ADDIS ABABA

INSTITUTE OF TECHNOLOGY

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CHEMICAL ENGINEERING DEPARTEMENT

REMOVAL OF BASIC DYES FROM TEXTILE WASTEWATER BY APPLYING ADVANCED OXIDATION PROCESS USING FENTON REAGENTS

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Acronyms &Chemical Formulas

AOP	Advanced oxidation process
BOD	Biological oxygen demand
BBD	Box-Behneken design
COD	Chemical oxygen demand
[ ]	Concentration
DSA	Dimensionally stable anode
EPA	Environmental Protection Agency
Fe^{2+} (Fe(II))	Ferrous ion
Fe^{3+} (Fe(III))	Ferric ion
$FeSO_4.7H_2O$	Hydrated ferrous sulfate
H_2SO_4	Sulfuric acid
PCBs	Poly chlorinated biphenyls
H_2O_2	Hydrogen peroxide
HO.	Hydroxyl radical
HO_2.	Per hydroxyl radical
HTHP	High Temperature High Pressure
mg	milligram
mg/L	milligram per liter
NTU	Nephelometric Turbidity Units
O_2^{-1}	superoxide anion
O_3	Ozone
Pt. Co/L	Platinum/cobalt color
NaOH	sodium hydroxide
RSM	Response surface methodology
TS	Total solid
TSS	Total suspended solid
TiO_2	Titanium dioxide
TOC	Total organic carbon
UV	Ultraviolet

Abstract

In this study Advanced oxidation process using Fenton reagents is considered for the application of textile dye-house wastewater treatment. A representative basic dye-house wastewater sample has been brought from K.K. Textile Factory and its characteristic is analyzed and the result shows that dye-house wastewaters, containing basic dyes, are hazardous to the environment since their COD & BOD values are higher than the free discharge limit values and also they are highly colored even at the lower dye concentration operation cases. After characterizing the wastewater, advanced oxidation of a Basic Blue 41 dyes using solar -Fenton treatment was investigated in batch experiments using Box–Behnken statistical experiment design and the response surface analysis. Dyestuff, H_2O_2 and Fe^{2+} concentrations were selected as independent variables in Box–Behnken design while color and COD removal were considered as the response functions. Color removal increased with increasing H_2O_2 and Fe^{2+} concentrations up to a certain level. High concentrations of H_2O_2 and Fe^{2+} adversely affected the color and COD removals due to hydroxyl radical scavenging effects of high oxidant and catalyst concentrations. Both H_2O_2 and Fe^{2+} concentration had profound effects on decolorization. Percent color removal was higher than COD removal indicating formation of colorless organic intermediate. The optimal H_2O_2 / Fe^{2+} / dyestuff ratio resulting in for the 99.75% color removal & 87.56% COD removal is found to be 1045mg/L / 52mg/L / 12mg/L (0, 0, -0.09 coded value).

Key Words: advanced oxidation process, Box –Behnken experimental design, Fenton reagents, Percent color removal , percent COD removal

1. INTRODUCTION

1.1 Back ground

Textile industry is a very diverse sector in terms of raw materials, processes, products and equipment and has very complicated industrial chain. The textile finishing covers the bleaching, dyeing, printing and stiffening of textile products in the various processing stages (fiber, yarn, fabric, knits, finished items). The purpose of finishing is in every instance the improvement of the service ability and adaptation of the products to meet the ever-changing demands of fashion and function. The impacts on the environment by textile industry have been recognized for some time, both in terms of the discharge of pollutants and of the consumption of water & energy [1].

Environmental problems of the textile industry are mainly caused by discharges of wastewater. The textile sector has a high water demand. Its biggest impact on the environment is related to primary water consumption (80–100 m^3/ton of finished textile) and waste water discharge (115– 175 kg of COD/ton of finished textile, a large range of organic chemicals, low biodegradability, color, salinity). Therefore, reuse of the effluents represents an economical and ecological challenge for the overall sector. Main pollution in textile wastewater comes from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Because all of them are not contained in the final product, become waste and caused disposal problems. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances [1].

Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Discharge standards restrict color to a maximum value of 10 mg Pt. Co/L. [2]. The Provisional Environmental Standard for Ethiopia, proposed by the Environmental Protection Authority (EPA) sets discharge limits of 5 mg/L of adsorbable organic halogenated compounds [2].

In Ethiopia textile industry is among the largest manufacturing industries, which government has given special attention. Following the promotion and incentive given to the textile sector by the government, significant number of textile factories are currently operating in the country. Most of them are engaged in processing natural fibers, specially cotton. There are more than fourteen

major state-owned and private textile and garment factories [3]. But most of them lack effluent treatment plants. Instead, they directly discharge untreated colored and toxic effluent into the nearby canals, rivers, lakes, and streams [3].

All organic and inorganic chemicals in wastewater are much higher than allowable limits and extremely harmful to aquatic flora and fauna and can reach human beings through food chains. This wastewater has serious negative impact not only on underground, surface water bodies and land in the surrounding area but also on the aquatic ecological system [4].

In general, several difficulties are encountered in removal of dyes from wastewaters. By design, dyes are highly stable molecules, made to resist degradation by light, chemical, biological and other exposures. Furthermore, dyeing wastewater compositions are not simple solutions of dye in water, but include many other materials such as particulates, processing assistants, salts, surfactants, acids and alkalis [5].

The fulfillment of severe quality standards is especially claimed for those substances exerting toxic effects on the biological sphere preventing the activation of biological degradation processes. The destruction of toxic pollutants as also that of the simple biologically recalcitrant compounds must be therefore demanded to other, non biological technologies. These technologies consist mainly of conventional phase separation techniques (adsorption processes, stripping techniques) and methods which destroy the contaminants (chemical oxidation/ reduction) [6].

Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, at their transformation into harmless products. Obviously the methods based on chemical destruction, when properly developed, give complete solution to the problem of pollutant abatement differently from those in which only a phase separation is realized with the consequent problem of the final disposal [6].

Many of the synthetic dyestuffs are resistant to biological degradation due to the presence of large degree of aromatics, and hence color removal by bio processing is difficult and not complete (Carliell et al., 1996). Recent studies indicate that several advanced oxidation processes (AOPs), such as photolysis, ozone and hydrogen peroxide system which generate strong oxidant

(OH.) may be an alternative for the oxidation of many organic compounds from water and wastewater. Degradation of commercial reactive dyestuffs by heterogeneous and homogeneous AOPs resulted in higher treatment efficiencies in terms of color, TOC, COD). Among the different AOPs, Fenton's reagent (a mixture of H_2O_2& Fe^{2+}) has been lately used for different treatment processes because of its ease of operation and low cost. The Fenton and photo-Fenton reaction using Fe^{2+}, H_2O_2 and UV light have been shown to be effective in mineralizing several recalcitrant pollutants like polychlorinated biphenyls (PCBs), chlorinated herbicides, chlorophenols, perhalogenated alkanes and dye effluents [7].

1.2 Problem Statement

In almost all cases, the Ethiopian industries (textile, paper, plastic, leather, food, cosmetic, etc) release their untreated or partially treated wastewaters into municipal sewers or directly into nearby drains, rivers, stagnant, ponds, lagoons, or lakes. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at large. It has been estimated that more than 10% of the total dyestuff used in dyeing processes is released into the environment .use of large amounts of dyestuffs during the dyeing stages of the textile manufacturing processes is the cause of pollution, which has a negative impact on the landscape and results in major environmental problems

Textile dyes are relatively resistant to microbial degradation due to their complicated structures. Among the various classes of dyes, basic dyes are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high. The presence of very small amounts of dyes in water (less than 1ppm for some dyes) is highly visible and undesirable. Consequently, the removal of dyes from effluents is required. But, because of the high cost and inefficient processes of conventional methods of dye removal, our textile factories using these basic dyes are directly discharging their untreated wastewater into their nearby streams. Consequently, such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at large. It is evident, therefore, that removal of such colored agents from aqueous effluents is of significant environmental, technical and commercial importance [9].

1.3 Objective of the Research

1.3.1 General objective

The main objective of the research is to remove basic dyes from textile wastewater by applying advanced oxidation processes and using Fenton reagents.

