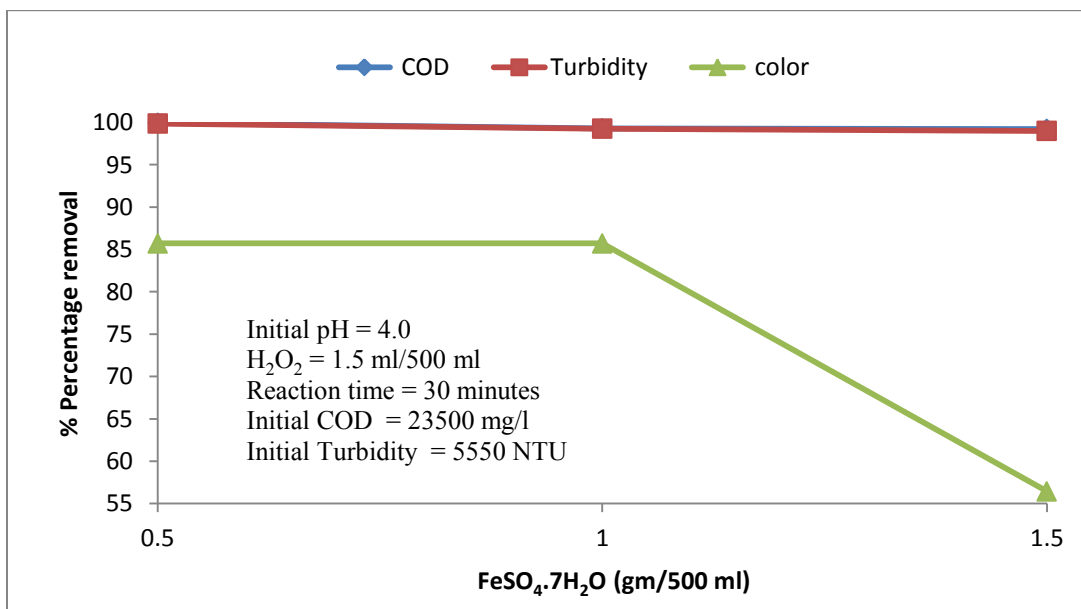
Figure 4.7: Effect of various doses of $FeSO_4.7H_2O$ on COD and Color removal (oxidation) (Finishing effluent)

Figure 4.7 shows the removal efficiencies for finishing effluent. It was observed that 85.7% color was removed at optimum ferrous doses of 0.5 gm/500ml. Based on results it is seen that the

removal for finishing effluent by Fenton process requires relatively lower doses of H_2O_2 and Fe^{2+} than used for cotton dyeing.

4.3.4 Effect of Fenton's oxidation reaction time on COD, Color and Turbidity removal

For discovering the optimum reaction time of Fenton oxidation process, 500 ml of sample was taken. The amount of H_2O_2 was taken 2.0 ml & 1.5 ml and the amount of Fe^{2+} was taken 1gm & 0.5 gm respectively for dyeing and finishing effluent. After mixing Fenton's reagents with sample, different reaction time from 10 minutes to 30 minutes was given and then rapid mixing and slow mixing were performed sequentially, followed by sedimentation was provided to settle down the produced sludge. The removal efficiency is shown in appendix. The maximum removal was observed in reaction time 20 minutes for cotton dyeing effluent and 30 minutes for finishing effluent. The result obtained in Figures 4.8 and 4.9 show reaction time as important parameter in Fenton oxidation. The results demonstrated that organic materials were rapidly degraded by Fenton reagent.
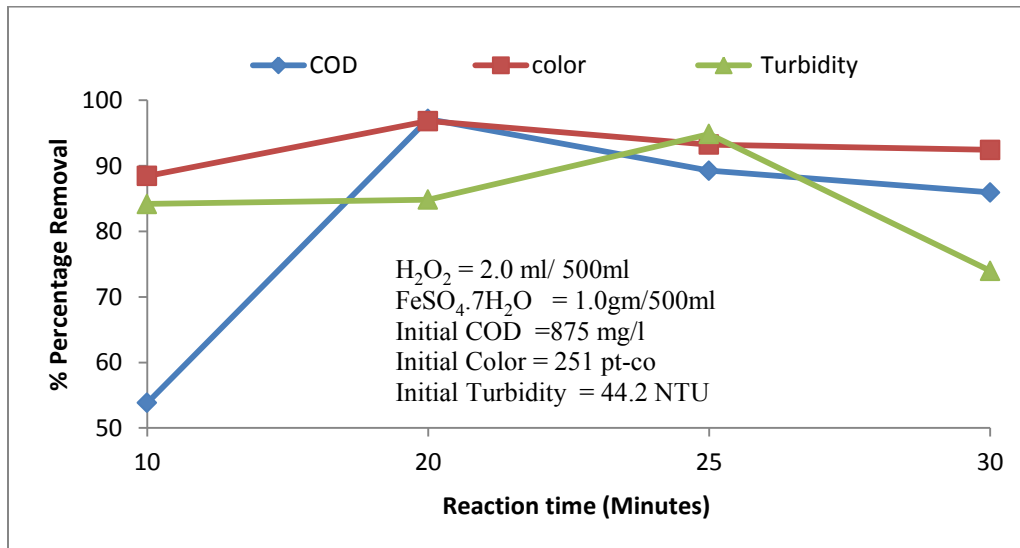
Figure 4.8: Effect of Fenton's oxidation reaction time on COD, Color and Turbidity removal at pH = 4.0 (Cotton dyeing)

Residual COD, Color, Turbidity was measured in all test runs. The experimental results for cotton dyeing effluent showed that the COD decreased by about 97.2% within 20 minutes and a higher reaction time did not lead to further significant COD reduction. The maximum color and Turbidity removal was 96.8% and 94.86% respectively for cotton dyeing effluent. Lin and Lo 1997 investigated effect of reaction time on treatment of desizing wastewater by Fenton process. The result shows that after 120 minutes reaction time degradation did not improve and after this reaction time H_2O_2 remained in solution.

