ADDIS ABABA UNIVERSITY
INISTITUTE OF TECHNOLOGY
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DEPARTMENT OF CHEMICAL ENGINEERING

Ayka Addis Textile Wastewater Treatment by the Fenton's Reagent

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Mekibib Soresa

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A Thesis Submitted to the Graduate Studies of Addis Ababa University in Partial Fulfillment of the Degree of Masters of Science in Chemical Engineering
(Process Engineering)

June - 2011
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ACKNOWLEDGEMENTS

Apart from the personal efforts and steadfastness to work, constant inspiration and encouragement given by a number of individuals served as the driving force and enabled me to submit this thesis in the present form. I am privileged to evince a word of thanks to everyone who played a positive role in the completion of my project with the grace of God, who have enlighten and empowered me to complete my work successfully.

First of all; I take this opportunity to express my deep sense of gratitude to my advisor, Eng. Teshome Worku, who gives me guidance, endless patience, help, constructive critism and affectionate attitude.

I also feel very much obliged to Dr. -Ing Zebene Kifle, head of chemical engineering department, for his guidance and suggestions. My gratitude is due to all department members of chemical engineering for their constant support and also I show gratitude to the department of environmental science workers especially Miss. Marta for allowing me to use their laboratory facilities.

Not forgetting laboratory assistances of chemical engineering department and laboratory workers of JIJE laboglass plc; I thank them all for their assistance, guidance and support during my laboratory season.

I wish to express my heartfelt thanks to Miss. Tenawork and Degnet for their kind cooperation in providing me with textile effluents (wastewater sample) and the necessary information about Ayka Addis textile and investment group plc.

Finally, I owe special thanks to my family and all my friends especially Miss. Mahalet Takele, Mr. Abeje Keskis, Mr. Semen Alemu, Mr. Aman Kassaye and Mr. Siyum Adere for their love and endless support of me and my work.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
AOX	Absorbable Organic Halide
BOD	Biological Oxygen Demand
BOD_5	Five Days Biological Oxygen Demand
CMC	Carboxy Methyl Cellulose
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EEPA	Ethiopian Environmental Protection Authority
EOP	Electrochemical Oxidation Potential
MDL	Method Detection Level
NHE	Normal Hydrogen Electrode
NTU	Nephelometric Turbidity Unit
PCP	Poly Chlorinated Phenols
Pt-Co	Platinum Cobalt Unit
PVA	Polyvinyl Alcohol
SS	Suspended Solids
TFE	Tetra Fluoro Ethylene
TOC	Total Organic Carbon
TS	Total Solid
TSS	Total Suspended Solids
UV	Ultraviolet
VS	Volatile Solid

ABSTRACT

Treatment of wastewater is one of the biggest challenges faced by textile manufacturers. One of the textile industries in Addis Ababa at Alem Gena, Ayka addis textile and investment group plc, is experiencing high concentration of COD and color in the final effluent, due to the absence of appropriate treatment facility, as a result of this the effluent wastewater exceeds the standard discharge limits.

The use of conventional textile wastewater treatment processes becomes drastically challenged to environmental engineers with increasing more and more restrictive effluent quality by water authorities. Conventional treatment such as biological treatment discharges will no longer be tolerated as 53 % of 87 colors are identified as non-biodegradable.

The purpose of this study was to investigate the suitability of using Fenton's reagent for treatment of Ayka Addis textile effluent wastewater and reduction of COD and color from the wastewater. The oxidation experiments was carried out using Fenton's reagent (hydrogen peroxide (H_2O_2) and ferrous sulphate ($FeSO_4.7H_2O$)), and to adjust the pH of the wastewater sample hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used.

In this work, optimum conditions such pH, reaction time and stirrer speed on COD and color removal efficiency were examined and after determination of the appropriate experimental conditions, the optimum dosages of Fenton's reagent were determined, at the optimal treatment conditions and dosages a satisfactory results were obtained.

It is found that the tested Ayka Addis textile wastewater revealed high susceptibility to treatment using a combined action of ferrous salts and hydrogen peroxide. The main characters of the wastewater, such as color and chemical oxygen demand (COD) were reduced by considerable amount. The result of this investigation shows a marked increase in degradation of pollutants by Fenton's reagent oxidation.

Keywords: Fenton's reagent, textile wastewater treatment, advanced oxidation process

1. INTRODUCTION

1.1. Background

Textile mills are major consumers of water with an average water consumption of 160kg per kg of finished product [1] and consequently one of the largest groups of industries causing intense water pollution. Generated wastewaters comprise different effluents coming from different manufacturing unitary operations such as sizing, desizing, scouring, bleaching, dyeing, soaping and softening [2].

These complex operations, subjected to frequent changes as a result of shifting consumer's preference, are the cause of the variable volume and the wide diversity of chemical products found in these wastewaters. Though their characteristics depend on the specific operations performed, they commonly present suspended solids, high temperature, unstable pH, high chemical oxygen demand (COD), low biological oxygen demand (BOD) and high colorization [3].

Color of textile effluents is caused by dyes employed in dyeing processes. In this sense, it is interesting to remark that about 10^6 tons and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used in dyeing and printing industries [4, 5].

Other major pollutant types identified are biocides used in the growing or storage of the fiber (e.g., chlorinated aromatics), starches, solvents, fats and greases, heavy metals (e.g., chromium), salts (e.g., carbonate, sulphate, chloride), nutrients (e.g., ammonium salts, urea, phosphate based buffers), oxidizing agents (e.g., hydrogen peroxide, dichromate), reducing agents (e.g., sodium sulphide), bleaching agents (e.g., hypochlorite, hydrogen peroxide) and adsorbable organic halogens (AOX) formed as a result of the use of bleaching chemicals containing chloride [6].

Price competition, demand for high quality products, new and innovative products that are highly durable put further pressure on the textile factory as it has to use more dosage of chemicals and continually change to new chemicals to suit the market demand. This finally results in the complication in the wastewater that is being discharged [7, 8].

Such wastewaters composition would cause serious impacts when encountering in natural environments. High contents of organic matter originate depletion of dissolved oxygen, which has an adverse effect on marine ecological system. Nitrogen and phosphorous nutrients content causes an increase of biomass production in aquatic environments, this situation also creates to a depletion of dissolved oxygen namely eutrophication [9].

Regarding high colorization, not only aesthetic pollution occurs (e.g., the eye can detect concentrations of 0.005 mg/l of reactive dye in water [10]), but it also produces strong prevention of absorption of the sunlight responsible for the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [11].

Conventional oxidation treatments have found difficulty to oxidize dyestuffs and complex structure of organic compounds at low concentration. To ease the stated problems advanced oxidation processes (AOPs), such as oxidation with Fenton's reagent have been developed to generate hydroxyl free radicals and then to oxidize the color and COD. This process is the combination of hydrated ferrous sulfate ($FeSO_4.7H_2O$) and hydrogen peroxide (H_2O_2), which showed the great promise to treat Ayka Addis textile wastewater [12]

1.2. Statement of the Problem

Textile processes produce multi-component wastewater which is difficult to treat. This wastewater can cause serious environmental problems due to their high color, large amount of suspended solids and high chemical oxygen demand [10, 12].

This wastewater cannot be readily degraded by conventional biological processes (e.g. activated sludge process) because the structure of most commercial dye compounds are generally complex and many dyes are non-biodegradable, this is due to their chemical nature and molecular size [11].

At present, several methods have been developed to treat textile wastewater but they cannot be used individually because this wastewater has high salinity, color and non-biodegradable organics. For instance, in coagulation process, large amount of sludge is created which may become a pollutant itself and increase the treatment cost. Oxidation process such as ozonation effectively decolorizes almost all dyes except disperse dyes but its COD removal efficiency is very low. There is no single process capable of adequate treatment of textile wastewater mainly due to the complex nature of this effluent. The use of combined processes has been suggested recently to overcome the disadvantages of individual unit processes [14, 13].

Most of the existing processes include an initial step of activated sludge treatment or biological treatment to remove the biodegradable organic matters and then oxidation with advanced oxidation process (AOP), such as oxidation with Fenton's reagent and also using other technologies like membrane separation or adsorption are recommended as a post-treatment options to minimize cost of treatment and for better removal of the effluent wastewater organic matters [15].

Oxidation with Fenton's reagent is an effective method for lowering the concentration of dissolved dyes and organic matters in textile effluent wastewater, this condition results in reduction of color and COD of textile wastewater [16].

Generally, the absence of effective techniques to reduce color and COD from textile wastewater initiates me to investigate the suitability of oxidation with Fenton's reagent capable of reducing chemical oxygen demand (COD) and color from Ayka Addis textile effluent wastewater.

1.3. Objective of the Study

1.3.1. General Objective

The main objective of this work was to study the treatment of Ayka Addis textile wastewater to reduce color and chemical oxygen demands (COD) by using Fenton's reagent and establishing the optimum Fenton's reagent dosage.

1.3.2. Specific Objectives

The specific objectives of this work include:

- Characterization of Ayka Addis textile factory wastewater, such as COD, BOD_5, TS, VS, TSS, color, temperature, turbidity and pH.
- Determination of the effect of process parameters, such as pH, stirrer speed and reaction time on treatment performance of Fenton oxidation.
- Determination of the optimum Fenton's reagent dosage (i.e. hydrogen peroxide and ferrous sulphate).
- Evaluation of the results of the experiment through regression analysis.

1.4. Study Variables

In this work the following are major study variables:

- COD concentration of the wastewater before and after the treatment
- Color of the wastewater before and after the treatment
- Appropriate treatment conditions, such as pH of the media, stirrer speed and reaction time.
- Optimum Fenton's reagent dosage

1.5. Significance of the Study

Advanced oxidation processes like oxidation with Fenton's reagent hold great promise to provide alternative, better treatment and protection of the environment. It has been applied as a post-treatment option to degrade non-biodegradable organic matters like COD and color in pigmented textile wastewater [15].

There are various types of advanced oxidation processes (AOPs) that are applicable for wastewater treatment but most of them do not degrade organic matters effectively like ozonation process and they require higher energy consumption and treatment cost like UV- assisted Fenton process [13].

But oxidation with Fenton's reagent has many advantages, such as the experiment need simple and easily available laboratory equipments, we can conduct the experiments with few chemicals/reagents, the reagents are environmentally safe and the reaction is fast and begins by itself without additional energy. Due to these advantages, oxidation with Fenton's reagent has been selected to treat Ayka Addis textile wastewater.

2. LITERATURE REVIEW

2.1. Processing of Cotton Based Textiles

Cotton based textiles are processed through three main stages, comprising spinning, knitting/weaving and wet processing [17]. In general, we can classify the overall processes of cotton based textiles in to two classes; these are dry process and wet process. The dry process includes; spinning, weaving/knitting and the wet process includes; sizing, desizing, scoring, bleaching, mercerizing, dying and printing.

2.1.1. Dry Process

2.1.1.1. Spinning

Spinning is the process which converts raw fiber into yarn or thread. The fibers are prepared and then drawn out and twisted to form the yarn, which is then wound onto a bobbin or cone. The spinning process is entirely dry, although some yarns may be dyed and finished as a final customer product [18, 19]. The spinning process is illustrated in Figure 2.1.

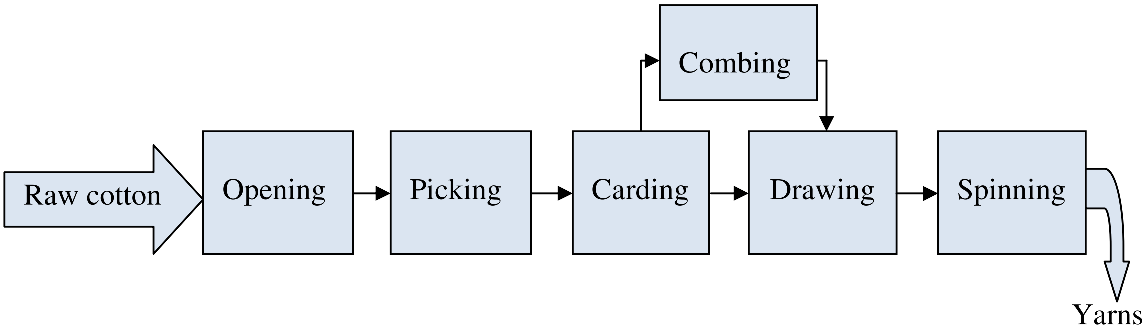


Figure 2.1**:** Main stages in the spinning of raw cotton.

2.1.1.2. Knitting

Knitting is carried out by interlocking a series of yarn loops, usually using sophisticated, high speed machinery. This process is almost completely dry, although some oils may be applied during the process for lubrication. These are removed by subsequent processing and enter in to the wastewater stream [12].

2.1.1.3. Weaving

Weaving is the most common method used for producing fabrics. The process is carried out on a loom which interlaces lengthwise yarns (warp yarns) with widthwise ones (weft or filling yarns).

Prior to weaving, the warp threads are coated with a size, to increase their tensile strength and smoothness [13].

The sizing compound is dried on the threads and remains a part of the cloth until it is removed in the subsequent processes. Other chemicals, such as lubricants, agents, and fillers, are often added to impart additional properties to a fabric [12, 13]. The knitting and weaving processes are illustrated in Figure 2.2.