1.3.2 Specific objectives

i. To characterize the effluent from the dye house waste water.
ii. To remove COD & color from wastewater containing dyes.
iii. To study the effect of the experimental parameters such as dye dosage, $[Fe]^{2+}$ and $[H_2O_2]$.
iv. To optimize the process parameters.

2. LITERATURE REVIEW

2.1 Dyes

Dyes are organic compounds. Like all organic compounds, their atomic orbital combine to form molecular orbital. Dye molecules comprise of two key components: the chromophores, responsible for producing the color, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers. Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified both by their chemical structure and their application to the fiber type. Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes [14]. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. m^3on full production

Dyes are manufactured through different stages involving nitration, reduction, halogenation, amination, sulfonation, diazotization and oxidation using benzene, toluene, xylene, naphthalene, anthracene, as raw materials. Dyes can be classified according to their use as follows [14].

Acid Dyes: used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food, and cosmetics. They are generally water soluble. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.

Cationic (Basic) Dyes: used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too. Originally they were used for silk, wool, and tannin-mordanted cotton. These water soluble dyes yield colored cations in solution and that's why are called as cationic dyes. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.

Disperse Dyes: used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibers. These are substantially water-insoluble non ionic dyes used for hydrophobic fibers from aqueous dispersion. They generally contain azo, anthraquinone, styryl, nitro, and benzo difuranone groups.

Direct Dyes: used in the dyeing of cotton and rayon, paper, leather, and, to some extent to nylon. They are water-soluble anionic dyes, and, when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulosic fibers. Generally the dyes in this class are poly azo compounds, along with some stilbenes, phthalocyanines and oxazines.

Reactive Dyes: generally used for cotton and other cellulosics, but are also used to a small extent on wool and nylon. These dyes form a covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands, and the dyeings are brighter making them advantageous over direct dyes.

Solvent Dyes: used for plastics, gasoline, lubricants, oils, and waxes. These dyes are solvent soluble (water insoluble) and generally non polar or little polar, i.e., lacking polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. The principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triaryl methane are also used.

Sulfur Dyes: used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper, and wood. They have intermediate structures and though they form a relatively small group of dyes the low cost and good wash fastness properties make this class important from an economic point of view.

Vat Dyes: used for cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool too. These water-insoluble dyes are with principal chemical class containing anthraquinone (including polycyclic quinones) and indigoids. Besides these, there are some other classes too like azoic having azo groups used for cotton and other cellulosic materials; fluorescent brighteners having stilbene, pyrazoles, coumarin and naphthalimides used for soaps and

detergents, fibers, oils, paints, and plastics and mordant having azo and anthraquinone used for wool, leather, natural fibers after pretreating with metals and anodized aluminium.

2.2 Dye House Operations

For a dye house to turn grey goods into a finished product, several sequential steps must occur, including fabric preparation, scouring, bleaching and finishing (dyeing, printing e.t.c.). Of all the fabric finishing unit processes; scouring, bleaching, dyeing and finishing are the most water-intensive and are therefore key targets for the use of tertiary-treated recycled water. While many of these steps are performed at specialized fabric preparation or finishing facilities, some of these operations are employed by dye houses in most industries [15].

2.2.1 Fabric Preparation

Fabric preparation is a series of treatment steps to remove impurities that may interfere with the subsequent dyeing, printing and finishing processes. The preparation treatments usually include desizing , scouring and bleaching, but may also include singeing (a dry process) and mercerizing.

Desizing: Sizing agents are added to fibers in order to improve their strength and bending behavior during the weaving process. Water-soluble sizes are used for synthetic fabrics and water-insoluble starches are used for natural fibers. Once the fibers are woven, the sizing agents need to be removed from the fabric in a process called desizing . Desizing involves a hot water wash for synthetic fibers or an enzyme wash for natural fibers [15]. It is important to remove sizing agents from natural fibers because the starches can react and cause color changes when exposed to sodium hydroxide during the scouring process [15].