Figure 4.9 shows the effect of Fenton's oxidation reaction time on COD, Turbidity and Color removal for finishing effluent. COD removal was maximum 99.9% for a reaction time of 30 minutes and shorter reaction time did not have any significant reduction. COD and Turbidity removal are improved by increasing reaction time than required for cotton dyeing effluent. Removal efficiency of color was also maximum at 30 minutes reaction time with pH 4.0. Determining the completion of the reaction is troublesome. Wastewaters will typically darken upon H_2O_2 addition and clear up as the reaction reaches completion.
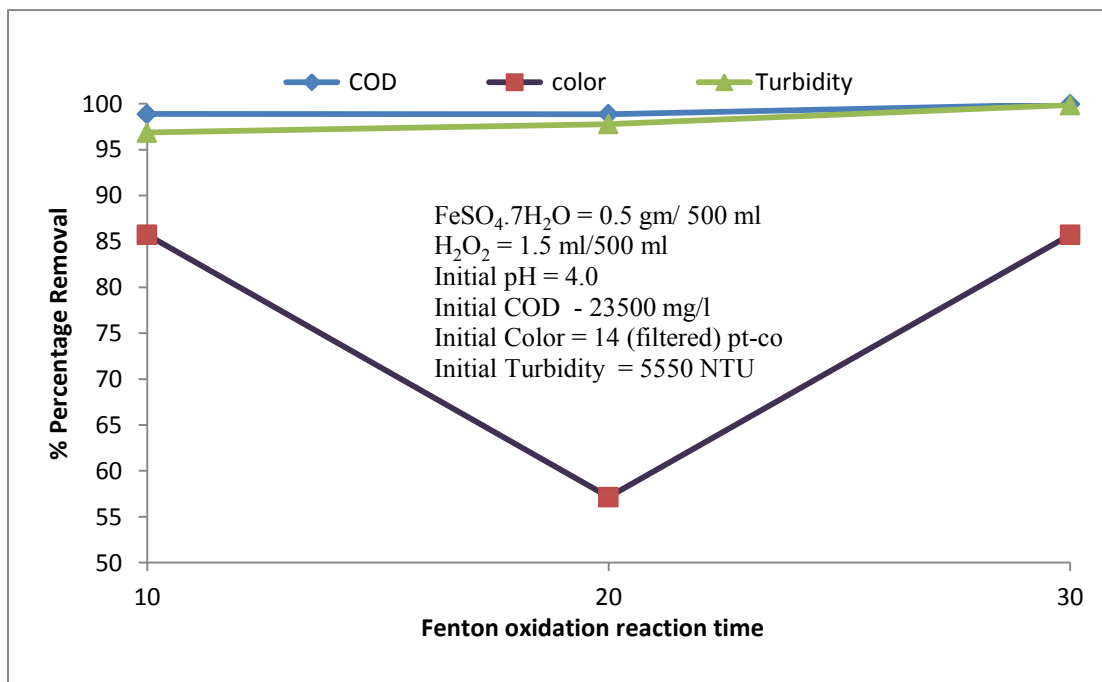
Figure 4.9: Effect of Fenton's oxidation reaction time on COD, Turbidity and Color removal
(Finishing effluent)

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4.3.5 Effect of Final pH after Fenton's oxidation on COD, Color and Turbidity removal

Effluent pH subsequent to Fenton's oxidation is typically adjusted to convert dissolved iron to iron sludge. The effect of pH during Fenton's coagulation on COD, color and Turbidity removal are shown in Figure 4.10 and 4.11.
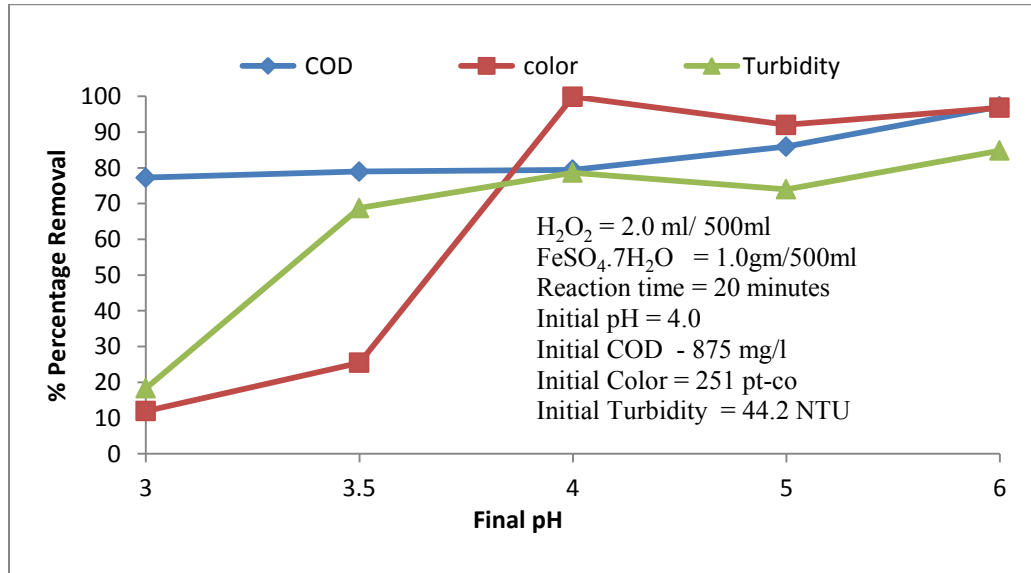
Figure 4.10: Effect of Final pH on COD, Color and Turbidity removal (Cotton dyeing)
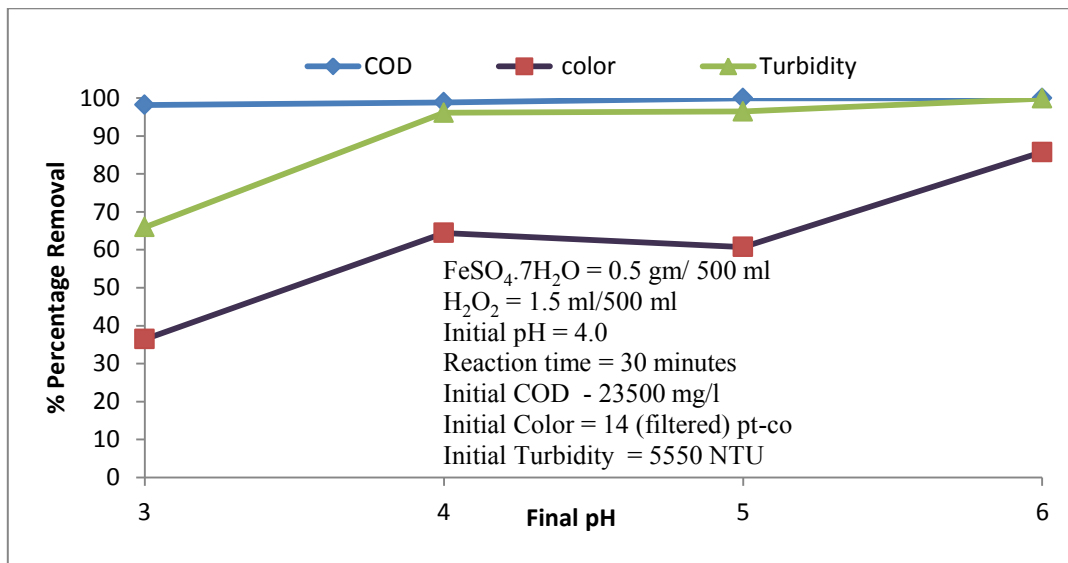
Figure 4.11: Effect of Final pH on COD, Color and Turbidity removal (Finishing effluent)