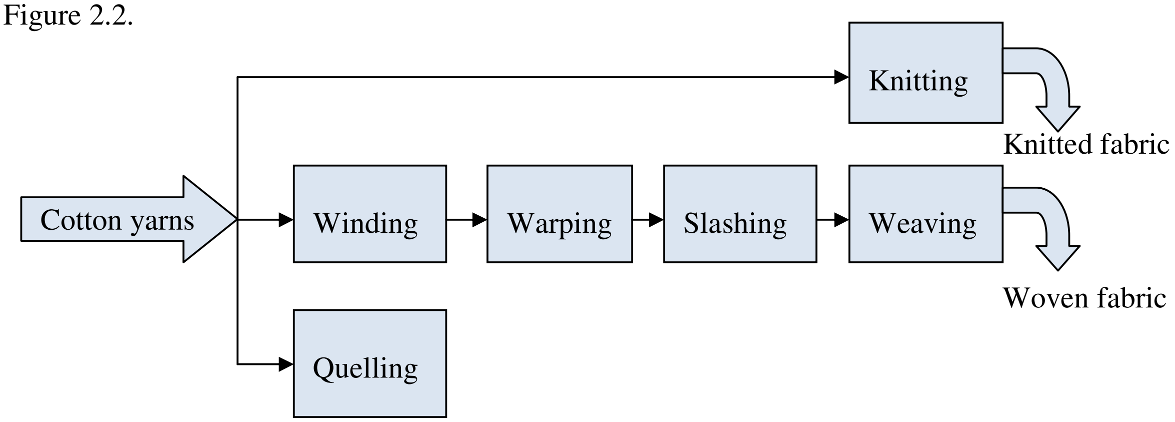


Figure 2.2: Main stages in the weaving and knitting of cotton yarns.

2.1.2. Wet Process

The stages of wet processing of cotton textiles, both woven and knitted, are shown in Figure 2.3 and 2.4 [13]:

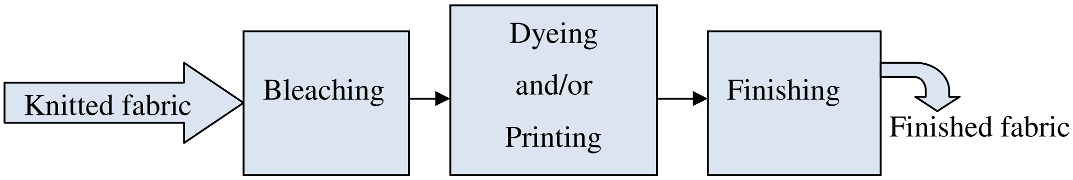


Figure 2.3: Wet processing of knitted cotton fabrics.

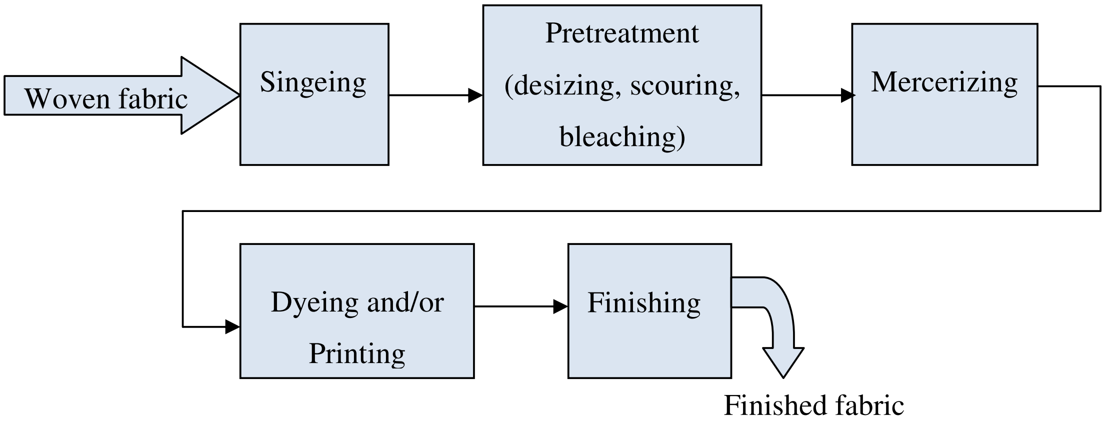


Figure 2.4: Wet processing of woven cotton fabrics.

2.1.2.1. Sizing and Desizing

Both sizing and desizing are among from pretreatment processes. Sizing is carried out before the weaving process by using starch to increase the tensile strength and smoothness of the yarn, to reduce yarn breakages [12].

Desizing, either with acid or enzymes then removes size or starch from the fabric, so that chemical penetration of the fabric in later stages is not inhibited. Desizing effluents have very high organic concentrations, contributing 40 – 50 % of the total organic load from the preparatory sequences. Gums and polyvinyl alcohol (PVA) may be removed by a simple hot wash but starch and its derivatives have to be made soluble by soaking with acids, enzymes or oxidants before being removed by a hot wash [14].

2.1.2.2. Scouring

Scouring is carried out to remove impurities that are present in cotton, both natural (e.g. waxes, fatty acids, proteins, etc.) and acquired (such as size, dirt and oil picked up during processing). This is usually done at high temperatures (above 100 °C) with sodium hydroxide and produces strongly alkaline effluents (around pH = 12.5) with high organic loads. They tend to be dark in color and have high concentrations of total dissolved solids (TDS), oil and greases [13].

The scouring is normally done either on a Kier, a J Box, or an open width pad roll system, or on open width continuous plant. Common scouring agents include detergents, soaps, alkalis, antistatic agents, wetting agents, foamers, defoamers and lubricants [14].

2.1.2.3. Bleaching

Bleaching is used to whiten fabrics and yarns using sodium hypochlorite or hydrogen peroxide. Many cotton processing factories use sodium hypochlorite as it is cheaper than hydrogen peroxide. However, this is highly toxic and is now strictly limited or banned in many countries. It can also break down to form absorbable organo-halogen compounds, which are both toxic and carcinogenic. Bleaching generates effluents with a low organic content, high TDS levels and strong alkalinity (pH between 9 - 12). Once bleaching is complete, the bleaching agent must be completely removed, either by a thorough washing or using enzymes [12, 14].

2.1.2.4. Mercerizing

In this process, the cotton yarn or fabric is treated with an alkali (sodium hydroxide, NaOH) to improve luster, strength and dye uptake. It also removes immature fibers. The process is normally carried out on dry fabric; wet mercerization reduces the steam consumption, but requires stringent control of the operational parameters, such as sodium hydroxide concentration [12].

Excess sodium hydroxide is normally recovered for reuse in either the scouring or other mercerization stages. The rinse wastes are alkaline, high in inorganic solids and caustic alkalinity, and low in BOD. With increasing trend toward cotton polyester blends, much less mercerizing is being carried out [13, 15].

Combined mercerizing: Where scouring is carried out simultaneously with the mercerization in hot conditions, is now becoming popular, as the mercerization increases the rate of scouring. This combined process reduces capital cost, space requirements, energy costs, labor requirement and chemical costs [15, 16].

2.1.2.5. Dyeing

The major classes of dyestuffs used in the textile industry are includes [17]:

Acid dyes: mainly used on wool, silk and polyamide fibers. They give very bright colors, whose fastness ranges from very poor to very good.

Basic dyes: usually applied to acrylics and polyesters to produce very bright colors.

Direct dyes: commonly applied to rayon and cotton.

Disperse dyes: applied to cellulose acetate, polyamide and polyester fibers.

Reactive dyes: this group produces a range of bright shades, and commonly used for cellulose textiles.

Sulphur dyes: most commonly used for dyeing cotton, rayon and cotton synthetic blends and produce strong, deep colors in the final fabric.

Vat dyes: these cover an almost full range of shades and are particularly important in the dyeing of cellulose fibers (such as cotton).

Azoic dyes: produce deep shades of blue, violet, yellow, orange and scarlet.

2.1.2.6. Printing

Printing is a process that is used for applying color to a fabric. Unlike dyeing, it is usually only carried on prepared fabric where it is applied to specific areas to achieve a planned design. The color is applied to the fabric and then treated with steam, heat or chemicals to fix the color on the fabric. Different printing techniques and their application area are shown in Table 2.1 [18, 19].

Table 2.1: Most commonly used printing techniques.

Printing Techniques	**Application**
Pigment printing	Commonly used for all fabric types
Wet printing	Uses reactive dyes for cotton and generally has a softer feel than pigment printed fabrics
Discharge printing	Creates patterns by first applying color to the fabric and then removing selected areas
Final washing	It is carried out to remove excess paste and leave a uniform color

2.1.2.7. Finishing

The finishing process imparts the final aesthetic, chemical and mechanical properties to the fabric as per the end user requirements [20, 21]. Common finishing processes include:

Wrinkle resistant/crease retentive: using synthetic resins.

Water/Oil repellent: using silicones and other synthetic materials (e.g. fluorocarbon resins).

Flame retardant: Most commonly carried out on synthetic fabrics, by co-polymerization of the flame retardant into the fabric itself; introduction of an additive during processing; application as a textile finish. Natural fibers such as cotton can only be made flame retardant by applying a chemical finish.

Mildew resistance: using hazardous substances such as mercury, copper, arsenic and poly chlorinated phenols (PCP).

2.2. Textile Wastewater

The amount of wastewater varies widely depending on the type of process operated at the mill. Various toxic chemicals such as complexing agents, sizing, wetting, softening, anti-felting and finishing agents, wetting agents, biocides, carriers, halogenated benzene, surfactants, phenols, pesticides, dyes and many other additive are used in wet processing, which are washing scouring, bleaching, mercerizing, dyeing, finishing. The water employed in the process eventually ends up as wastewater [23, 24].

Main pollutants from dyeing and finishing units include high suspended solids (SS), chemical oxygen demand (COD), biological oxygen demand (BOD), heat, color, acidity, basicity, and other organic pollutants [25].

Government legislation is becoming more stringent in most developed and developing countries regarding the removal of dyes from industrial effluent. Due to this most textile industry is developing onsite or in plant facilities to treat their own effluent before discharging into the environment [26].

2.2.1. Sources of Wastewater in Textile Manufacturing

The main sources of wastewater normally come from cleaning water, pretreatment, dyeing and finishing process water, non-contact cooling water and others. The water consumption varies widely in the industry depending on the mill, processes, equipment used and type of materials produced. Each textile processes utilizes large amount of water, which will finally become wastewater [22].

The most significant sources of wastewater among various process stages are pretreatment, dyeing, printing, and finishing of textile materials. At the pretreatment stage, desizing is the industry's largest source of wastewater [28]. During desizing, all the sizes used during weaving are removed from the fabric and discarded into the wastewater. In scouring, dirt, oil, waxes from natural fibers are removed from the fabric and washed into wastewater stream. Normally desizing and scouring are combined and these two processes may contribute to 50 % of BOD in the wastewater in the wet processing. Wastewater from the peroxide bleaching is not a major problem [29, 30].

Dyeing process generate the largest portion of the total wastewater. The source of wastewater is from the dye preparation, spent dye bath and washing processes. Dyeing wastewater contains high salt, alkalinity and color. Finishing processes generate organic pollutants such as residue of resins, softeners and other auxiliaries [31, 32].

2.2.2. Textile Wastewater Characteristics and Environmental Impact

Normal textile dyeing and finishing operations dyestuff usage can vary from day to day and sometimes even several times a day because of the batch wise nature of the processes. Frequent changes of dyestuff employed in the dyeing and finishing processes cause considerable variation in the wastewater characteristics particularly the pH, color and COD [32, 33].

Strong color is another important component of the textile wastewater which is very difficult to deal with. Color is noticed in the wastewater effluent and the presence of small concentrations of dyes in water is highly visible and may affect their transparency and aesthetics [34].

Dye house wastewater from textile mills is a serious pollution problem because it is high in both color and organic content. A dye is a colored substance that can be applied in solution or dispersion to a substrate in textile manufacturing, thus giving a color appearance to textile materials. Discharging of dyes into water resources even in a small amount can affect the aquatic life and their food web and also causes allergic dermatitis and skin irritation on human being [35, 36].

The primary concern about effluent color is not only its toxicity but also its undesirable aesthetic impact on receiving waters. Non-biodegradable nature of most of the dyes reducing aquatic diversity by blocking the passage of sunlight through the water represents serious problems to the environment. Since many dyes have adverse effect on aquatic life and human beings, the removal of color from the effluent or process has appeared of importance for ensuring healthy environment [34].

Table 2.2: Effluent characteristics from textile industry.

Process	**Effluent Composition**	**Characteristics**
Sizing	Starch, wax, carboxy methyl cellulose (CMC), poly vinyl alcohol (PVA), wetting agents	High in BOD, COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins	High in BOD, COD, SS, dissolved solid (DS)
Bleaching	Sodium hypochlorite, Cl_2, NaOH, H_2O_2, acids, surfactants, $NaSiO_3$, sodium phosphate , short cotton fiber	High alkalinity, high SS
Mercerizing	NaOH, cotton wax	High pH, low BOD, high DS
Dyeing	Dyestuffs urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents	Strongly colored, high BOD, DS, low SS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly colored, high BOD, oily appearance, slightly alkaline

The discharge of organic pollutant either BOD or COD to the receiving stream can lead to the depletion of dissolved oxygen and thus creates anaerobic condition. Under anaerobic condition foul smelling compound such as hydrogen sulfides may be produced. This will consequently upset the biological activity in the receiving stream [37, 38].

Hence, it is imperative that a suitable treatment method should be applied. The color of the effluent discharges into receiving water affects the aquatic flora and fauna and causes many water born diseases. Some of dyes are carcinogen and others after transformation or degradation yield compound such as aromatic amines, which may carcinogen or otherwise toxic. In addition, dyes accumulate in sediments at many sites, especially at location of wastewater discharge, which has an impact on the ecological balance in the aquatic system. These pollutants because of leaching from soil also affect ground water system [39, 40].

The color of reactive dyes is due to the presence of -N=N- azo bonds and chromophoric groups. The dyes are first absorbed on the cellulosic and then fiber. After fixation of the dyes on the fiber about 10 – 15 % of initial loading is present in the dye bath effluent [40]. Reactive dyes in both ordinary and hydrolyzed form are not easily biodegradable and thus even after treatment color may be present in the effluent. [41].

With regard to environmental pollution through wastewater, Ayka Addis textile factory discharges the wastewater without proper treatment except addition of sulfuric acid to reduce its pH and urea to balance the fertility of the contaminated soil; due to this they are polluting the environment and causing the above mentioned impacts on the surrounding environment. The wastewater discharge to the environment is shown in Figure 2.5.

Figure 2.5: Ayka Addis textile factory wastewater discharged to the environment.