Scouring: Scouring is performed to remove any impurities present in the fabric. The impurities (i.e. lubricants, dirt, surfactants, residual tints) are removed using an alkaline solution, typically sodium hydroxide, at high temperatures to breakdown or emulsify and suspend impurities. The specific scouring procedures vary with the type of fiber or cloth construction [15]. Because soaps and detergents used during scouring may precipitate in hard water, process water is usually softened prior to the start of the scouring process [15].

Bleaching: Bleaching is the removal of unwanted color from the textile fibers and typically involves the use of one of three main bleaching agents: hydrogen peroxide, sodium hypochlorite or sodium chlorite [15]. Hydrogen peroxide bleaching is performed under alkaline conditions and, as a result, may be combined with the scouring process [15].

The bleaching process includes three main steps:

(1) Saturating the fabric with the bleaching agent and other necessary chemicals;

(2) Raising the temperature to the recommended level for the particular textile and maintaining that temperature for a set period of time; and

(3) Thoroughly washing and drying the fabric

2.3 Dyeing process in the textile Industries

Dyeing is the application of color to the whole body of a textile material with some degree of Color fastness. Textiles are dyed using continuous and batch processes and dyeing may take place at any of several stages in the manufacturing process (i.e., prior to fiber extrusion, fiber in staple form, yarn, fabric, garment). Most of textile dyeing is done in finishing departments of basic textile manufacturing facilities, although there are also several commission dye houses. From an environmental perspective, dyeing has typically been viewed as a wastewater issue due to the large quantities of water, chemicals, and auxiliaries (such as salt) includes a depiction of a typical fabric dyeing operation [16].

Dyeing is essentially a mass transfer process where the dye diffuses in solution, adsorbs onto the fiber surface, and finally, within the fiber. Dyeing is complicated by the fact that there are many sources of color variations, such as dyes, substrate, reparation of substrate, dyeing auxiliaries (such as salt) used, and water. Processing variables such as time, temperature, and dye liquor ratio (pounds of dyebath to pounds of cloth) also affect dyeing results [16].Table 2.1 depicts classes of dye-stuff and their corresponding fibers.

Table 2.1: Major Dye Classes and Substrate Fibers [16].

Dye Classes	Fibers
Acid	Wool ,silk and nylon
Azoic	Cotton and cellulose
Basic	Acrylic, certain polyesters
Chrome	Wool, silk and nylon
Direct	Cotton, rayon and other cellulosic
Disperse	Polyester, acetate and other synthetic
Fiber Reactive	Cotton and other cellulosic, wool
Naphtol (azoic)	Cotton, rayon, other cellulosic
Mordant (absolute)	Natural fiber(pre treat with metals)
Pigment	All(requires binders)
Solvent	Synthetic(rarely used in commerce)
Sulfur	Cotton and other cellulosic
Vat	Cotton and other cellulosic

Since this research is concerned with basic dyes, polyester & acrylic fibers dyeing processes only will be considered in the following paragraphs.

2.3.1 Polyester Fiber Dyeing

Dispersed dyestuffs are used for dyeing of polyester fiber. The dyeing operation starts with loading a predetermined quantity of fiber into the carrier with the help of water and manual pressing. The loaded carrier is then transferred into the HTHP fiber dyeing machine. The dye bath solution containing the requisite quantities of dispersed dyes, leveling agent, formic/acetic acid to maintain pH at about 4, and water is prepared in a separate vessel and pumped into the machine. The temperature of the dye bath is raised to 132^0C with the help of steam and mixing of the solution is achieved by internal recycling. At the end of dyeing, the machine is gradually cooled to 70-80^OC and the dye bath solution is drained. This dyeing operation is followed by other operations such as reduction clearing at 80^0C (only in case of heavy dark and dark shade), soaping at 70 ^{O}C, hot and cold wash, neutralization and anti-static finishing treatment at 50^oC. After completion of these operations, dyed fiber is removed from the carrier and subjected to hydro-extraction to remove excess liquid carried by the fiber. Hydro-extracted fiber is dried in a hot air blower to get the final dyed fiber.