The corresponding values of reduced COD, color and Turbidity is given in Tables A-6 and B-6. With 2ml of H_2O_2 and 1 gm of Fe^{2+} on 500 ml sample, the maximum COD, color and turbidity removal occurred at pH 6.0 for the samples collected from cotton dyeing section and the removal efficiency is above 80 %. With 1.5 ml of H_2O_2 and 0.5 gm of Fe^{2+} on 500 ml sample, the maximum COD, color and turbidity removal occurred at pH 6.0 for the samples collected from finishing section and the removal efficiency is above 85 %.

4.4 Analysis of Effluent after Fenton's Treatment

To know the efficacy of Fenton's process treated effluent with optimum doses of reagents were further analyzed. The value of pH was reduced to 6.38 from 9.75 for cotton dyeing effluent and from 7.7 to 6.2 for finishing effluent after Fenton's treatment. Reduction in different water quality parameters like pH, color, Turbidity, EC, Alkalinity in textile effluent collected from cotton dyeing and finishing section before and after Fenton process are shown in figure 4.12 and 4.13 respectively.

Figure 4.12: Reduction in different water quality parameters in an textile effluent before and after Fenton's process (cotton dyeing)

The removed Color for cotton dyeing and finishing section is 8 pt-co and 2 pt-co unit respectively. Alkalinity after Fenton's treatment was reduced to74 mg/l and 69 mg/l for cotton

dyeing and finishing effluent respectively. EC reduced to 58.2% and 48.8%. Turbidity removal for cotton dyeing and finishing effluent was 84.8% and 99.9% respectively. Electrical conductivity is directly related to the concentration of salts dissolved in water. Electrical conductivity increases with the number of ions in solution which may be lost from the solution after treatment resulting in lower value of EC. EC of the collected samples were found to be different due to the effect of temperature on the viscosity of water or can be due to the presence of fine sediment.

Figure 4.13: Reduction in different water quality parameters in an textile effluent before and after Fenton's process (Finishing effluent)

Test results of Nitrate and Nitrite, Ammonia Nitrogen, Sulphate and Sulphide of raw sample and treated sample are shown in bar graph 4.14 and 4.15 for effluent collected from cotton dyeing and finishing section respectively. Nitrate reduction in cotton dyeing effluent was 95.27%. Nitrite reduction was 28% and 57.3% for samples. NO_3 was reduced to 0.9 mg/l to 0.2 mg/l for finishing effluent.

Ammonia nitrogen concentration was measured after Fenton's process. No reduction was observed for either of the samples. Fenton's degradation of nitrogen contained in organic

compounds produces ammonia and traces of nitrate hence increase the concentration of ammonia.
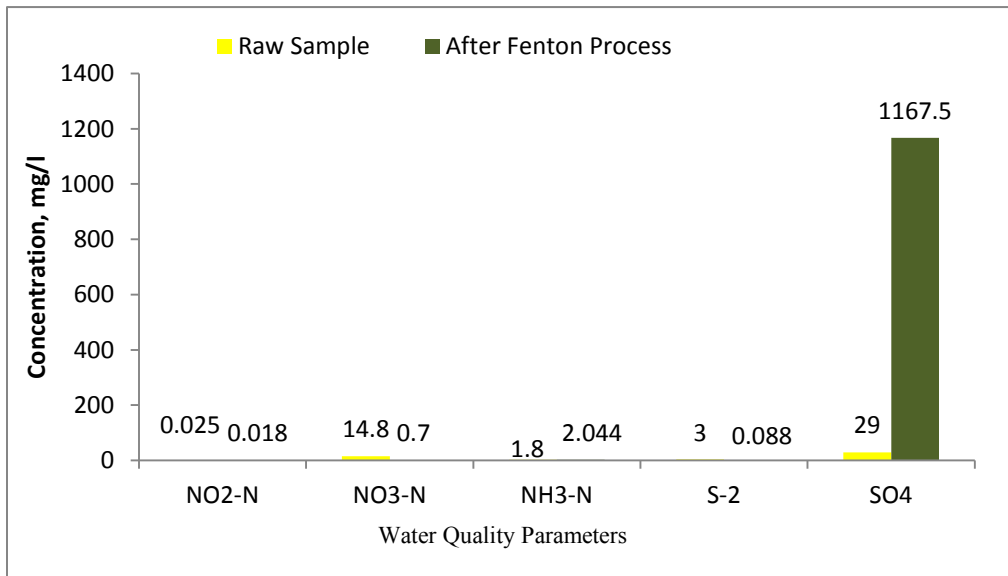
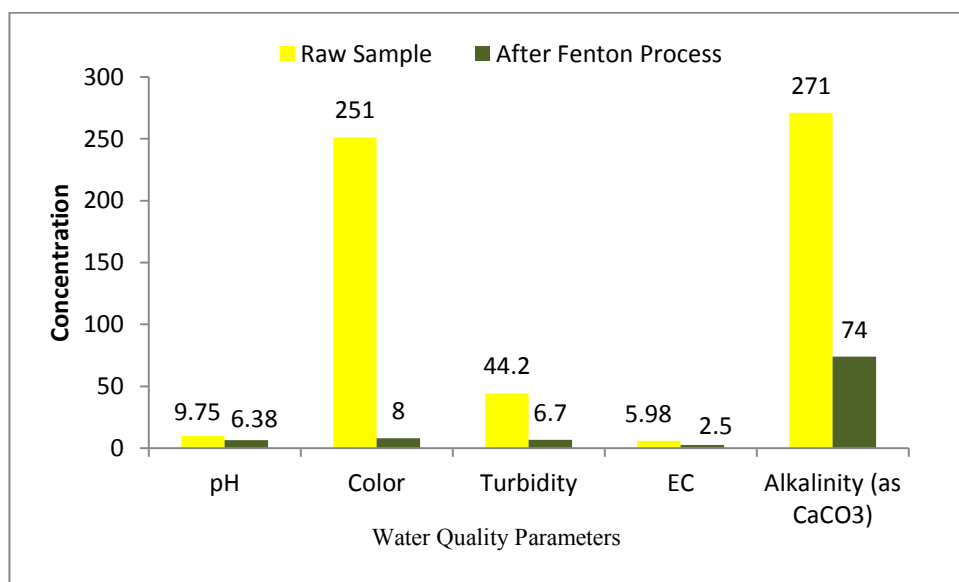