2.3. Treatment of Textile Wastewater

The dye contained in textile wastewater can vary daily and even hourly. The hot and strongly colored wastewater contains large amount of suspended solids, high chemical oxygen demand and greatly fluctuating pH which can be difficult to be treated. Hundreds of small scale dyeing industries is facing closure since they are not treating their effluent as it is not economical [41].

After every effort to reduce waste strength and volume by conservation and good housekeeping there are still problems of disposing the effluent without affecting the receiving stream. There are many ways for treating textile wastewater. The treatment methods differ from plant to plant depending on the size, type of waste and degree of treatment needed. Generally, treatment options can be divided into three main categories namely biological, chemical and physical methods [43].

a) Biological Method: There are many types of biological treatment methods. Among them include trickling filters, activated sludge process, anaerobic process, oxidation ponding etc. To date the commonest treatment of textile wastewater has been based on mainly on aerobic biological process, consisting mainly conventional and extended activated sludge system. The trickling filters simulate stream flow by spraying wastewater over a broken medium such as stone or plastic. The medium serves as a base for biological growth, which attacks the organic matter of wastewater and uses it as food [44].

In activated sludge process, the wastewater flows into a tank after primary settling. The microorganism in activated sludge is suspended in the wastewater as aggregates. The sludge and wastewater is kept in suspension by compressed air, which also supplies the oxygen, necessary for biological activities. The aerated waste is continuously withdrawn and settled and a portion of the sludge is returned to the influent [45].

Biological methods of removing pollutants from textile wastewater, by using natural process involving bacteria and other microorganism for oxidation of the organic waste are generally cheap and simple to apply and are currently used as a pretreatment option to remove biodegradable organics from textile wastewater. Anaerobic and aerobic treatments have been used together or separately for the treatment of textile effluents. Hence aerobic treatment is not effective in color removal from textile wastewater that contains azo dyes [46].

Generally, conventional biological treatment process are not effective for treating dyed wastewater because many commercial dyes are toxic to organism being used and result in the problems of sludge bulking, rising sludge and pin flock. Because of low biodegradability of many textile chemicals and dyes, biological treatment alone is not always effective for treatment of textile wastewater [44, 46].

b) Chemical Method: Includes coagulation or flocculation and oxidation. The main advantage of the conventional coagulation and flocculation is removal of the waste stream due to the removal of dye molecules from the dye bath effluent and not due to partial decomposition of dyes which can lead to an even more potentially harmful and toxic aromatic compound [46].

Physical and chemical treatment techniques are effective for color removal but use more energy and chemicals than biological processes. They also concentrate the pollution into solid or liquid side streams requiring additional treatment of disposal. The major disadvantage is the production of sludge. In coagulation process large amount of sludge is created which may become a pollutant itself and increase the treatment cost [47].

Chemical oxidation uses strong oxidizing agents such as hydrogen peroxides, chlorine and others to force degradation of resistant organic pollutant. Chemical oxidation is the most commonly used method of decolorization by chemical owing to its simplicity and the main oxidizing agent is hydrogen peroxide [46, 47].

Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenol, pesticides and aromatic hydrocarbon. One of the major advantage of ozonation is it does not increase the volume of wastewater and sludge. A major disadvantage of this process is its short half life typically being 20 minutes [47].

c) Physical Method: Includes membrane filtration such as nano-filtration, reverse osmosis and adsorption. Membrane filtration is an effective means of removing pollutant from the wastewater. However the initial investment cost is very huge and the periodic replacement of membrane is remarkably high [48].

Adsorption is an effective method of lowering the concentration of dissolved dyes in the effluent resulting in color removal. The adsorption on activated carbon without pretreatment is impossible because the suspended solids rapidly clog the filter. This procedure is therefore only feasible in combination with flocculation - decantation treatment or a biological treatment. The combination permits a reduction of suspended solids and organic substances, as well as a slight reduction in the color, but the cost of activated carbon is high [48, 49].

Reverse osmosis membranes have a retention rate of 90 % or more for most types of ionic compounds and produce a high quality of permeate [50]. Decoloration and elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step by reverse osmosis. It 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 [51].

Ultra-filtration enables elimination of macromolecules and particles, but the elimination of polluting substances, such as dyes, is never complete, it is only between 31 % and 76 % [52]. Even in the best of cases, the quality of the treated wastewater does not permit its reuse for sensitive processes, such as dyeing of textile emphasize that 40 % of the water treated by ultra-filtration can be recycled to feed processes termed "minor" in the textile industry (rinsing, washing) in which salinity is not a problem. Ultra-filtration can only be used as a pretreatment for reverse osmosis or in combination with a biological reactor [54, 53].

Micro-filtration is suitable for treating dye baths containing pigment dyes, as well as for subsequent rinsing baths. The chemicals used in dye bath, which are not filtered by micro-filtration, will remain in the bath. It can also be used as a pretreatment for nano-filtration or reverse osmosis [53].

2.3.1. Advanced Oxidation Processes (AOPs)

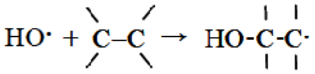
The AOP term was firstly coined by *Glaze et al. in 1987* and includes all those chemical oxidations based on the generation of highly reactive hydroxyl free radicals ($OH^\bullet$) as principal oxidants [31]. The standard potential (E^o = 2.80 V versus normal hydrogen electrode (NHE)) is shown along with the ones of some common oxidants in Table 2.3. Following fluorine, hydroxyl free radical is the most powerful known oxidant [31, 57].

Table 2.3: Standard potential of some relevant oxidants (at 25°C).

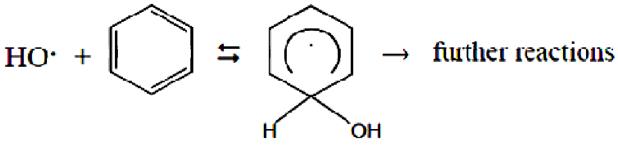
Oxidizing Agent	**Electrochemical Oxidation Potential (EOP), V**
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

As a difference to other conventional oxidant species, the hydroxyl free radical is capable to completely oxidize (i.e., mineralize) even the less reactive pollutants. It reacts non-selectively with organic compounds, principally by means of electrophilic, addition to unsaturated bonds, addition to aromatic rings, abstraction of hydrogen, or by electron transfer, Equations (2.1) – (2.4) [33].

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \qquad (2.1)$$



(2.2)



(2.3)

$$HO^{\bullet} + RH \rightarrow [RH]^{\cdot +} + HO^{-} \qquad (2.4)$$

Mineralization end products generally are carbon dioxide, water and inorganic ions, without a large residues generation. The rate constants of most reactions involved are usually in the order of 10^6 - 10^9 l/mol. s [59].

Advanced oxidation processes usually operate at or near to ambient temperature and pressure. They can be classified according to the reaction phase, homogeneous and heterogeneous and depending on the method used to generate hydroxyl free radical species, chemical, electrochemical, photochemical, sono-chemical and radiolytic techniques [31, 60]. Among them, the most extensively used include, heterogeneous photo-catalysis with TiO_2 single or with H_2O_2, treatment with ozone often combined with H_2O_2, and /or UV systems and Fenton type reactions such as Fenton, photo-Fenton, or electro-Fenton processes [31, 60].

The main disadvantage of some AOPs is the operational cost associated with their high electrical energy input particularly UV radiation generation. In fact, only wastewaters with relatively small concentrations (COD $\leq$ 5,000 mg/l) can be economically treated with these technologies [62, 63].

However, not all photochemical AOPs require irradiation of the same wavelength. Whereas direct O_3 or H_2O_2 photolysis requires photons of short wavelength (below ~ 300 nm), heterogeneous photo-catalysis with TiO_2 and photo-assisted Fenton processes may employ photons of wavelengths up to around 400 nm and 550 nm, respectively [64].

To overcome this energy consumption, AOPs can effectively treat textile wastewater under solar irradiation, wavelengths greater than 300 nm, reduces significantly the economic burden in a more environmentally benign manner. This fact is especially interesting for the large scale application of these processes [55, 65].

Another important strategy that could lead to minimize such AOPs drawbacks is combining it with biological treatments. Under mild conditions, conventional biological treatment can be implemented as a pre-treatment step, aimed to turn bio-recalcitrant pollutants into bio-compatible new compounds and those of AOPs as a post-treatment step to abate the pollutants left after the biological treatment [66]. Types of advanced oxidation processes (AOPs) are listed below;

- $H_2O_2/UV/Fe^{2+}$ (photo-assisted Fenton)
- H_2O_2/Fe^{2+} (Fenton)
- Ozone/UV (also applicable in the gas phase)
- Ozone/H_2O_2
- Ozone /UV/H_2O_2
- Ozone/TiO_2/Electron-beam irradiation
- Ozone/TiO_2 /H_2O_2
- Ozone and electron beam irradiation
- Ozone/ultrasonic
- H_2O_2/UV

Table 2.4: Possible treatments for textile wastewater and their advantages and disadvantages.

Processes	**Advantages**	**Disadvantages**
Biodegradation	Rates of elimination by oxidizable substances about 90 %	Low biodegradability of dyes
Coagulation - flocculation	Elimination of insoluble dyes	Production of sludge blocking filter
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Cost of activated carbon
Ozone treatment	Good decolorization	No reduction of the COD
Electrochemical processes	Capacity of adaptation to different vol. and pollution loads	Iron hydroxide sludge

In this work oxidation with Fenton's reagent (H_2O_2/Fe^{2+}) is selected due to its advantages over other treatment techniques in Table 2.3. Its advantages includes, the experimental set up is simple, laboratory equipments are easily available, the reagents are environmentally safe and the reaction is fast and to start the reaction no need of additional energy.

2.3.1.1. Fenton's Oxidation Process

It is accepted that the "classical" mechanism described in 1934 by Haber and Weiss where in Fenton reaction, Equation (2.5), it is firstly reported by H.J.H. Fenton in 1894, hydroxyl free radicals are generated by interaction of hydrogen peroxide (H_2O_2) with ferrous salts namely the Fenton reagent. For simplification, H_2O ligands on iron sphere coordination will be omitted from here on [57, 65].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (k = 53 – 76 \text{ l/mol. s}) \qquad (2.5)$$

Generated Fe^{3+} can be reduced by reaction with exceeding H_2O_2 to form again ferrous ion and more hydroxyl free radicals. This second process is called Fenton-like reaction; it is slower than Fenton reaction and allows Fe^{2+} regeneration in an effective cyclic mechanism, Equation (2.6) and (2.7). When iron is added in small amounts, it acts as a catalyst while hydrogen peroxide is continuously consumed [66].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (k = 1 – 2*10^{-2} \text{ l/mol. s}) \qquad (2.6)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \quad (k = 0.33 - 2.1*10^{6} \text{ l/mol. s}) \qquad (2.7)$$

The rate limiting step is the regeneration of Fe^{2+}, Equation (2.6) and (2.7). Ferrous ion remains at trace levels, with approximately constant Fe^{3+} concentration in aqueous solution.

Equations (2.8) – (2.10), show other important reactions involving ferrous ion and hydrogen peroxide in the absence of other interfering ions and organic substances. The following radical-radical reactions as well as the auto-decomposition of H_2O_2 take part in the complex process, Equation (2.11) – (2.14) [66, 67].

$$Fe^{2+} + HO_2^{\bullet} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \quad (k = 0.72 – 1.5*10^{6} \text{ l/mol. s}) \qquad (2.8)$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \quad (k = 2.6 – 5.8*108 \text{ l/mol. s}) \qquad (2.9)$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (k = 1.7 – 4.5*10^{7} \text{ l/mol. s}) \qquad (2.10)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (2.11)$$

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (k = 5 - 8*10^9 \text{ l/mol. s}) \qquad (2.12)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (k = 0.8 - 2.2*10^6 \text{ l/mol. s}) \qquad (2.13)$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \quad (k = 1.4*10^{10} \text{ l/mol. s}) \qquad (2.14)$$

The rate constants are those reported by Sychev and Isaak [58]. It is important to note that some of the reactions are believed to occur in multiple steps.

2.3.1.1.1. Kinetics of Fenton Reactions

The kinetics of Fenton reactions can be quite complex because of the large number of steps involved. The general rate equation for the reaction of target organic compound may be written as follows [54]:

$$\frac{dC_{RH}}{dt} = k_{HO\bullet} * C_{HO\bullet} * C_{RH} + \sum_{i}(k_{OXi} * C_{OXi} * C_{RH}) \qquad (2.15)$$

where;

ox_i represents additional oxidants other than $HO^{\bullet}$ that may also be present, such as ferryl, C_{OXi} is their concentration, $C_{HO\bullet}$ is the hydroxyl free radical concentration and C_{RH} is the target organic compound concentration.

Since hydroxyl free radical is usually regarded as the sole or most important reactive species, Equation (2.15) can be rewritten as:

$$-\frac{dC_{RH}}{dt} = k_{HO\bullet} * C_{HO\bullet} * C_{RH} \qquad (2.16)$$

Considering that the concentration of reactive species must quickly reach a stationery state regimen during the processm and provided that $C_{HO\bullet}$ may be considered constant, the rate law may be treated as being of pseudo-first order in terms of consumption of the target organic compound, Equation (2.16) can be rewritten as:

$$-\frac{dC_{RH}}{dt} = k_{app} * C_{RH} \qquad (2.17)$$

Finally, by integrating Equation (2.17), a plot of $\ln C_{RH}$ versus time generates a straight line whose slope corresponds to the apparent rate constant value (k_{app}) of the target organic compound degradation, Equation (2.18):

$$\ln C_{RH} = \ln C_{RH_0} - k_{app} * t \qquad (2.18)$$

where;

C_{RH0} is the initial concentration of the target organic compound.

2.3.1.1.2. Operational Conditions

The performance of such a complex reactive system is clearly pH dependent particularly in Fenton-like and photo-Fenton reactions with the maximum catalytic activity occur at pH = 3 [69].

For higher pH values, low activity is detected because of the decrease of free iron species due to ferric oxyhydroxides precipitation. On the other hand, the decrease of activity for pH values below the optimum is understandable taking into account (i) the inhibition of the complexation of Fe^{3+} with H_2O_2 in Equation (2.6) and (ii) the photo-activity of Fe^{2+} species present in solution.