2.3.2 Acrylic Fiber Dyeing

The process of acrylic fiber dyeing is similar to polyester fiber dyeing with the exception that in the dye bath, basic dyestuffs and retarder are used in place of dispersed dyes and leveling agent. Acrylic fiber dyeing does not involve the reduction clearing operation of polyester fiber dyeing. The schematic process flow diagram for acrylic fiber dyeing is shown in Figure 2. 1 .

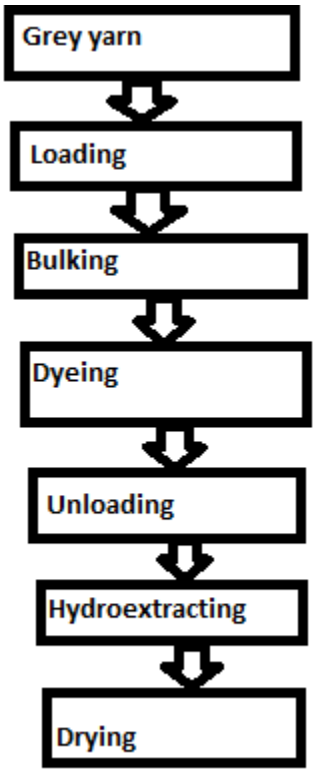


Figure 2.1: Process flow chart for acrylic fiber dyeing

Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances [17]. COD values of composite wastewater are extremely high compare to other parameter. In most cases BOD/COD ratio of the composite textile wastewater is around 0.25 that implies that the wastewater contains large amount of non biodegradable organic matter [17]. Besides the parameters and values mentioned in the table 2.2 many discharge standards doesn't allow visible color in the wastewater at all [17]. As a result of all these problems treating the wastewater before discharge is becoming mandatory.

Table 2.2: Limit values for discharge to in land water [18]

Parameter	Limit values
Temperature	40^{o}C
BOD5 at 20^{o}C	6-9
Total nitrogen (as N)	50mg/L
COD (mg O_2/l)	40mg/L
Total phosphorous (as P)	150 mg/L
Suspended solids	10mg/L
Total ammonia (as N)	30mg/L
Oil, fats and grease	20mg/L
Phenols	1mg/L
Mercury (as Hg)	0.001mg/L
Nickel (as Ni)	2mg/L
Cobalt (as Co)	1mg/L
Lead (as Pb)	0.5mg/L
Antimony (as Sb)	2mg/L
Tin (as Sn)	5mg/L
Chromium (as Cr VI)	0.1mg/L
Chromium (as total Cr)	1mg/L
Arsenic (as As)	0.25mg/L
Cadmium (as Cd)	1mg/L
Zinc (as Zn)	5mg/L
Copper (as Cu)	2mg/L
Mineral oils (Interceptors)	20mg/L
Benzene, toluene and xylene (combined)	1mg/L
Mineral oils (Biological Treatment)	5mg/L
Organochlorine pesticides (as Cl)	0.03mg/L
Organophosphorous pesticides (as P)	0.003mg/L
Adsorbable organic halogen compounds (AOX)	5mg/L
Sulfides (as S)	2mg/L

2.4 Technologies Available For Dye Removal

There are several methods for the removal of pollutants from effluents (Table2.3). The technologies can be divided into three categories: biological, chemical and physical. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries [19].

Table 2.3: Methods of removal of pollutants [20]

	Technology	Advantage	Disadvantage
Conventional treatment process	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problem
	Biodegradation	Economically attractive, publicity acceptable treatment	Slow process, necessary to create an optimal favorable environment maintenance and nutrition requirement
	Adsorption on activated carbon	The most efficient adsorbent ,great capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes ,the regeneration is expensive and results in loss of the adsorbent, non- destructive process
Established recovery process	Membrane separation	Removes all the dyes, produce a high quality treated effluent	High pressure, expensive ,incapable treating large volume
	Ion -exchange	No loss of adsorbent on regeneration, effective	economic constraint, not effective for disperse dyes
	oxidation	rapid &efficient process	high energy cost ,chemical required
Emerging removal process	Advanced oxidation process	No sludge production, little or no consumption of chemicals efficient for recalcitrant dyes	Economic constraints.
	Selective bio adsorbents	Economically attractive, regeneration is not necessary,high selectivity	Requires chemical modification ,non- destructive process
	Biomass	low operating cost ,god efficiency and selectivity, no toxic effect on organisms	slow process ,performance depends on some external factors (pH, salts)

At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [21]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way.