Figure 4.14: Reduction in different water quality parameters in an textile effluent before and after Fenton's process (cotton dyeing)
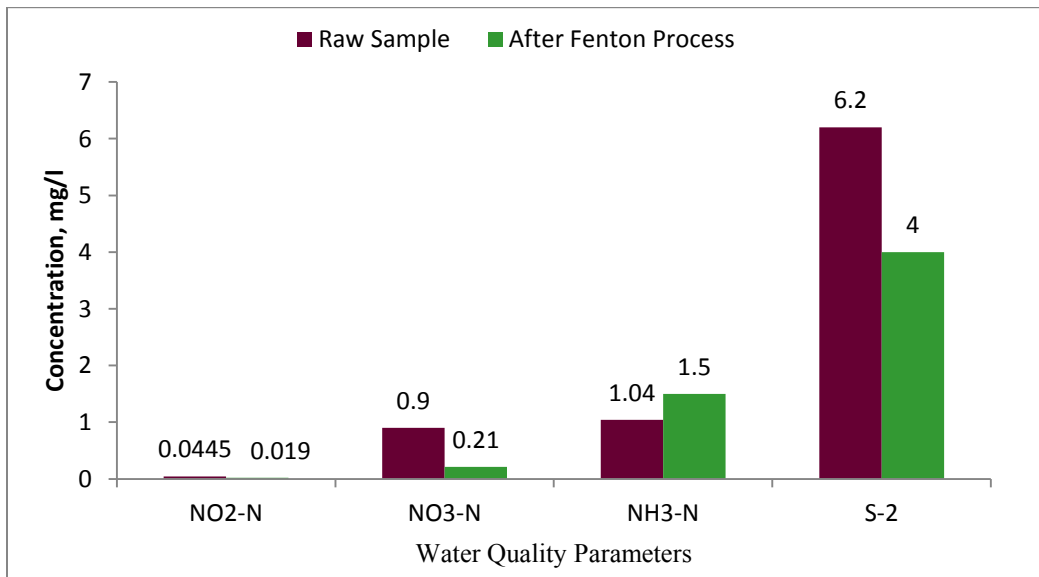
Figure 4.15: Reduction in different water quality parameters in an textile effluent before and after Fenton's process (finishing effluent)

Ammonia can be oxidized to nitrite, but only under special conditions and in small concentrations (Meyer and Pietsch, 1996). Organic nitrogen can be decomposed to form ions and gases, for example, as nitrate, nitrite, ammonia, molecular nitrogen or nitrogen monoxide (Maletzky and Bauer, 1998). Several authors have reported that only for high H_2O_2 concentration it is possible to eliminate ammonia nitrogen and the main byproducts are gaseous N_2 and nitrate (Zoh and Stenstrom, 2002; Goi and Trapido, 2002).