Another important factor influencing the efficiency of these processes is the initial Fe^{2+} and H_2O_2 dosage. Although Fenton type reactions have been widely studied, there is no agreement on the ratio of H_2O_2 to Fe^{2+} that leads to the best mineralization results. Different authors have reported different reactant ratios and it seems difficult to attain a universal criterion for all type of substrates when the reaction pathways and even the oxidative species may differ in each case [62, 70].

The optimum treatment conditions depend on the degree of degradation that is to be achieved. In any case, it has to be taken into account the detrimental effect of large concentrations of either H_2O_2 or Fe^{2+} since they can act themselves as radical scavengers, Equation (2.9) and (2.10). Undesirable competitive reactions, such as given by Equation (2.110 – (2.14), could also be favored by using inappropriate Fe^{2+}/H_2O_2 ratios [63, 70].

As other AOPs, Fenton and photo-Fenton processes are generally carried out at room temperature. However, temperature is a key parameter that has to be taken into account. It is known that thermal Fenton process is accelerated with increasing temperature, although too high values (above 40 ^oC) may decompose hydrogen peroxide, Equation (2.11) precluding the extent of mineralization. When photo-assisted reactions are controlling the process, no beneficial effect is observable [63].

Obviously, incident irradiation intensity is also another factor affecting the rate of generation of hydroxyl free radicals at photo-assisted processes and hence the rates of degradation of pollutants [63].

Finally, it has been reported that incorporation of molecular oxygen into the complex reaction mechanism of the Fenton and photo-Fenton systems leads to greater mineralization of target pollutants into CO_2 [32, 64].

Oxygen (O_2) consumption may be caused by different processes. It reacts with intermediate organic radicals to generate oxygenated intermediates, Equation (2.19), forming photo-labile Fe^{3+} complexes and thus promoting overall mineralization [56, 65].

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow \text{Non-radical oxygenated products} \qquad (2.19)$$

The intermediate organo-peroxides formed serve to oxidize Fe^{2+} to Fe^{3+}, which is photo-active, Equation (2.20).

$$RO_2^{\bullet} + Fe^{2+} \rightarrow RO_2^{-} + Fe^{3+} \qquad (2.20)$$

Finally, it generates $HO_2^{\bullet}$ by means of the "Dorfman" mechanism, Equation (2.21) [57, 60], which is shown below:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \rightarrow ROH + HO_2^{\bullet} \qquad (2.21)$$

The direct oxidation of Fe^{2+} by O_2 (auto-oxidation) is too slow to be important in acidic solution [62].

2.3.1.1.3. Application to Wastewater Treatments

The degradation of organic pollutants present in wastewater by means of Fenton and more especially of photo-Fenton systems is a fast growing field of applied research.

Oxidation with Fenton's reagent can be used to treat different industrial effluent wastewater such as pesticide manufacturing effluents, agricultural effluents (wine-distilleries and black olive plants), pulp and paper bleaching effluents and dye containing textile effluents [68].

2.3.1.1.4. Benefits and Limitations

Among the different AOPs, Fenton and especially the photo-Fenton processes are considered the most promising for the remediation of highly contaminated wastewaters. They constitute an attractive oxidative system since do not require neither expensive reagents nor sophisticated instrumentation for pollutant destruction [62].

Iron is the fourth most abundant element on the earth, as well as non-toxic and safe, whereas hydrogen peroxide, compared with other bulk oxidants, is reasonably priced, easy to handle and environmentally benign [69].

At the same time, the Fenton reagent is considered a "clean" reagent. Once the treatment is over, dissolved iron can be removed by precipitation and physical separation, just increasing the pH ~ 8.5

of the media [63]. Moreover, if the employed catalyst amount is small enough (in order of few mg/l), it could remain dissolved without affecting the quality of the resulting water. Likewise, any residual hydrogen peroxide readily decomposes to O_2 and H_2O, Equation (2.11), posing no lasting environmental threat [55, 57].

Fenton type processes are capable to carry out a deep mineralization of pollutants, in many cases, oxidative effectiveness clearly superior than other AOPs. It makes use of photons with wavelengths from the near-UV up to visible (~ 550nm), with the possibility of be driven under solar irradiation [36].

Other associated drawbacks are the instability of the reagent mixture, the necessity of pH change, the interference by some substances that complex iron ions and the possible iron oxide sludge generation and subsequent disposal. In this sense, recent studies aim at the application of iron as a heterogeneous catalyst, providing an easy separation and the possibility of working without pH adjustment [39, 59].

3. MATERIALS AND METHODS

3.1. Materials

The following main materials and equipments were utilized during the experiment work:

- Wastewater sample collected from Ayka Addis textile factory around Addis Ababa city at Alem Gena
- Chemicals (Fenton's reagent such as hydrogen peroxide (H_2O_2), hydrated ferrous sulphate ($FeSO_4.7H_2O$)) and to adjust the pH of the wastewater sample, hydrochloric acid (HCl) and sodium hydroxide (NaOH)
- Laboratory equipments such as pH meter, stirred tank reactors, beakers different in size and capacity, digital or analog type of balance, spatula, filter paper, oven, BOD incubator, COD and TOC analyzer and HACH model spectrophotometer are necessary.

3.2. Methods

3.2.1. Analytical Methods

The measured parameters of wastewater during the experiments were chemical oxygen demand (COD, mg/l), biological oxygen demand (BOD, mg/l), total organic carbon (TOC, mg/l), total suspended solids (TSS, mg/l), total solids (TS, mg/l), color (Pt-Co unit), pH, turbidity (NTU).

The experiment is conducted according to procedures given in standard methods for the examination of water and wastewater [69]. Some of the experimental procedures which are relevant with the objectives of this work are described in the following sections.

3.2.1.1. COD Analysis

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Because of its unique chemical properties, the dichromate ion ($Cr_2O_7^{2-}$) is the specified oxidant used in this experiment.

Chemical oxygen demand (COD) measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, titrimetric method 5220 C [69].

Apparatus used

a) Digestion vessels: Preferably use borosilicate culture tubes, 16 × 100 mm, 20 × 150 mm, or 25 × 150 mm, with tetra-fluoro-ethylene (TFE) lined screw caps.

b) Block heater or similar device to operate at a temperature of 150 ± 2 °C, with holes to accommodate digestion vessels. Do not use an oven because of the possibility of leaking samples generating a corrosive and possibly explosive atmosphere.

c) Microburet

d) Ampule sealer: Use only a mechanical sealer to insure strong and consistent seals.

Reagent used

a) Standard potassium dichromate digestion solution, 0.01667M: Add to about 500 ml distilled water 4.903 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150 ^{0}C for 2 hr, 167 ml H_2SO_4, and 33.3 g $HgSO_4$. Dissolve, cool to room temperature, and dilute to 1000 ml.

b) Sulfuric acid reagent: Add Ag_2SO_4, reagent or technical grade, crystals or powder, to H_2SO_4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4.

c) Ferroin indicator solution: Dissolve 1.485 g 1,10-phenanthroline monohydrate and 695 mg $FeSO_4 \cdot 7H_2O$ in distilled water and dilute this reagent by a factor of 5 (1 + 4).

a) Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10 M: Dissolve 39.2 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml H_2SO_4, cool, and dilute to 1000 ml.

b) Standardize solution daily against standard $K_2Cr_2O_7$ digestion solution as follows: Pipet 5.00 ml digestion solution into a small beaker.

$$\text{Molarity of FAS solution} = \frac{\text{Vol. of 0.01667M } K_2Cr_2O_7 \text{ solution titrated, ml}}{\text{Vol. of FAS used in titration, ml}} * 0.1$$

c) Sulfamic acid: Required only if the interference of nitrites is to be eliminated.

d) Potassium hydrogen phthalate (KHP) standard, $HOOCC_6H_4COOK$: Lightly crush and then dry KHP to constant weight at a temperature of 110 ^{0}C. Dissolve 425 mg in distilled water and dilute to 1000 ml.

Experimental procedure

a) Wash culture tubes and caps with 20 % H_2SO_4 before first use to prevent contamination.

b) Place tubes or ampules in block digester preheated to 150 °C and reflux for 2 hrs behind a protective shield.

c) Cool to room temperature and place vessels in test tube rack.

d) Remove culture tube caps and add small tetraflouro ethylene (TFE) covered magnetic stirring bar. If ampules are used, transfer contents to a larger container for titrating.

e) Add 0.05 to 0.10 ml (1 to 2 drops) ferroin indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10 M FAS.

f) The end point is a sharp color change from blue-green to reddish brown, although the blue-green may reappear within minutes. In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.

Figure 3.1: Wastewater sample analysis for COD determination.

Calculation

Chemical oxygen demand (COD) concentration was calculated using the following formula:

$$\mathrm{COD}\left(\frac{\mathrm{mg}}{\mathrm{l}}\right) = \frac{(\mathrm{FAS_S} - \mathrm{FAS_P}) * \mathrm{N} * \mathrm{f}}{\mathrm{V_S}}$$

where;

FASs: used ferrous ammonium sulphate concentration for sample, mg/l, FASp: used ferrous ammonium sulphate concentration for pure water, mg/l, f: dilution factor (8000), N: normality of FAS and Vs: sample volume, ml

3.2.1.2. Color Measurements

A HACH model spectrophotometer was used for the color measurements in Pt-Co unit. The following are the experimental procedures followed to determine the color of the wastewater before and after treatment:

- Wipe the blank (deionized water) and place it into the cell holder and touch zero, the display will show 0 Pt-Co and,

- Wipe the prepared wastewater sample and place it into the cell holder and touch read, the result will appear in Pt-Co unit.

Figure 3.2: Spectrophotometer (HACH model) used for determination of the color of wastewater.

3.2.1.3. Five Day BOD Test

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 day. Dissolved oxygen (DO) is measured initially and after incubation, and the BOD_5 is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

Five days biological oxygen demand (BOD_5) measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, 5 – days BOD test 5210 B. [69].

Apparatus used

a) Incubation bottles: Use glass bottles having 60 ml or greater capacity (300 ml bottles having a ground glass stopper and a flared mouth are preferred). Clean bottles with a detergent, rinse thoroughly and drain before use.

b) Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

Required reagent

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles.

a) Potassium hydroxide (KOH) to absorb carbon dioxide gas (CO_2)

b) Nitrification inhibitor, 2 – chloro – 6 - (trichloromethyl) pyridine.to avoid nitrification

c) Dilution water: Use demineralized, distilled, tap, or natural water for making sample dilutions

d) Acid and alkali solutions, 1 N of NaOH and HCl, for neutralization of caustic or acidic wastewater samples.

Experimental procedures

Preparation of the sample

a) Select the volume for the wastewater sample

b) The sample volume is related to the expected BOD_5 value. The BOD_5 incubator is designed to operate with the following BOD_5 ranges and sample volume allowing BOD_5 measurement.

   i) BOD_5 range 0 - 400 mg/l use the sample without dilution

   ii) BOD_5 range 0 - 2000 mg/l, the expected sample volume is 56 ml with 3 drop of nitrification inhibitor and 3 - 4 drop of potassium hydroxide (KOH) addition.

   iii) BOD_5 range 0 - 4000 mg/l the expected sample volume is 21.2 ml with 1 drop of nitrification inhibitor and 3 - 4 drop of potassium hydroxide (KOH) addition.

c) Carry out the necessary pretreatment of the wastewater sample, setting pH between 6.5 - 7.5, if higher or lower adjust by HCl and NaOH and mix well and allow the sample to settle and filtrate of the sample

d) Measure the wastewater sample precisely using appropriate overflow and if necessary add nitrification inhibitor

e) Insert magnetic stirring rod

f) Place 3 - 4 drop of KOH solution into the seal gasket and insert gasket in the neck of the bottle, screw the BOD sensors to the sample bottle and then place the bottle in the bottle rack

g) Finally, incubate the sample for 5 days at a temperature of 20 ^{0}C.

Calculation

For each test bottle meeting the 2.0 mg/l minimum dissolved oxygen (DO) depletion and the 1.0 mg/l residual DO, calculate BOD_5 as follows:

$$\mathrm{BOD_5, mg/l} = \frac{D_1 - D_2}{P}$$

Where;

D_1 = DO of diluted sample immediately after preparation, mg/l,

D_2 = DO of diluted sample after 5 day incubation at 20 °C, mg/l,

P = decimal volumetric fraction of sample used,

Figure 3.3: Wastewater samples in BOD_5 incubator.

3.2.1.4. TOC Analysis

The sample is homogenized and diluted as necessary and a micro portion is injected into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide, platinum group metals, or barium chromate. The water is vaporized and the organic carbon is oxidized to CO_2 and H_2O. The CO_2 from oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a non-dispersive infrared analyzer, or titrated coulometrically.

Total organic carbon (TOC) measurements were carried out according to procedures given in standard methods for the examination of water and wastewater, high temperature combustion method 5310 B [69].

Apparatus used

a) Total organic carbon analyzer, using combustion techniques
b) Sampling, injection, and sample preparation accessories
c) Sample blender or homogenizer
d) Magnetic stirrer and tetrafluoro ethylene (TFE) - coated stirring bars
e) Filtering apparatus and 0.45 μm pore - diameter filters. Preferably use syringe filters with no detectable TOC blank.

Reagent used

a) Reagent water: Prepare reagents, blanks, and standard solutions from reagent water with a TOC value less than 2 × the method detection level (MDL).
b) Acid: Sulfuric acid, H_2SO_4
c) Organic carbon stock solution**:** Dissolve 2.1254 g anhydrous primary-standard-grade potassium biphthalate ($C_8H_5KO_4$) in carbon-free water and dilute to 1000 ml.
d) Inorganic carbon stock solution: Dissolve 4.4122 g anhydrous sodium carbonate (Na_2CO_3) in water, add 3.497 g anhydrous sodium bicarbonate ($NaHCO_3$) and dilute to 1000 ml.
e) Carrier gas: Purified oxygen or air, CO_2 - free and containing less than 1 ppm hydrocarbon (as methane).
f) Purging gas: Any gas free of CO_2 and hydrocarbons.