Reduction in values of different heavy metals for the samples collected from cotton dyeing section and finishing section are shown in figure 4.16 and 4.17. Significant reduction occurs for Cu, Pb and Zn. Chromium toxicity damages the liver, lungs and causes organ hemorrhages, though is an essential trace nutrient and a vital component for glucose tolerance factor (WHO, 1988). Cr reduction was achieved 87.5% for dyeing effluent and 88.9% for finishing effluent. Cadmium was absent in both samples.
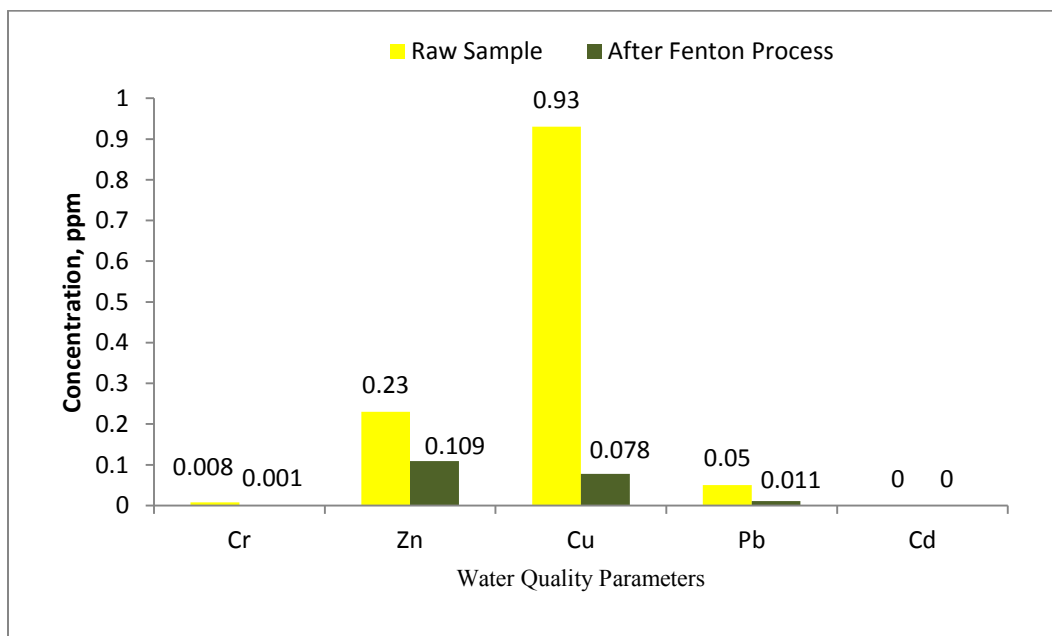
Figure 4.16: Representation of reduction in different heavy metal before and after treatment with Fenton's reagent (Cotton dyeing)
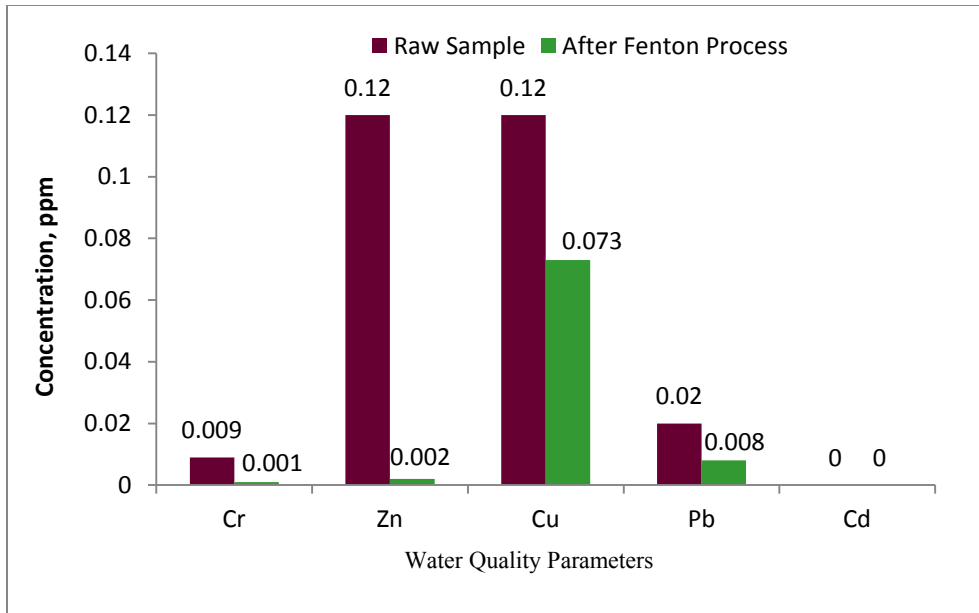
Figure 4.17: Representation of reduction in different heavy metal before and after treatment with Fenton's reagent (Finishing effluent)
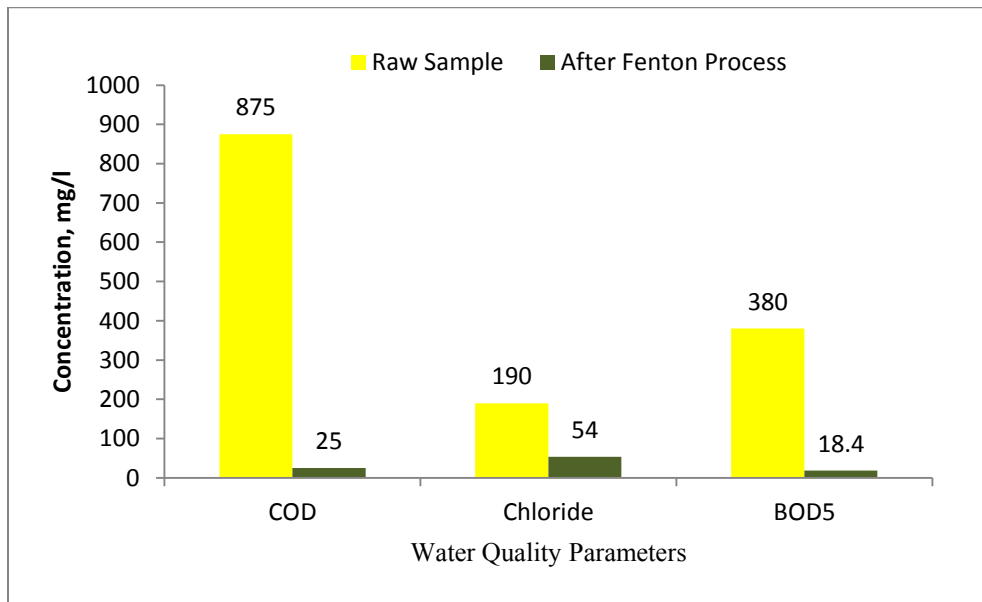
Figure 4.18**:** Representation of reduction in different parameters before and after treatment with Fenton's reagent (Cotton dyeing)
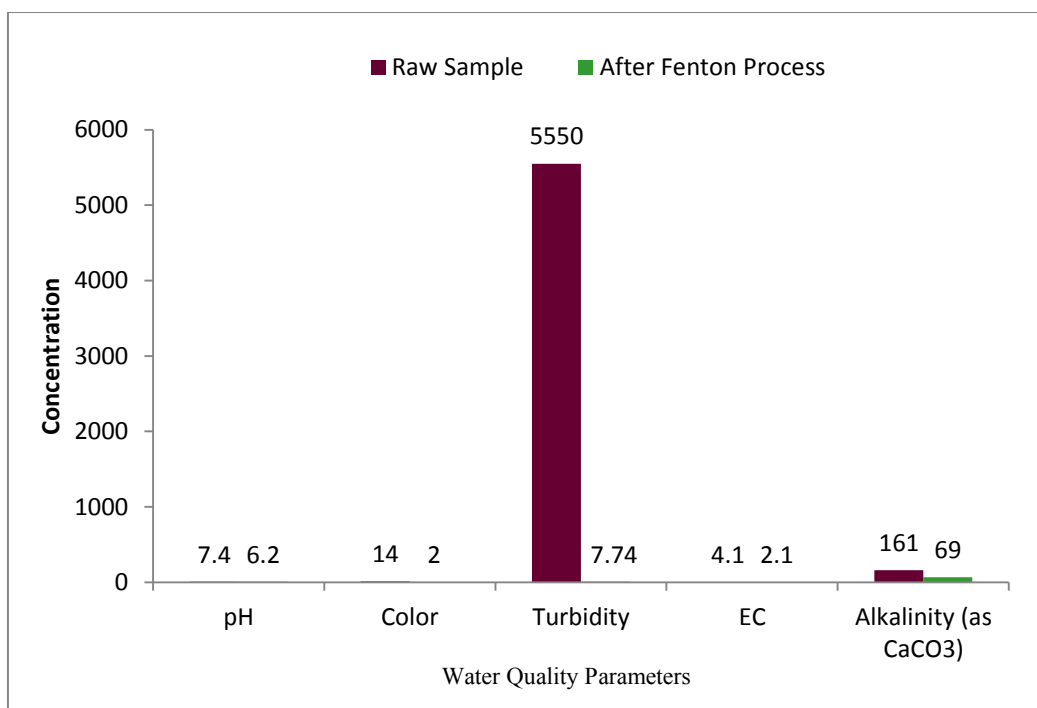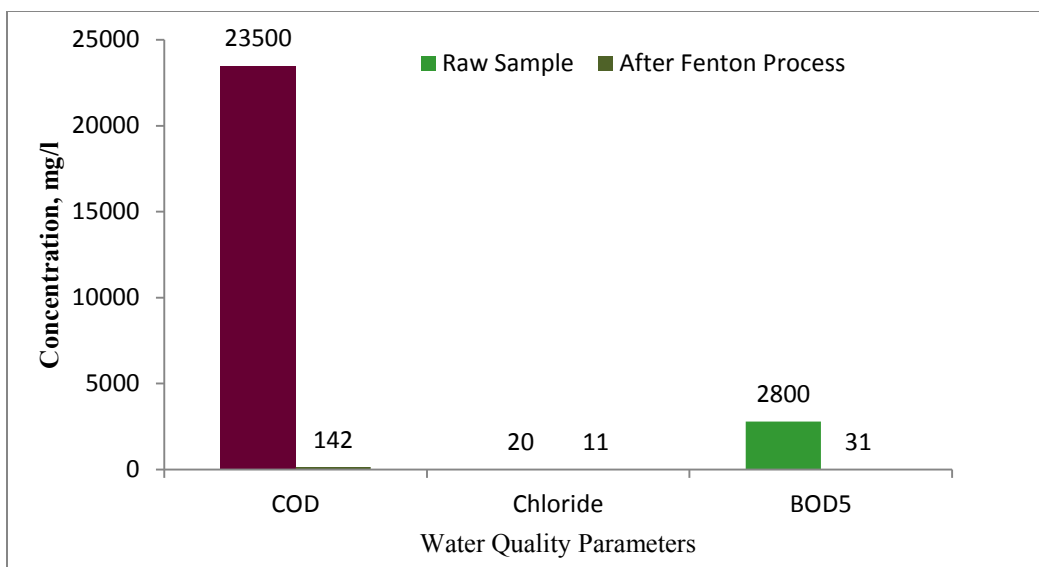
Figure 4.19: Reduction in different water quality parameters in an textile effluent before and after Fenton's process (finishing effluent)

Representation of test results of different parameters like COD, Chloride and BOD$_5$ in raw sample and treated sample are shown in figure 4.18 and 4.19 for Cotton dyeing and finishing section respectively. No substantial change of chloride in finishing effluent was observed. COD values of wastewater are extremely high compare to other parameter. Removal efficiency was 97.1% and 99.4%.

4.5 Fenton's treatment of combined effluent

Raw samples were analyzed to know the characteristics of the sample. Different parameters were tested after Fenton's treatment also. Findings of the experiments are listed in table 4.2

Treated samples were analyzed directly after Fenton's Process and reduction in different parameters like COD, BOD$_5$, Sulfide, and Nitrate were observed significant. COD, BOD$_5$, NO$_3$ and S^{2-} were removed up to 77%, 77%, 50% and 89.5% respectively. Major problems associated with textile effluent treatment are high concentration of TDS and Sulfate which cannot be reduced even with filtered sample. Concentration of ammonia nitrogen is also increased after Fenton's treatment.

Table 4.2: Concentration of different parameters after and before Fenton treatment

Parameters	Raw Sample	Treated Water	Treated Water (Filtered Sample)
pH	8.37	5.67	6.10
COD, mg/l	551	127	103
BOD_5, mg/l	90	20	18
TDS	2975	3938	
TSS, mg/l	76	87	
TS, mg/l	3051	4025	
NO_3, mg/l	0.8	0.4	
Sulfides, mg/l	285	30	15
Sulfate	1650	3388	2975
NH_3, mg/l	3.4	10.9	10.1
Turbidity, NTU	146	149	86.6

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

Bangladesh is heavily involved in textile production and export. A lot of textile mills were established in the country mostly in and around Dhaka city. A large number of these mills generate and discharge waste waters. It was reported by the various organization and monitoring authority that the pollution of the rivers and canals in and around Dhaka is well above their acceptable level. Various agencies are trying to safeguard the clean environment. Bangladesh Government has already issued various forms of warning and red alerts to the concerned industries. A lot of textile wet processing industries have already installed effluent treatment plants (ETP) and many of them are at various stages of installing ETP's. Several physico-chemical decolonization techniques have been used by textile industries e.g. adsorption, chemical transformation, incineration, photo catalysis, Ozonation or membrane separation but their lack of implementation has been largely due to high cost, low efficiency and inapplicability to a wide variety of dyes and here necessities advanced oxidation process. The following conclusions can be made from the study.

5.2 Conclusions

1. Optimum pH was found to be 4.0 for Fenton's reagent to oxidize organic matter for cotton dyeing and finishing effluent. At an extremely low pH, removal efficiency decreased.

2. Optimum final pH for Fenton coagulation and hence maximum removal of Color, COD and Turbidity was 6.0.

3. Fenton treatment of Textile effluent of dyeing section gives satisfactory results with respect to the removal of COD, color and turbidity. By using Fenton's reagent maximum COD, color and Turbidity removal was 97.2%, 96.8% and 84.8% for cotton dyeing effluent and 99.9%, 85.7% and 99.9% for finishing effluent.

4. Considering the removal efficiencies, optimum dose of hydrogen peroxide is found to be 2.0 ml/500 ml and 1.5 ml/500 ml for cotton dyeing and finishing effluent, respectively. The concentration of OH^- is increase with increasing hydrogen peroxide doses, leading to increased oxidation rates of color and organic compounds (COD).

5. Optimum dose of ferrous sulphate were 1.0 gm/500 ml and 0.5 gm/500ml for cotton dyeing and finishing effluent, respectively.

6. Maximum COD, Color and Turbidity removal occurred at the 20 minutes reaction time for cotton dyeing effluent and 30 minutes reaction for finishing effluent.

7. The ratio of BOD_5 to COD indicates that Finishing effluents are more non-biodegradable than dyeing effluent. Fenton i.e. Chemical oxidation is found to be most effective in Turbidity and COD removal of the finishing effluent which are resistant to biological treatment. But one major problem of this method is generation of sludge through the flocculation of the reagents.

5.3 Recommendations for further study

1. In this study only $FeSO_4.7H_2O$ were used as catalyst, other coagulants like Mohr salt, Fecl$_3$ can also be used to test the effectiveness of Fenton coagulation on the treatment of textile effluent.

2. Fenton method for treatment of textile effluent can be compared with other AOP such as Photo catalytic oxidation with TiO_2, Ozonation, Ozone combined with UV and H_2O_2, UV irradiation with H_2O_2.

3. In this study only Fenton process as AOP was performed. Some physical, Physico-chemical and Biological treatments can also be done to find out the effective removal of color, COD and Turbidity.

4. In further study tests can be done using any other less expensive oxidizing agents like chlorine, ozone, potassium permanganate in place of hydrogen peroxide to explore their efficiency.

5. Tests can be performed considering different stoichiometric ratio of Ferrous and hydrogen peroxide.

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Appendix A

Test Results of Cotton Dyeing Section

Table A-1: Concentration of different parameters of textile effluent. Samples were collected from cotton dyeing section on 28/11/2012.