Experimental procedure

a) Instrument operation: Adjust to optimum combustion temperature before using instrument; monitor temperature to insure stability.
b) Sample treatment: If a sample contains gross solids or insoluble matter, homogenize until satisfactory replication is obtained. If inorganic carbon must be removed before analysis,

transfer a representative portion (10 to 15 ml) to a 30 ml beaker, add acid to reduce pH to 2 or less, and purge with gas for 10 min.

c) Sample injection: Withdraw a portion of prepared sample using a syringe fitted with a blunt tipped needle. Stir samples containing particulates with a magnetic stirrer. Inject samples and standards into analyzer and record response. Repeat injection until consecutive measurement is obtained, that is reproducible to within ± 10%.

d) Preparation of standard curve: Prepare standard organic and inorganic carbon series by diluting stock solutions to cover the expected range in samples within the linear range of the instrument. Dilute samples higher than the linear range of the instrument in reagent water. Inject and record peak height or area of these standards and a dilution water blank.

e) Plot carbon concentration in milligrams per liter against corrected peak height or area on rectangular coordinate paper.

Calculations

Calculate corrected instrument response of standards and samples by subtracting the reagent - water blank instrument response from that of the standard and sample. Prepare a standard curve of corrected instrument response versus TOC concentration. Subtract procedural blank from each sample instrument response and compare to standard curve to determine carbon content.

3.2.1.5. Total Solids and Volatile Solids (TS and VS) Analysis

a) Total Solids (TS): Total solids are a measure of the suspended and dissolved solids in water. Matter suspended or dissolved in water or wastewater is considered as solids. A high amount of solids in water generally makes it not desirable for consumption.

Figure 3.4: Wastewater samples in the oven for total solid analysis.

Solid analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations. A limit of 500 mg dissolved solids/l is set by Ethiopian Environmental Protection Authority (EEPA) as secondary standard for drinking water.

b) Volatile Solids (VS): Volatile solids are those solids lost on ignition (heating to 550 ^{0}C.) They are useful to approximate the amount of organic matter present in the solid fraction of wastewater, activated sludge and industrial wastes.

Figure 3.5: Wastewater samples in muffle furnace for volatile solid analysis.

Apparatus used

a) Evaporating dishes
b) Desiccators, provided with a desiccant containing a color indicator of moisture
c) Drying oven operating at a temperature of 103 – 105 ^{0}C, for total and suspended solid analysis, Figure 3.4.
d) Analytical balance
e) Graduated cylinder and beaker
f) Muffle furnace operating at a temperature of 550 ^{0}C, for volatile solid analysis, Figure 3.5.

Experimental procedure

Preparation of evaporating dish:

a) Ignite clean evaporating dish at a temperature of 550^{o}C for 1 hr in a muffle furnace for volatile solid analysis
b) Heat clean dish at a temperature of 103 – 105 ^{0}C for 1 hr for total solid analysis
c) Store and cool dish in desiccators at room temperature until needed
d) Weigh the dish immediately before use

Analysis of the sample:

a) Add a measured volume of well mixed sample to a pre-weighed dish
b) Evaporate to dryness on drying oven for 24 hrs
c) If necessary add successive sample portions to the same dish after evaporation
d) Cool dish in desiccators to balance temperature and weigh it immediately
e) Ignite the residue produced in a muffle furnace for 3 hrs
f) Transfer to a desiccators for final cooling in a dry atmosphere

Calculations

The amounts of total solid and volatile solid in the sample can be computed using Equation (3.2) and (3.3) respectively.

$$\frac{\text{Total solid, mg}}{\text{l}} = \frac{(\text{A} - \text{B})}{\text{Vample volume, ml}} * 100 \qquad (3.2)$$

where;

A = weight of dried residue + dish, mg, and B = weight of dish, mg.

$$\frac{\text{Volatile solid , mg}}{\text{l}} = \frac{(\text{A} - \text{B})}{\text{Sample volume, ml}} * 100 \qquad (3.3)$$

where;

A = weight of dried residue + dish before ignition, mg and B = weight of residue + dish after ignition, mg.

3.2.1.6. pH Measurements

pH measurements were carried out by using 890 MD pH meter. The pH meter was calibrated by using deionized water before use.

3.2.2. Experiments Using Fenton's Reagent

Before the experiment was conducted, it is necessary to convert the reagents in to easily available measuring units as described below;

a) Conversion of H_2O_2 from mg/l to ml unit:

Hence, hydrogen peroxide is available in solution form so that, to convert it in ml unit we should have to use Equation (3.6).

$$30\% \, * \, \text{density of } \mathrm{H_2O_2} \qquad (3.4)$$

$$\frac{30\text{ g}}{100\text{ g}} * \frac{1.11 * 10^3\text{ mg}}{\text{ml}} = 333\frac{\text{mg}}{\text{ml}} \qquad (3.5)$$

$$\mathrm{H_2O_2}, \text{ml} = \frac{\text{ml}}{333\text{ mg}} * \mathrm{H_2O_2}, \frac{\text{mg}}{\text{l}} * \text{wastewater vol.}, \text{l} \qquad (3.6)$$

b) Conversion of Fe^{2+} from mg/l to mg unit:

Hence, ferrous sulfate is available in solid form so that, to convert it in mg unit we should have to use the following formula.

$$\mathrm{FeSO_4 \, . \, 7H_2O}, \text{mg}$$

$$= \frac{1\text{ mmol}}{56\text{ mg of Fe}^{2+}} * \frac{278.01\text{ mg of } \mathrm{FeSO_4 \, . \, 7H_2O}}{\text{mmol}} * \mathrm{Fe}^{2+}, \frac{\text{mg}}{\text{l}} * \text{wastewater vol.}, \text{l}$$

3.2.2.1. Experimental Design

In this work, the study was carried out at four different stages to fulfill the specified objectives and each stage is described as follows;

First stage: H_2O_2 and Fe^{2+} dosages fixed at 600 mg/l, stirrer speed and reaction time were kept constant at 30 rpm and 30 min respectively, to determine the optimum pH providing maximum COD and color removal. Here the only experimental factor was pH and its range was between 2 and 6.

Second stage: optimum reaction time was investigated by providing optimum pH from the first stage and taking a constant dosage of H_2O_2 and Fe^{2+}, 600 mg/l and fixed value of stirrer speed, 30 rpm were used. Here the only experimental factor was reaction time and its range was 5 - 30 min.

Third stage: optimum stirrer speed was investigated by providing the optimum pH and reaction time of first and second stage of experiment and by providing a constant dosage of H_2O_2 and Fe^{2+}, 600 mg/l. Here the only experimental factor was stirrer speed and its range was 5 - 30 rpm.

Fourth stage: the optimum H_2O_2 and Fe^{2+} dosage is determined, by providing the optimum pH, reaction time and stirrer speed from the previous stages. Here the experimental factors were H_2O_2 and Fe^{2+} dosage and their ranges were classified in to four series these are;

a) Series – 1: Fe^{+2} dosage was kept constant at 1,200 mg/l while H_2O_2 dosage was altered from 200 to 1,200 mg/l, to observe the effect of H_2O_2 dosage on COD and color removal.
b) Series – 2: H_2O_2 dosage was kept constant at 600 mg/l while Fe^{2+} dosage was altered from 200 to 1,200 mg/l, to observe the effect of Fe^{2+} dosage on COD and color removal.
c) Series – 3: Fe^{2+} dosage was kept constant at 600 mg/l while H_2O_2 dosage was altered from 100 to 600 mg/l, to observe the effect of H_2O_2 at lower dosage on COD and color removal.
d) Series – 4: both H_2O_2 and Fe^{2+} dosage was altered from 100 to 600 mg/l, to observe the effects of both H_2O_2 and Fe^{2+} at lower dosages on COD and color removal.

3.2.2.2. Experimental Procedure

To conduct the oxidation experiment with Fenton's reagent, the wastewater sample is necessary. So that I collect the wastewater sample from Ayka Addis textile factory at the outside of the factory's discharge point on 24th January - 2011 at 4: 25 o'clock.

During this time the discharge was the combination of reactive dye, dispersed dye and vat dye. So, the experiment was done using this combined wastewater sample. The wastewater sample point is shown bellow in Figure 3.6.

Figure 3.6: Ayka Addis textile factory wastewater discharge and sample point.

Experiments were conducted using hydrogen peroxide (H_2O_2) (30 %, w/w) and hydrated ferrous sulfate ($FeSO_4.7H_2O$) and samples' pH value was adjusted using 1M hydrochloric acid (HCl) and 1M sodium hydroxide (NaOH). It was carried out in jar test apparatus.

Before doing the experiment it is necessary to reduce the pH of the wastewater sample by using 0.1 M hydrochloric acid (HCl) solution and then after measuring the desired dosages of $FeSO_4.7H_2O$ put it in to 250 ml of wastewater sample and then add the desired amount of H_2O_2 in to the same sample and after doing this, expose the wastewater sample for stirrer to mix the contents in the wastewater sample. After the treatment, the treated wastewater should be allowed to settle for more than 20 min.

Settled sample then placed into new beaker with a volume of 500 ml and pH was adjusted to 7.6 with 0.10 M sodium hydroxide (NaOH) solution then the treated wastewater sample used for further investigations like COD and color. The overall experimental set-up is shown in Figure 3.7.

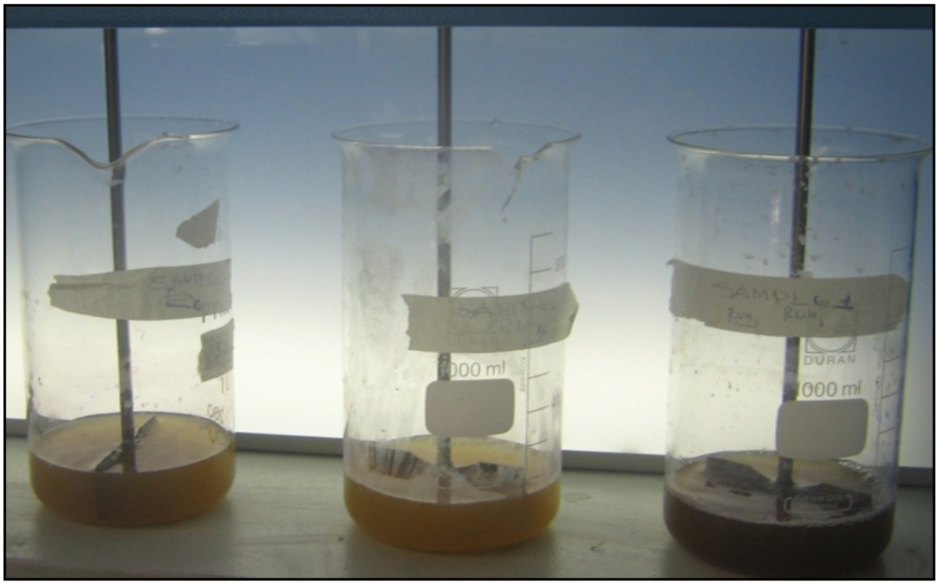


Figure 3.7: Wastewater treatment process and experimental set-up.

4. RESULTS AND DISCUSSIONS

4.1. Ayka Addis Textile Wastewater Characteristics

For the characterization of Ayka Addis textile factory wastewater effluents that are used in chemical oxidation experiment using Fenton's reagent, COD, BOD_5, TOC, color, TS, VS, TSS, TDS, pH and turbidity analysis were made according to the procedures described in section 3.2.1. These results were presented in Table 4.1.

Table 4.1: Characteristics of Ayka Addis textile wastewater.

Parameters	**Value**
pH	8.5
Biological Oxygen Demand (BOD_5) (mg/l)	230
Chemical Oxygen Demand (COD) (mg O_2/l)	1,122.70
Total Organic Carbon (TOC) (mg/l)	69.01
Total Solids (TS) (mg/l)	4,000
Total Suspended Solids (TSS) (mg/l)	1, 000
Volatile Solid (VS) (mg/l)	1,250
Total Dissolved Solids (TDS) (mg/l)	3,000
Turbidity (NTU)	195
Color (Pt-Co)	2,000

4.2. The Effect of pH on Fenton Oxidation

The effect of pH on removal of COD and color were investigated by changing the pH values from 2 to 6 with a single replica, at fixed concentrations of 600 mg/l H_2O_2 and 600 mg/l Fe^{+2} and at 30 minutes reaction time and 30 rpm stirrer speed. Optimum pH value was found to be 3 and used for all other experiments as optimal condition. The results obtained from this experiment were illustrated in Table 4.2. The maximum COD and color removal efficiency was found to be 78 %

and 97 %, respectively at pH = 3. The removal efficiency of COD and color as a function of pH value is shown on Figure 4.1.