Parameters	Unit	Raw Sample	Treated Sample
pH	-	9.75	6.38
COD	mg/l	875	25
BOD_5	mg/l	380	18.4
TDS	mg/l	1275	-
TSS	mg/l	80	-
TS	mg/l	1355	-
Color	pt-co	251	8.0
Turbidity	NTU	44.2	6.7
Cr	ppm	0.008	0.001
Zn	ppm	0.23	0.109
Cu	ppm	0.93	0.078
Cd	ppm	0.0	0.000
Pb	ppm	0.05	0.011
Chloride	mg/l	190	54
Alkalinity	mg/l	271	74
NO_3-N	mg/l	14.8	0.7
NH_3-N	mg/l	1.8	2.044
NO_2-N	mg/l	0.025	0.018
SO_4	mg/l	29	1167.5
S^{-2}	mg/l	3.0	0.088
EC	ms/cm	5.98	2.50

Table A-2: Effect of pH during Fenton's oxidation on COD, Color and Turbidity removal

pH during Fenton oxidation	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
3.0	107	87.77	32	87.25	7.14	83.85
3.5	26	97.03	11	95.62	7.6	82.81
4.0	25	97.2	8.0	96.8	6.7	84.8
5.0	125	85.71	20	92.03	12	72.85
6.0	196	77.6	117	53.39	22.8	48.42

Table A-3: Effect of various dosages of H_2O_2 on COD, Color and Turbidity removal at pH 4.0 (Fenton's process)

Reagent Dose	Amount of H_2O_2, ml/500ml	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
Dose 1	0.5	60	93.14	71	71.71	10.1	77.15
Dose 2	1.0	28	96.8	9.0	96.42	4.76	89.92
Dose 3	1.5	27	96.92	13	94.82	5.8	86.88
Dose 4	2.0	25	97.2	8.0	96.8	6.7	84.8

Table A-4: Effect of various dosage of FeSO$_4$.7H$_2$O on COD and Color removal (oxidation)

Reagent Dose	Amount of FeSO$_4$.7H$_2$O gm/500 ml	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
Dose 1	0.5	102	88.34	139	44.62	41.4	6.33
Dose 2	1.0	25	97.2	8.0	96.8	6.7	84.8
Dose 4	2.0	107	87.77	198	21.11	38.2	13.57
Dose 5	4.0	48	94.52	115	54.23	6.2	85.97

Table A- 5: Effect of Fenton's oxidation reaction time on COD, Turbidity and Color removal at pH 4.0

Reaction time (minutes)	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
10	404	53.83	29	88.45	6.99	84.19
20	25	97.2	8.0	96.8	6.7	84.8
25	94	89.26	17	93.23	2.27	94.86
30	123	85.94	19	92.43	11.5	73.98

Table A-6: Effect of Final pH on COD, Color and Turbidity removal with initial pH = 4.0.

Final pH	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
3.0	199	77.26	221	11.95	36.1	18.33
3.5	184	78.97	187	25.49	13.8	68.77
4.0	180	79.43	1.0	99.92	9.45	78.62
5.0	123	85.94	19.0	92.03	11.5	73.98
6.0	25	97.2	8.0	96.8	6.7	84.8

Appendix B

Test Results of Finishing Section

Table B-1: Concentration of different parameters of textile effluent. Samples were collected from finishing section on 27/12/2012.

Parameters	Unit	Raw Sample	Treated Sample
pH	-	7.45	6.2
COD	mg/l	23500	142
BOD_5	mg/l	2800	31
TDS	mg/l	1005	-
TSS	mg/l	7288	-
TS	mg/l	8293	-
Color	pt-co	14 (filtered)	2.0
Turbidity	NTU	5550	7.74
Cr	ppm	0.009	0.001
Zn	ppm	0.12	0.002
Cu	ppm	0.12	0.073
Cd	ppm	0	0
Pb	ppm	0.02	0.008
Chloride	mg/l	20	11
Alkalinity	mg/l	161	69
NO_3-N	mg/l	0.9	0.21
NH_3-N	mg/l	1.040	1.5
NO_2-N	mg/l	0.0445	0.019
SO_4	mg/l	11.6	-
S^{-2}	mg/l	6.2	4.0
EC	ms/cm	4.1	2.1

Table B-2: Effect of pH during Fenton's oxidation on COD, Color and Turbidity removal

pH during Fenton oxidation	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity	Percentage Turbidity removal, %
3.0	161	99.31	222	0	287	94.83
4.0	142	99.9	2.0	85.7	7.74	99.9
5.0	213	99.09	31	0	16.8	99.7

Table B-3: Effect of various dosages of H_2O_2 on COD, Color and Turbidity removal at pH=4 (Fenton's process)

Reagent Dose	Amount of H_2O_2, ml/500ml	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
Dose 1	1.0	232	99.01	10.3	26.43	63.7	98.85
Dose 2	1.5	142	99.9	2.0	85.7	7.74	99.9
Dose 3	2.0	504	97.85	1.0	92.86	84.3	98.48

Table B-4: Effect of various dosage of $FeSO_4.7H_2O$ on COD, Color and Turbidity removal (oxidation) at pH= 4.0

Reagent Dose	Amount of $FeSO_4.7H_2O$ gm/ 500 ml	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
Dose 1	0.5	142	99.9	2.0	85.7	7.74	99.9
Dose 2	1.0	164	99.30	2.0	85.7	41.4	99.25
Dose 3	1.5	186	99.21	4.1	56.43	56.1	98.99

Table B-5: Effect of Fenton's oxidation reaction time on COD, Color and Turbidity removal at pH = 4.0

Reaction time (minutes)	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
10	279	98.88	2.0	85.7	174	96.86
20	312	98.87	6.0	57.14	120	97.78
30	142	99.9	2.0	85.7	7.74	99.9

Table B-6: Effect of Final pH on COD, Color and Turbidity removal with initial pH = 4.0

Final pH	Residual COD, mg/l	Percentage COD removal, %	Residual Color, mg/l	Percentage color removal, %	Residual Turbidity NTU	Percentage Turbidity removal, %
3.0	432	98.16	8.9	36.43	1890	65.95
4.0	294	98.85	5.0	64.43	216	96.11
5.0	160	99.93	5.5	60.72	198	96.43
6.0	142	99.9	2.0	85.7	7.74	99.9

Appendix C

Figure C-1: Raw samples collected from textile- Dying section.

Figure C-2: Samples prepared for Fenton's tests.

Figure C-3: Addition of Fenton's reagents during experiment.

Figure C-4: Taking of sample with 500 ml measuring cylinder.

Figure C-5: Foam formation after addition of H_2O_2

Figure C-6: After addition of Fenton's reagent.

Figure C-7: Formation of Flocs during addition of H_2O_2

Figure C-8: Samples set in the flocculation unit to accelerate the coagulation process.

Figure C-9: Addition of the titrant during Chloride Test.

Figure C-10: Filtration of sample for TDS tests.

Figure C-11: Samples heating in a water for preparation of samples for heavy metals tests.

Figure C-12: Sample prepared for heavy metal tests.

Figure C-13: Samples prepared for BOD test.

Figure C-14: Samples were preserved in an incubator.

Figure C-15: Sepernatant collected for further analysis of the samples.

Figure C-16: Weighing of $FeSO_4.7H_2O$ for the supply of Fe^{2+}

Figure C-17: Sample collected from finishing section.

Figure C-18: Sedimentation of the sample after Fenton's oxidation process.

Figure C-19: Formation of flocks after adding H_2O_2

Figure C-20: After coagulation process samples allowed to precipitate.

Appendix D

Table D-1: Standards for wastes from Industrial units or projects waste (DoE 1997)

Sl No.	Parameter	Unit	Places for determination of standards		
			Inland surface water	Public Sewerage system connected to treatment at second stage	Irrigated land
1	Ammoniacal Nitrogen (N molecule)	mg/l	50	75	75
2	Ammonia (free Ammonia)	mg/l	5	5	15
3	Arsenic	mg/l	0.2	0.5	0.2
4	BOD_5 20^0C	mg/l	50	250	100
5	Boron (B)	mg/l	2	2	2
6	Cadmium (Cd)	mg/l	0.05	0.5	0.5
7	Chloride (Cl-)	mg/l	600	600	600
8	Chromium (Total Cr)	mg/l	0.5	1	1
9	COD	mg/l	200	400	400
10	Chromium (hexavalent Cr)	mg/l	0.1	1	1
11	Copper (Cu)	mg/l	0.5	3	3
12	Dissolved Oxygen (DO)	mg/l	4.5-8	4.5-8	4.5-8
13	Electrical Conductivity	mg/l	1200	1200	1200
14	Total Dissolved Solids (TDS)	mg/l	2100	2100	2100
15	Fluoride (F)	mg/l	7	15	10
16	Sulfide (S)	mg/l	1	2	2
17	Iron (Fe)	mg/l	2	2	2
18	Total Kjeldahl Nitrogen (N)	mg/l	100	100	100
19	Lead (Pb)	mg/l	0.1	0.1	0.1
20	Manganese (Mn)	mg/l	5	5	5
21	Mercury (Hg)	mg/l	0.01	0.01	0.01
22	Nickel (Ni)	mg/l	1	1	1
23	Nitrate (N molecule)	mg/l	10	undetermined	10
24	Oil & grease	mg/l	10	20	10
25	Phenol compounds (C_6H_5OH)	mg/l	1	5	1
26	Dissolved Phosphorus (P)	mg/l	8	8	8
27	Radioactive materials: As determined by Bangladesh Atomic Energy Commission				
28	pH	mg/l	6-9	6-9	6-9
29	Selenium (Se)	mg/l	0.05	0.05	0.05
30	Zn (Zn)	mg/l	5	10	10
31	Temperature	Centigrade			
	Summer	mg/l	40	40	40
	Winter	mg/l	45	45	45
32	Total Suspended Solid (TSS)	mg/l	150	500	200
33	Cyanide (CN)	mg/l	0.1	2	0.2

Table D-2: list of some waste materials generated at each level of cotton textile processing

(Babu B. R., Parande A. K., Raghu S., and Kumar T. P., 2007)

process	Air emissions	wastewater	Residual wastes
Fiber preparation	Little or no more air emissions generated	Little or no wastewater generated	Fiber waste; packaging waste; hard waste.
Yarn spinning	Little or no more air emissions generated	Little or no wastewater generated	Packaging waste; sized yarn; fiber waste; cleaning and processing waste.
Slashing/sizing	Volatile organic compounds	BOD, COD, metals; cleaning waste, size	Fiber lint; yarn waste; packaging waste; unused starch-based sizes.
Weaving	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; yarn and fiber scraps; off-spec fabric; used oil.
Knitting	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; yarn and fiber scraps; off-spec fabric.
Tufting	Little or no air emissions generated	Little or no wastewater generated	Packaging waste; yarn and fiber scraps; off-spec fabric.
Desizing	Volatile organic compounds from glycol ethers and scouring solvents	BOD from water-soluble sizes; synthetic size; lubricants; biocides; anti-static compounds	Packaging waste; fiber lint; yarn waste; cleaning materials, such as wipes, rags and filters; cleaning and maintenance wastes containing solvents.
Scouring	Volatile organic compounds from glycol ethers and	Disinfectants and insecticide residues; NaOH; detergents;	Little or no residual waste generated.

	scouring solvents	fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents	
Bleaching	Little or no air emissions	Hydrogen peroxide, sodium silicate or organic stabilizer; high pH.	Little or no residual waste generated.
Singeing	Small amounts of exhaust gasses from the burners	Little or no wastewater generated.	Little or no residual waste generated.
Mercerizing	Little or no air emissions	High pH; NaOH.	Little or no residual waste generated.
Heat setting	Volatilization of spin finish agents applied during synthetic fiber manufacture.	Little or no wastewater generated.	Little or no residual waste generated.
Dyeing	VOC	Metals; salt; surfactants; toxics; organic processing assistance, cationic materials; color; BOD; sulfide; acidity/alkalinity; spent solvents.	Little or no residual waste generated.
Printing	Solvents. Acetic acid from dyeing and curing oven emissions; combustion gasses;	Suspended solids; urea; solvents; color; metals; heat; BOD; foam.	Little or no residual waste generated.

	particular matter.		
Finishing	VOC; contaminants in purchased chemicals; formaldehyde vapor; combustion gasses; particular matter.	BOD; COD; suspended solids; toxics; spent solvents.	Fabric scraps and trimming; packaging.
Product fabrication	Little or no air emissions generated	Little or no wastewater generated.	Fabric scraps.

Table D-3: Standards for composite Textile plant and large processing unit as per ECR-1997
(Schedule 12-B)

Parameters	Standard
pH	6.5-9
Suspended Solids, ppm	100
BOD_5*, 20OC, ppm	150
Oil and Grease, ppm	10
Total Dissolved Solids, ppm	2100
Wastewater flow (liter/kg fabric processed)	100
Total chromium, ppm	2**
Sulfide as S, ppm	2**
Phenolic compound as C_6H_5OH , ppm	5**
BOD limit of 150 ppm implies only with physico-chemical processing ** Special parameters based on type of dye used	