Table 4.2: The effect of pH on treatment performance of Fenton oxidation.

pH	Effluent COD (mg/l)	COD Removal Efficiency (%)	Effluent Color (Pt-Co)	Color Removal Efficiency (%)
Control	1,122.70	-	2,000	-
2	505.22	55	140	93
3	246.99	78	60	97
4	296.52	74	83	96
5	336.81	70	100	95
6	842.03	25	240	88

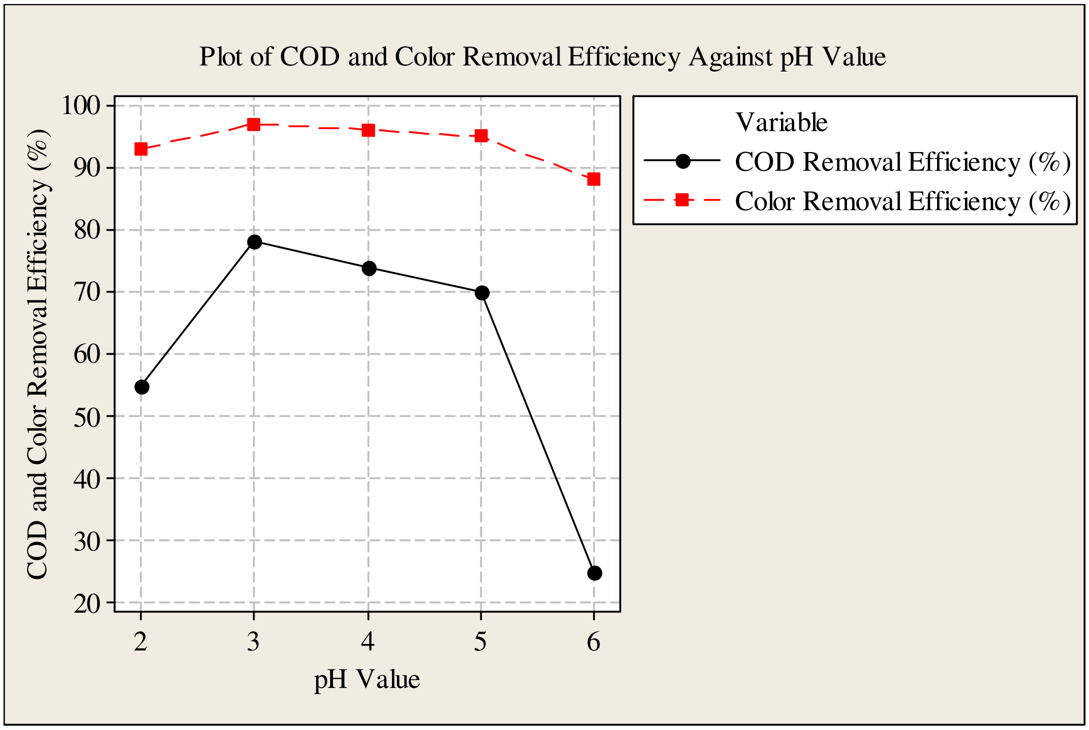


Figure 4.1: COD and color removal efficiency at different pH values

Figure 4.1 shows that, COD and color removal efficiency decline after pH value is equal to 3, this is because of coagulant formation, the decrease of free iron (II) species due to ferric oxyhydroxides precipitation, the decomposition of hydrogen peroxide to water and oxygen occurs more rapidly in alkali or at higher pH and at larger pH value there will be the occurrences of several side reactions rather than generation of hydroxyl free radicals ($OH^{\bullet}$). Therefore, the oxidation with Fenton's reagent is more favorable at pH value is equal to 3.

4.3. The Effect of Reaction Time on Fenton Oxidation

In this experiment reaction times were changed from 5 to 30 minutes with a single replica, in order to determine the effect of reaction time on COD and color removal efficiencies. The experiments were carried out at pH = 3 it is taken from the above experiment result and also by using the fixed concentrations of 600 mg/l of Fe^{+2} and 600 mg/l of H_2O_2 and 30 rpm of constant stirrer speed.

The optimum reaction time based on COD and color removal efficiencies were found at 30 minutes, at this reaction time the concentration of COD decreased to 246.99 mg/l with 78 % removal efficiency and color was reduced to 80 Pt-Co with a corresponding color removal efficiency of 96 %, the results of this experiment were presented in Table 4.3.

Table 4.3: The effect of reaction time on treatment performance of Fenton oxidation

Rxn. Time (min.)	**Effluent COD (mg/l)**	**COD Removal Efficiency (%)**	**Effluent Color (Pt-Co)**	**Color Removal Efficiency (%)**
Control	1,122.7	-	2,000	-
5	471.53	58	160	92
10	449.08	60	140	93
15	303.13	73	120	94
20	291.90	74	115	94
25	280.68	75	100	95
30	246.99	78	80	96

From this result, we can observe that as the time of reaction increases, the efficiency of COD concentration and color removal efficiency also increases. If the reaction proceeds over 30 miniuts we may have more COD and color reduction efficiency but in order to reduce or save time for other experiments and also to minimize energy consuption, it is better to stop the experiment at this reaction time (30 minutes) for this research experiments.

4.4. The Effect of Stirrer Speed on Fenton Oxidation

In this experiment stirrer speeds were changed from 5 to 30 rpm with a single replica, in order to determine the effect of stirrer speed on COD and color removal efficiencies. The experiments were carried out at pH = 3 from previous experiment result, using the fixed concentrations of 600 mg/l of Fe^{+2} and 600 mg/l of H_2O_2 and also at 30 minutes of reaction time which is obtained from the above experiment result.

The optimum stirrer speed based on COD and color removal efficiencies was found at 30 rpm. At this stirrer speed COD concentration decreased to 235.77 mg/l with 79 % removal efficiency and color was reduced to 60 Pt-Co with the corresponding color removal efficiency of 97 %, the results were presented in Table 4.4.

Table 4.4: The effect of stirrer speed on treatment performance of Fenton oxidation

Stirrer Speed (rpm)	Effluent COD (mg/l)	COD Removal Efficiency (%)	Effluent Color (Pt-Co)	Color Removal Efficiency (%)
Control	1,122.7	-	2,000	-
5	505.22	55	360	82
10	415.40	63	240	88
15	314.36	72	160	92
20	280.68	75	120	94
25	269.45	76	100	95
30	235.77	79	60	97

From this result we can observe that, as the stirrer speed increases, the efficiency of COD concentration and color removal efficiency increases. If the reaction proceeds over 30 rpm we may have more COD and color reduction efficiency but there is an increament of energy consumption. So that, to minimize energy consuption it is better to run the experiment at this stirrer speed for this research experiments. Since, COD and color reduction efficiency at this stirrer speed has a satisfactory result.

4.5. The Effect of Fenton's Reagent Dosages

In this study a series of experiments were carried out at different Fe^{+2} and H_2O_2 dosages, from previous experiments pH is equal to 3 and 30 minutes of reaction time and 30 rpm of stirrer speed were used to obtain optimum Fe^{+2} and H_2O_2 dosage. This experiment is divided in to four series, each series includes six different dosages and they were subjected to Jar test.

4.5.1. Effect of H_2O_2 Dosages on Effluent COD and Color Removal

In the first series Fe^{+2} dosage was kept constant at 1,200 mg/l while H_2O_2 dosage was altered from 200 to 1,200 mg/l. In this series, optimum Fe^{+2} and H_2O_2 dosage based on removal efficiencies were at 1,000 mg/l of H_2O_2 and 1,200 mg/l of Fe^{2+}.

Application of these dosages resulted with removal efficiencies of 88 % and 99 % for removal of COD and color, respectively which are bellow the limit value set by Ethiopian Environmental Protection Authority (EEPA) (Appendix II). The effects of H_2O_2 dosage on COD and color removal efficiencies were presented in Table 4.5.

Table 4.5: Results of series - 1 for Fenton's reagent dosages.

Dosages (mg/l)	**Effluent COD (mg/l)**	**COD Removal Efficiency (%)**	**Effluent Color (Pt-Co)**	**Color Removal Efficiency (%)**
Control	1,122.70	-	2,000	-
200 mg/l H_2O_2 + 1,200 mg/ Fe^{+2}	550.12	51	360	82
400 mg/l H_2O_2 + 1,200 mg/l Fe^{+2}	392.95	65	120	94

600 mg/l H_2O_2 + 1,200 mg/l Fe^{+2}	190.86	83	60	97
800 mg/l H_2O_2 + 1,200 mg/l Fe^{+2}	168.41	85	40	98
1,000 mg/l H_2O_2 + 1,200 mg/l Fe^{+2}	134.72	88	20	99
1,200 mg/l H_2O_2 + 1,200 mg/l Fe^{+2}	224.54	80	80	96

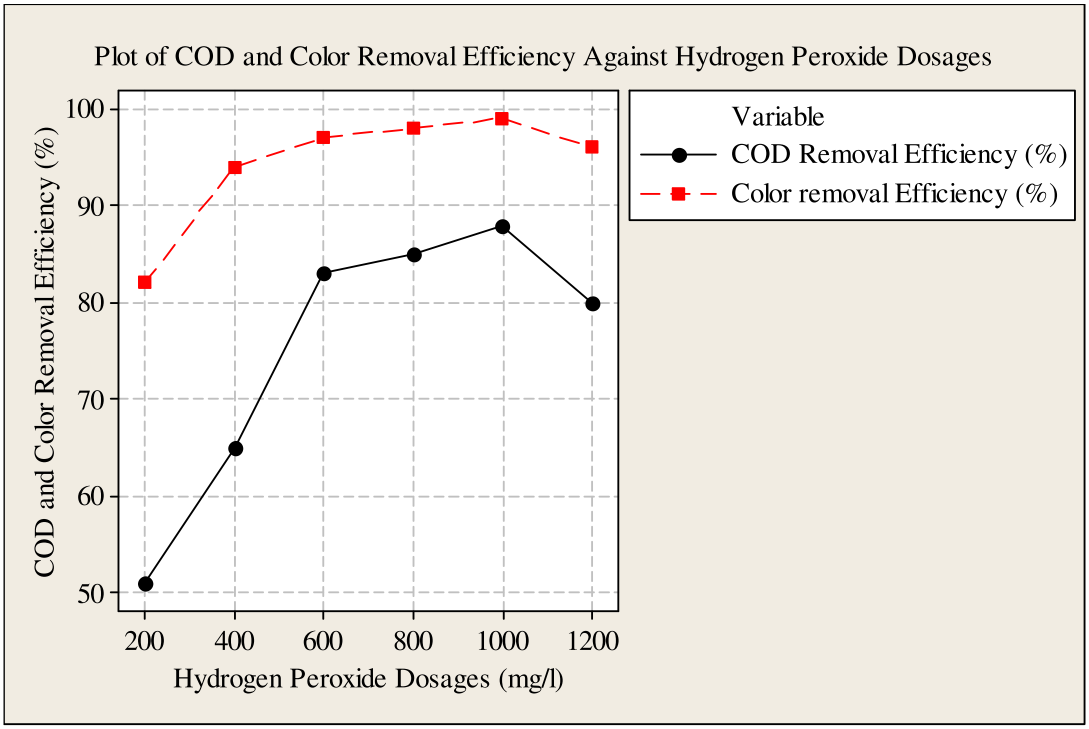


Figure 4.2: COD and color removal efficiency against H_2O_2 dosages at fixed dosage of Fe^{2+}.

From Figure 4.2, we can observe that, the removal efficiencies of COD and color increased when the amount of hydrogen peroxide (H_2O_2) increases up to 1000 mg/l, at a fixed dosage of ferrous ion (Fe^{2+}), 1200 mg/l.

After the maximum H_2O_2 dosage (1000 mg/l) the removal efficiency of COD and color becomes decreasing, this is due to the availability of different side reactions, reduction of free Fe^{2+} ion, this condition results the decrease of hydroxyl free radicals ($OH^{\bullet}$). Consequently, reduction of COD and color has resulted.

4.5.2. Effect of Fe^{2+} Dosages on Effluent COD and Color Removal

In second series Jar test was carried out at a fixed dosage of hydrogen peroxide (H_2O_2) = 600 mg/l and different Fe^{2+} dosages increasing from 200 mg/l to 1,200 mg/l. It was observed that removal efficiency increased with increasing dosage of Fe^{2+}.

Application of these dosages resulted with removal efficiencies of 85 % and 99 % for removal of COD and color, respectively. The effects of Fe^{2+} dosage on COD and color removal efficiencies were presented in Table 4.6.

Table 4.6: Results of series - 2 for Fenton's reagent dosages.

Dosages (mg/l)	Effluent COD (mg/l)	COD Removal Efficiency (%)	Effluent Color (Pt-Co)	Color Removal Efficiency (%)
Control	1,122.7	-	2,000	-
600 mg/l H_2O_2 + 200 mg/l Fe^{+2}	516.44	54	100	95
600 mg/l H_2O_2 + 400 mg/l Fe^{+2}	392.95	65	80	96
600 mg/l H_2O_2 + 600 mg/l Fe^{+2}	269.45	76	60	97
600 mg/l H_2O_2 + 800 mg/l Fe^{+2}	235.77	79	40	98
600 mg/l H_2O_2 + 1,000 mg/l Fe^{+2}	202.09	82	20	99
600 mg/l H_2O_2 + 1,200 mg/l Fe^{+2}	168.41	85	16	99

From Figure 4.3, we can observe that, the removal efficiencies of COD and color increased when the amount of ferrous ion (Fe^{2+}) increases up to 1200 mg/l, at a fixed dosage of hydrogen peroxide (H_2O_2), 600 mg/l. After the maximum ferrous ion (Fe^{2+}) dosage (1200 mg/l), the removal efficiency of color becomes unchanged this is due to the presence of excess amount of ferrous ion (Fe^{2+}) this phenomena indicates that further addition of ferrous ion (Fe^{2+}) (more than 1200 mg/l) gives no contribution on COD and color reduction rather than excess sludge formation.

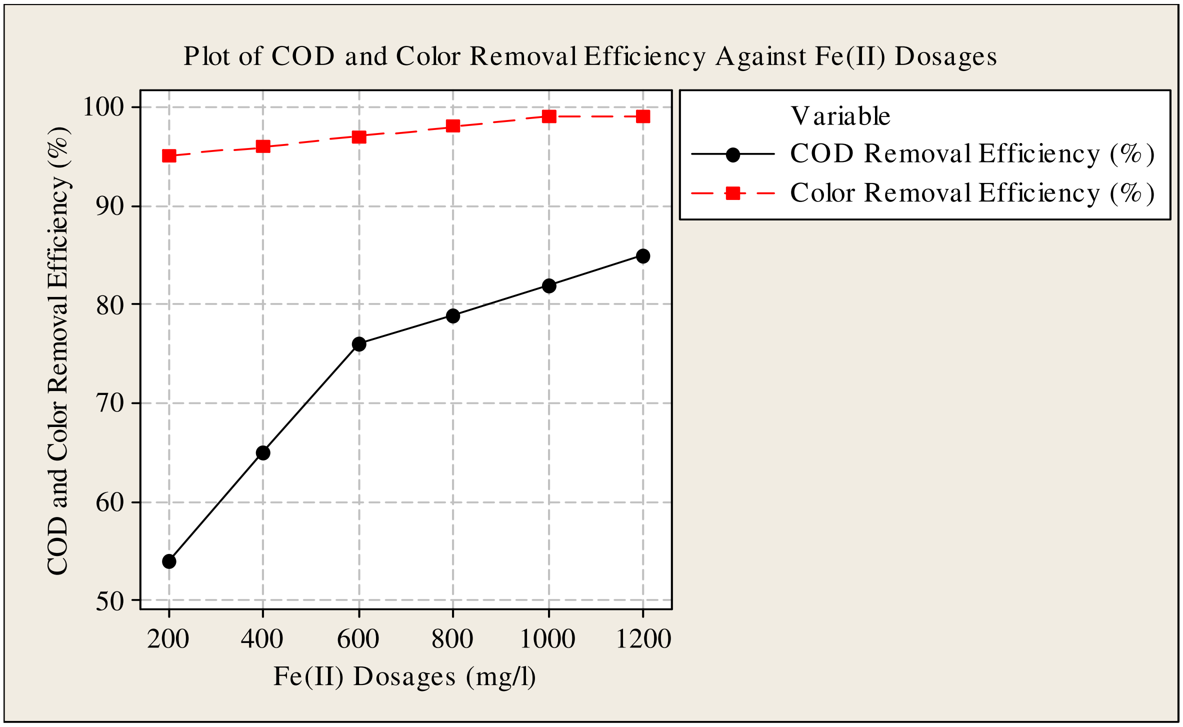


Figure 4.3: COD and color removal efficiency against H_2O_2 dosages at fixed dosage of (Fe^{2+}).

4.5.3. Effect of H_2O_2 at Lower Dosages on Effluent COD and Color Removal

In third series Jar test was carried out at a fixed dosage of ferrous ion (Fe^{2+}) = 600 mg/l and different hydrogen peroxide (H_2O_2) dosages increasing from 100 mg/l to 500 mg/l. It was observed that COD and color removal efficiency increases as the dosages of H_2O_2 increases.

Application of these dosages resulted with COD and color reduction of 291.90 mg/l and 80 Pt-Co, respectively. The corresponding COD and color removal efficiencies were 74 % and 96 % respectively.

Table 4.7: Results of series – 3 for Fenton’s reagent dosages

Dosages (mg/l)	**Effluent COD (mg/l)**	**COD Removal Efficiency (%)**	**Effluent Color (Pt-Co)**	**Color Removal Efficiency (%)**
Control	1,122.7	-	2,000	-
100 mg/l H_2O_2 + 600 mg/l Fe^{+2}	460.31	59	320	84

200 mg/l H_2O_2 + 600 mg/l Fe^{+2}	404.17	64	120	94
300 mg/l H_2O_2 + 600 mg/l Fe^{+2}	348.04	69	116	94
400 mg/l H_2O_2 + 600 mg/l Fe^{+2}	325.58	71	100	95
500 mg/l H_2O_2 + 600 mg/l Fe^{+2}	291.90	74	80	96

As the hydrogen peroxide dosage increases at constant lower dosage of ferrous ion (600 mg/l), the value of COD and color removal efficiencies also increases, but when the results of this experiment series compared to the results obtained at series one and two, it is not satisfactory result. The effects of Fe^{2+} at lower dosages on COD and color removal efficiencies were presented in Table 4.7.

4.5.4. Effect of H_2O_2 and Fe^{2+} Dosages on Effluent COD and Color Removal

In series four both hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) dosages increased from 100 mg/l to 500 mg/l. It was observed that, removal efficiencies were increases as the dosages of the reagent increases. Results of series four were illustrated in Table 4.8.

Application of these dosages resulted with COD and color reduction of 381.72 mg/l and 80 Pt-Co, respectively and the corresponding COD and color removal efficiencies were 66 % and 96 % respectively.

Table 4.8: Results of series - 4 for Fenton's reagent dosages.

Dosages (mg/l)	**Effluent COD (mg/l)**	**COD Removal Efficiency (%)**	**Effluent Color (Pt-Co)**	**Color Removal Efficiency (%)**
Control	1,122.7	-	2,000	-
100 mg/l H_2O_2 + 100 mg/l Fe^{+2}	752.21	33	1,040	48

200 mg/l H_2O_2 + 200 mg/l Fe^{+2}	583.80	48	500	75
300 mg/l H_2O_2 + 300 mg/l Fe^{+2}	527.67	53	240	88
400 mg/l H_2O_2 + 400 mg/l Fe^{+2}	415.40	63	140	93
500 mg/l H_2O_2 + 500 mg/l Fe^{+2}	381.72	66	80	96

When both hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) dosage increases, the value of COD and color removal efficiencies also increases, but when the results of this series compared to the result obtained at series one and two it is not satisfactory result. The effects of both hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) at lower dosages on COD and color removal efficiencies were presented in the above Table 4.8.

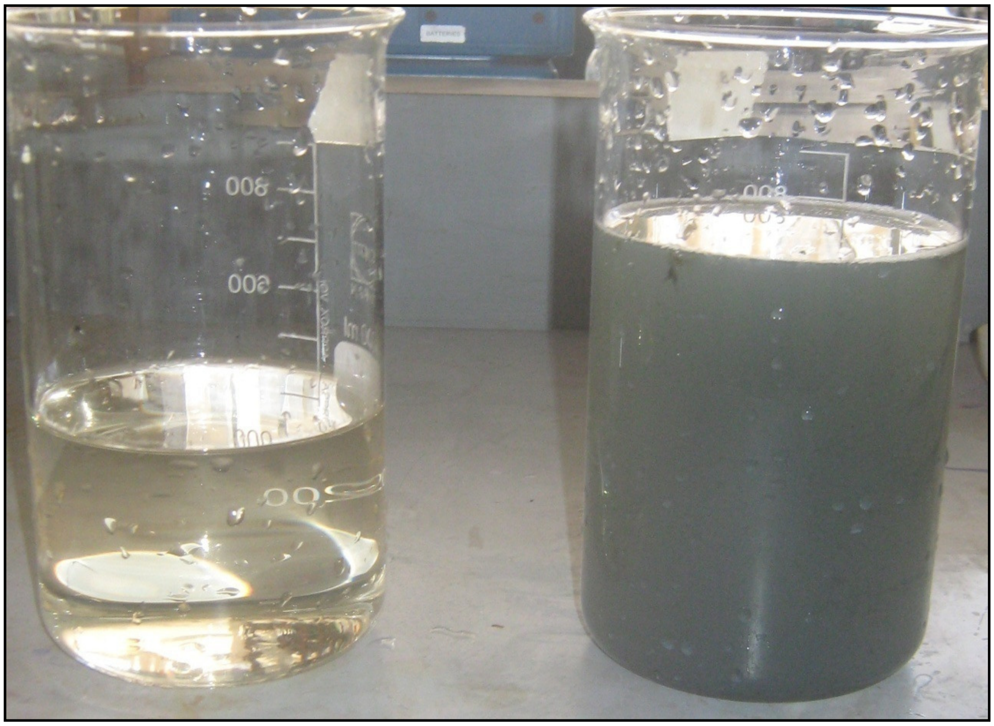


Figure 4.4: Wastewater after treatment (left) and before treatment (right).

Here in the above Figure 4.4, we can observe that how the treatment efficiency of oxidation with Fenton's reagent is better and significant. This result is obtained at series one experiment which is at the optimal treatment conditions (pH = 3, stirrer speed = 30 rpm and reaction time = 30 minutes) and at optimal Fenton's reagent dosage (H_2O_2 = 100 mg/l and Fe^{2+} = 1200 mg/l). At lower dosages of Fenton's reagent the removal efficiency is not satisfactory, this is because the less or minimum generation of hydroxyl free radicals.

4.6. Statistical Analysis

4.6.1. Regression Analysis

Regression analysis is used to investigate and model the relationship between a response variable and one or more predictors/factors. Minitab provides least squares and logistic regression procedures; use least squares procedures when your response variable is continuous and use logistic regression when your response variable is categorical.

Both least squares and logistic regression methods estimate parameters in the model so that the fit of the model is optimized. Least squares regression minimizes the sum of squared errors to obtain parameter estimates, whereas Minitab's logistic regression obtains maximum likelihood estimates of the parameters.

4.6.1.1. Effluent COD versus H_2O_2 and Fe^{2+} Dosages

Effluent COD values were affected by both hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) dosages and the regression equation is represented by;

Effluent COD (mg/l) = 636 - 0.296 H_2O_2 Dosage (mg/l) - 0.180 Fe^{2+} Dosage (mg/l)

Predictor	**Coef**	**SE Coef**	**T**	**P**
Constant	636.40	46.84	13.59	0.000
H_2O_2 Dosage (mg/l)	- 0.29590	0.08755	- 3.38	0.003
Fe^{2+} Dosage (mg/l)	- 0.18035	0.06247	- 2.89	0.009

S = 93.3075, R-Sq = 69.1%, R-Sq (adj) = 65.9%, R-Sq (pred) = 48.17%

Analysis of variance

Source of var.	DF	SS	MS	F	P
Regression	2	370,595	185,298	21.28	0.000
Residual Error	19	165,419	8,706		
Lack of Fit	18	165,167	9,176	36.41	0.130
Pure error	1	252	252		
Total	21	536,015			

Unusual observations

Obs	H_2O_2 Dosage (mg/l)	Effluent COD (mg/l)	Fit	SE Fit	Residual	St Resid.
1	200	550.1	360.8	52.4	189.3	2.45R
6	1200	224.5	64.9	56.1	159.6	2.14R

R denotes an observation with a large standardized residual. Durbin - Watson statistic = 0.961562

Lack of fit test

- Possible curvature in variable Fe^{2+} Dosage (P-Value = 0.007)
- Possible lack of fit at outer X - values (P - Value = 0.000)
- Overall lack of fit test is significant at P = 0.000

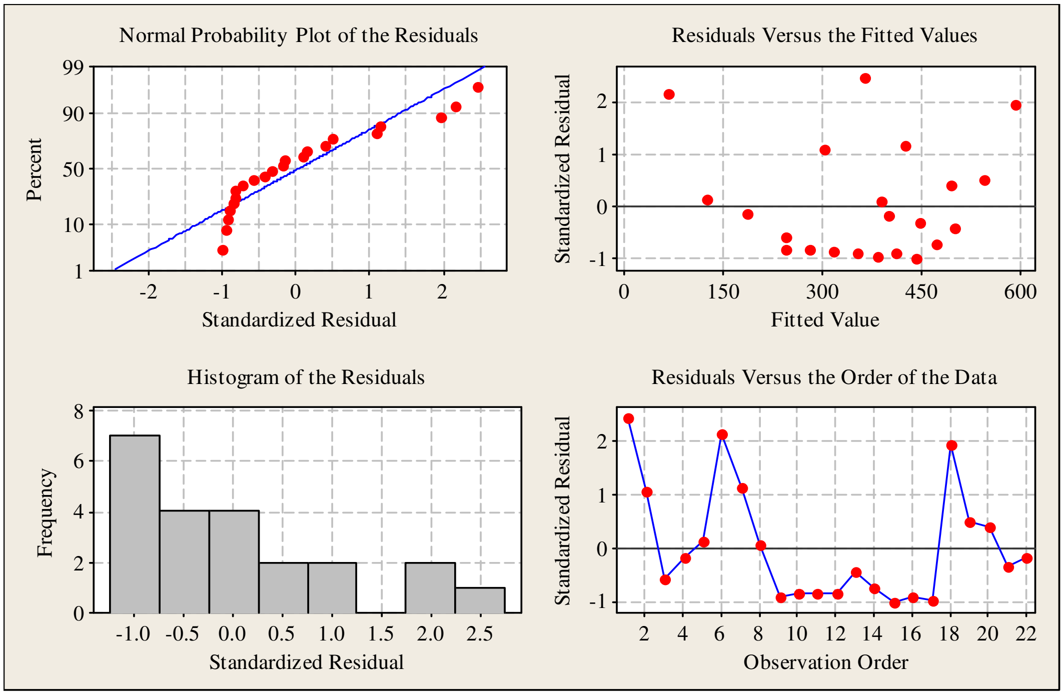


Figure 4.5: Residual plots for effluent COD.

4.6.1.2. Effluent Color versus H_2O_2 and Fe^{2+} Dosages

Effluent color values were affected by both hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) dosages and the regression equation is represented by;

Effluent Color (Pt-Co) = 463 - 0.394 H_2O_2 Dosage (mg/l) - 0.138 Fe^{2+} Dosage (mg/l)

Predictor	**Coef**	**SE Coef**	**T**	**P**
Constant	462.86	94.14	4.92	0.000
H_2O_2 Dosage (mg/l)	- 0.3936	0.1760	- 2.24	0.037
Fe^{2+} Dosage (mg/l)	- 0.1384	0.1256	- 1.10	0.284

S = 187.528, R-Sq = 39.6%, R-Sq(adj) = 33.3%, PRESS = 1041392, R-Sq(pred) = 5.93%

Analysis of Variance

Source of var.	**DF**	**SS**	**MS**	**F**	**P**
Regression	2	438,859	219,430	6.24	0.008
Residual Error	19	668,170	35,167		
Lack of Fit	18	667,202	37,067	38.29	0.127
Pure error	1	968	968		
Total	21	1,107,029			

Unusual Observations

Obs	**H_2O_2 Dosage (mg/l)**	**Effluent Color (Pt-Co)**	**Fit**	**SE Fit**	**Residual**	**St Resid.**
18	100	1,040.0	409.7	81.6	630.3	3.73R

R denotes an observation with a large standardized residual. Durbin-Watson statistic = 1.53760

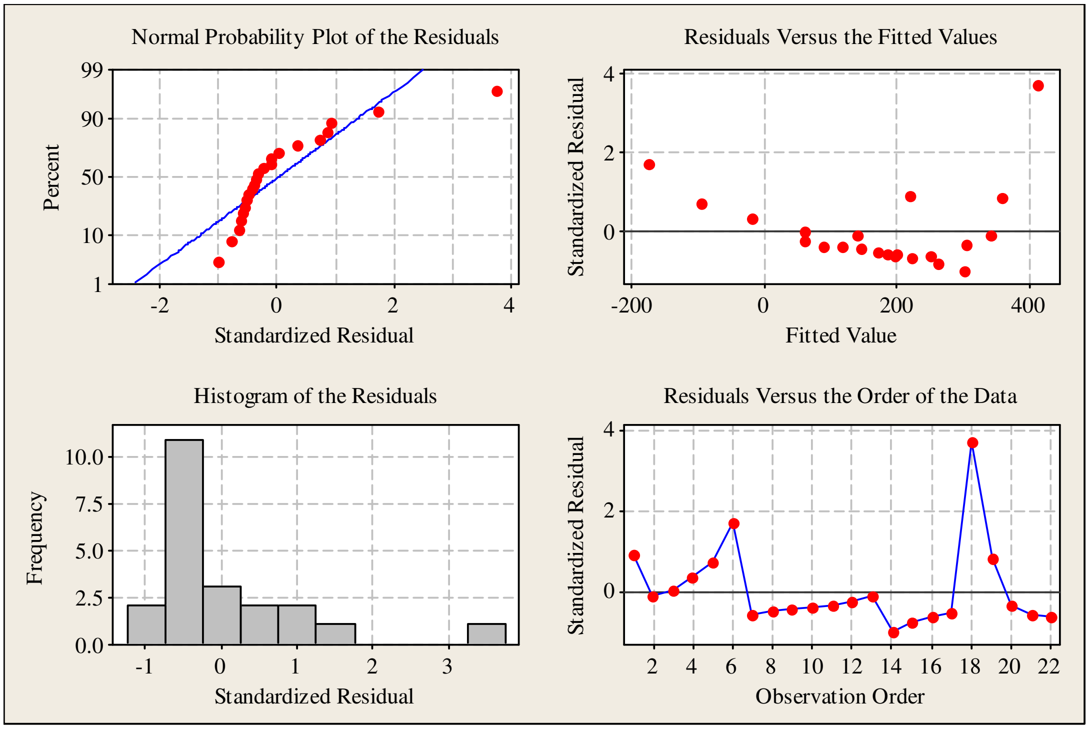


Figure 4.6: Residual plots for effluent color.

Lack of fit test

- Possible curvature in variable H_2O_2 Dosage (P - Value = 0.023)
- Possible curvature in variable Fe^{2+} Dosage (P - Value = 0.008)
- Possible interaction in variable Fe^{2+} Dosage (P - Value = 0.096)
- Possible lack of fit at outer X - values (P - Value = 0.000)
- Overall lack of fit test is significant at P = 0.000

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Advanced oxidation processes (AOPs) represent a powerful treatment for toxic pollutants in textile wastewaters. Oxidation with Fenton's reagent has showed better results for the treatment of Ayka Addis textile factory's wastewater to reduce COD and color.

Maximum removal efficiencies were obtained under the circumstances of at pH = 3, reaction time = 30 minutes, stirrer speed = 30 rpm and Fenton's reagent dosages of 1000 mg/l of H_2O_2 and 1200 mg/l of Fe^{+2}. The removal efficiencies obtained in these conditions were 88 % for COD and 99 % for color and the actual reduction values for COD and color were 134.72 mg/l and 20 Pt-Co unit respectively, which are bellow the limit value set by Ethiopian Environmental Protection Authority (EEPA).

The removal of COD and color is influenced by the dosage of Fe^{2+} and H_2O_2, pH of the media, reaction time and stirrer speed. The relationship between the Fenton's reagent dosage and the removal is non-linear and synergistic effect was observed. At lower pH has better treatment efficiency than higher pH value and when the reaction time and stirrer speed increases the reduction of COD and color also increases.

It has generally been observed that the efficiency of the Fenton oxidation process, in terms of degradation rate, increases with increasing Fe^{2+} dosage in the presence of sufficient H_2O_2. However, as the dosage increases further, the enhancement becomes trivial and at certain stage, reduces the efficiency of the process probably due to the scavenging of the radicals by Fe^{2+}.

Similar to ferrous ion dosage, increase in H_2O_2 dosage has been found to increase the degradation rate of Fenton oxidation process. However, excessive dosage of the hydrogen peroxide may inhibit the reaction, possibly due to the scavenging effect of H_2O_2 producing $HO_2^{\bullet}$ which is a less reactive species than $HO^{\bullet}$ or through recombination of $HO^{\bullet}$ due to its excessive concentration reproducing H_2O_2.

Enhancement of color removal by the coagulation process is mainly through elimination of the remaining ferrous ion rather than removal of the organics. The regression analysis also shows that the effluent COD and color reduction has a strong interaction with H_2O_2 and Fe^{2+}.

5.2. Recommendations

Fenton oxidation processes for water and wastewater applications by generating hydroxyl free radicals should be facilitated through either using artificial UV-light or solar light. These will advantageously increases the generation of hydroxyl free radicals. So, it is worthwhile to investigate the effect of these factors on effluent wastewater COD and color removal.

Future work must also investigate the effectiveness of these technologies in combination with other cost-effective treatments such as biological treatment for the treatment of bio-recalcitrant compounds, where each technology by itself may not be sufficiently effective for the degradation of toxic compounds.

It might be beneficial to carry out a cost analysis for the implementation of this technology, since economy is an important parameter.

For my experiment, due to the absence of treatment facilities in Ayka Addis Textile Factory except neutralization of the wastewater, samples were taken without treatment activities but samples should also be taken after the biological treatment facility in order to observe the effect of COD and color removals of Fenton oxidation process as a post-treatment facility.

The iron residues in the treated wastewater can be easily separated by increasing the pH of the treated wastewater and then it form precipitation, after physical separation of this precipitate, using this iron residue for the same purpose is possible by converting it to iron (II) form or for other purposes is recommended.

Finally, I recommend that Fish toxicity experiment may be conducted after wastewater treatment through chemical oxidation with Fenton's reagent to observe changes on aquatic environment.

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APPENDICES

Appendix I: Some Laboratory Procedures for Water and Wastewater Analysis

a) Heavy Metal Analysis

I) Method

APHA, procedure 3030E-nitric acid digestion

II) Apparatus used

1) Hot plate
2) Conical (Erlenmeyer) flasks,
3) Volumetric flasks
4) Watch glasses
5) Boiling chips
6) Pipette
7) AAS (flame system) model NOV AA 400, analytikjena company, Germany

III) Reagent

Nitric acid concentration analytical or trace metal grade

IV) Procedure

1) Transfer a measured volume (100 ml recommended) of well-mixed, acid preserved sample appropriate for the expected metals concentrations to a flask or beaker.
2) In a hood, add 5 ml concentrated HNO_3
3) If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels (>10 mg/l) are being determined.
4) Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 ml) before precipitation occurs.
5) Continue heating and adding conc. HNO_3 as necessary until digestion is complete as shown by a light-colored, clear solution. Do not let sample dry during digestion.
6) Wash down flask or beaker walls and watch glass cover (if used) with metal free water and then filter if necessary. Transfer filtrate to a 100-ml volumetric flask with two 5-mL portions of water, adding these rinsing to the volumetric flask. Cool, dilute to mark and mix thoroughly.

7) Take portions of this solution for required metal determinations.

b) Phosphorus Analysis

I) Method

1) HACH method 8190: Molybdovanadate with acid per-sulfate digestion
2) Adaptation of the standard method for examination of water and wastewater 20th ed. 4500 - PC, vanadomolybdophosphoric acid method. A persulfate digestion converts organic and condensed inorganic forms of phosphates to orthophosphate then the reaction between orthophosphate and the reagent cause a yellow tint in the sample

II) Required reagent

1) Potassium per-sulfate powder pillows
2) 1.54 N NaOH solution
3) Molybdovanadate reagent
4) Deionized water

III) Materials used

1) HACH reactor
2) HACH spectrophotometer model DR / 2010
3) Measuring cylinder
4) Pipette

IV) Measurement procedure

Reagent blank correction

1) This method needs a reagent blank correction
2) A single vial may be used more than once
3) The blank vial is stable up to one day (room temperature)
4) For most accurate measurement, run a blank for each set of measurements and always use the same lot of reagents for blank and sample
   i. Choose a homogeneous sample
   ii. Preheat the HACH reactor to 150 ^{0}C
   iii. Remove the cap from two reagent vials
   iv. Add exactly 5ml of sample to one vial (sample vial)
   v. Add exactly 5 ml of deionized water to the other (blank vial)

Replace the cap tightly and mix by inverting each vial a couple of times

1) Add the content of one potassium per-sulfate reagent powder pillows for phosphorus analysis to each vials
2) Replace the cap tightly and shake gently the vials until all the powder is completely dissolved
3) Insert the vials into the reactor and heat them for 30 minute at 150 ^{0}C
4) At the end of digestion period switch of the reactor and place the vials carefully in the test tube rack and allow cooling to room temperature
5) Select the program number corresponding to total phosphorus on the secondary LCD by pressing program increase or decrease symbol
6) Remove the cap from the vials and add exactly 2ml of sodium hydroxide solution (1.54 N) to each vial while keeping the vial at 45 degree
7) Replace the cap tightly and mix by inverting the vial a couple of time
8) Remove the cap from the vial and add exactly 0.5 ml of molybdovanadate reagent to each vial while keeping the vial at 45 degree
9) Replace the cap tightly and mix by inverting the vial a couple of time
10) Place the blank vial into the holder and push it completely down
11) Press timer and the display show the countdown prior to the measurement, alternatively, wait for 7 minute and pres zero in both cases ‘sip’ will blink on the display
12) The display will show ‘-0.0- ‘now the meter is zeroed and ready for measurement
13) Remove the blank vial
14) Place the sample vial into the holder and push it completely down
15) Press read direct and ‘sip’ will blink during measurement
16) Instrument directly displays concentration in mg/l of total phosphorus on the liquid crystal display
17) To convert the reading to mg/l of P_2O_5, multiply by a factor of 0.748
18) To convert the reading to mg/l of phosphorus concentration, multiply by a factor of 0.326

c) Nitrogen Analysis

I) Method

1) HACH method 10072: TNT per-sulfate digestion
2) Chromotropic acid method, a persulfate digestion converts all forms of nitrogen to nitrate. Then the reaction between nitrate and the reagents causes a yellow tint in the sample

II) Required reagent

1) Reagent vial-total nitrogen hydroxide reagent
2) Total nitrogen per-sulfate powder pillows
3) Total nitrogen reagent A powder pillows
4) Total nitrogen reagent B powder pillows
5) Deionized water

III) Materials used

1) HACH reactor
2) HACH spectrophotometer model DR / 2010
3) Measuring cylinder
4) Pipette

IV) Measurement procedure

Reagent blank correction

1) This method needs a reagent blank correction
2) A single vial may be used more than once
3) The blank vial is stable up to one week (room temperature)
4) For most accurate measurement, run a blank for each set of measurements and always use the same lot of reagents for blank and sample
    i. Choose a homogeneous sample
    ii. Preheat the HACH reactor to 105 ^{0}C
    iii. Remove the cap from two digestion vials
    iv. Add the content of one packet of total nitrogen per-sulfate reagent powder pillows
    v. Add exactly 0.5 ml of sample to one vial (sample vial)
    vi. Add exactly 0.5 ml of deionized water to the other (blank vial)

Replace the cap tightly and shake vigorously the vials for about 30 seconds until all the powder is completely dissolved

1) Insert the vials into the reactor and heat them for 30 minute at 105 ^{0}C
2) At the end of digestion period switch of the reactor and place the vial in test tube rack after digestion to cool at room temperature
3) Select the program number corresponding to total nitrogen on the secondary LCD by pressing program increase or decrease symbol

4) Remove the cap from the vials and add the content of one packet of total nitrogen reagent powder pillow to each vial. Replace the cap tightly and shake gently the vials for 15 seconds
5) Wait for 3 minute without shaking the vials to allow the reaction to complete
6) Remove the cap from the vials and add the content of one packet of total nitrogen reagent B powder pillows to each vial. Replace the cap tightly and shake gently the vials for 15 seconds
7) Wit for 2 minute without shaking to allow the reaction to complete
8) Remove the cap from two other reagent vials
9) Add exactly 2 ml of digested sample from the digested sample vial to one reagent vial (sample vial), and 2 ml of digested blank to other reagent vial (blank vial) while keeping the vial at 45 degree angle
10) Replace the cap tightly and invert the vials 10 times
11) Place the blank vial into the holder and push it completely down
12) Press timer and the display show the countdown prior to the measurement, alternatively, wait for 5 minute and pres zero in both cases ‘sip’ will blink on the display
13) The display will show ‘-0.0- ‘now the meter is zeroed and ready for measurement
14) Remove the blank vial
15) Place the sample vial into the holder and push it completely down
16) Press read direct and ‘sip’ will blink during measurement
17) Instrument directly displays concentration in mg/l of total nitrogen on the liquid crystal display
18) To convert the reading to NH_3, multiply by 1.22
19) To convert the reading to NO_3, multiply by 4.43
20) Interference
    i. Bromide above 240 mg/l
    ii. Chloride above 3000 mg/l

Appendix II: EEPA Emission Limits for Textile Manufacturing

Table A: Limit values for discharges to water.

Parameter	**Limit Values**
Temperature	40 °C
pH	6 – 9
BOD_5 at 20°C	90% removal or 50 mg/l, or less
Total nitrogen (as N)	80% removal or 40 mg/l, or less
COD (mg O_2 /l)	80% removal or 150 mg/l, or less
Total phosphorus (as P)	80% removal or 10 mg/l, or less
Suspended solids	30
Total ammonia (as N)	20
Oils, fats & grease	20
Phenols	1
Mercury (as Hg)	0.001
Nickel (as Ni)	2
Cobalt (as Co)	1
Lead (as Pb)	0.5
Antimony (as Sb)	2
Tin (as Sn)	5
Chromium (as Cr VI)	0.1
Chromium (as total Cr)	1
Arsenic (as As)	0.25
Cadmium (as Cd)	1
Zinc (as Zn)	5
Copper (as Cu)	2
Mineral oils (Interceptors)	20
Benzene, toluene and xylene (combined)	1
Mineral oils (Biological Treatment)	5
Organochlorine pesticides (as Cl)	0.03
Organophosphorus pesticides (as P)	0.003