2.4.1 Physical Methods

Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis,) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane

fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability.

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [22]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

2.4.2 Biological Methods

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants [23]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [24]. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes [25]. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin [26]. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.4.3 Chemical Methods

Commonly employed methods for color removal such as adsorption, coagulation–flocculation, oxidation and electrochemical methods are quite expensive and have operational problem.

However recent studies indicate that among different chemical methods, several advanced oxidation processes (AOPs), such as photolysis, ozone and hydrogen peroxide system which generate strong oxidant (OH.) may be an alternative for the oxidation of many organic compounds from water and wastewater. For example, the ozonation oxidation process can effectively decolorize wastewater containing soluble dyes, such as reactive dyes. However, ozonation oxidation cannot decolorize insoluble dyes, such as disperse dyes. Insoluble dyes can be effectively decolorized by coagulation, but coagulation is ineffective for soluble dyes. Finally, Fenton's reagent that has been demonstrable effectively in decolorizing both soluble and insoluble dyes.

2.4.3.1 Oxidation

Oxidation is a method by which wastewater is treated using oxidizing agents. Generally, two forms viz. chemical oxidation and UV assisted oxidation using chlorine, hydrogen peroxide, fenton's reagent, ozone, or potassium permanganate are used for treating the effluents, especially those obtained from primary treatment (sedimentation). They are among the most commonly used methods for decolorisation processes since they require low quantities and short reaction times [27].

They are used to partially or completely degrade the dyes (generally to lower molecular weight species such as aldehydes, carboxylates, sulfates and nitrogen). However, a complete oxidation of dye can theoretically reduce the complex molecules to carbon dioxide and water. It is worth to note that pH and catalysts play an important role in oxidation process.

Chlorine: is a strong oxidizing agent used and may also be applied as calcium hypochlorite and sodium hypochlorite. In addition to being the most widely used disinfectant for water treatment, it is extensively used for reduction of color like pulp and textile bleaching. Reactive, acid, direct and metal complex dyes, which are water soluble are decolorised readily by hypochlorite, but waterinsoluble disperse and vat dyes are resistant to decolorisation in this process [27].

It has been reported that decolorisation of reactive dyes generally require long reaction times, while metal complex dye solution remains partially colored even after an extended period of treatment. Dyes having amino or substituted amino groups on a naphthalene ring, are most

susceptible to chlorine and decolorize more easily than other dyes. Oxidation can be enhanced through control of pH and also by using catalysts, e.g., in the decomposition of metal complex dyes metals, like iron, copper, nickel and chromium, are liberated and these metals have a catalytic effect that increases decolorisation [27].

Though the use of chlorine gas is a low-cost methodology for decolorising dye wastewater, its use causes unavoidable side reactions, producing organo chlorine compounds including toxic tri halo methane, thereby increasing the absorbable organic halogens content of the treated water, also the liberation of metals in metal complex dyes may cause corrosion in metallic vessels [27].

Hydrogen peroxide (H_2O_2): is a very pale blue liquid which appears colorless in a dilute solution, slightly more viscous than water. It has strong oxidizing properties and is therefore a powerful bleaching agent that is used for bleaching paper besides other uses About 50% of the world's production of hydrogen peroxide in 1994 was used for paper and pulp bleaching . Hydrogen peroxide is also used for making peroxides enzymes, which are used for decolorisation of dyes. However, the process is pH dependent and produces sludge [27].

2.4.4 Strategies for the choice of appropriate treatment processes [28]

1- Possibility of recycling and reuse treated wastewater (pollution prevention).

2- If recycling of wastewater constituents is not suitable for any reason, biological processes are preferred because of low costs compared to other processes

3- If the wastewater contains non-biodegradable organic pollutants, microorganisms cannot degrade the main part of the organics, biological processes are not suitable.

4- Advanced oxidation processes (AOPs) are suitable alternatives for the treatment of the wastewater containing toxic or non-degradable pollutants

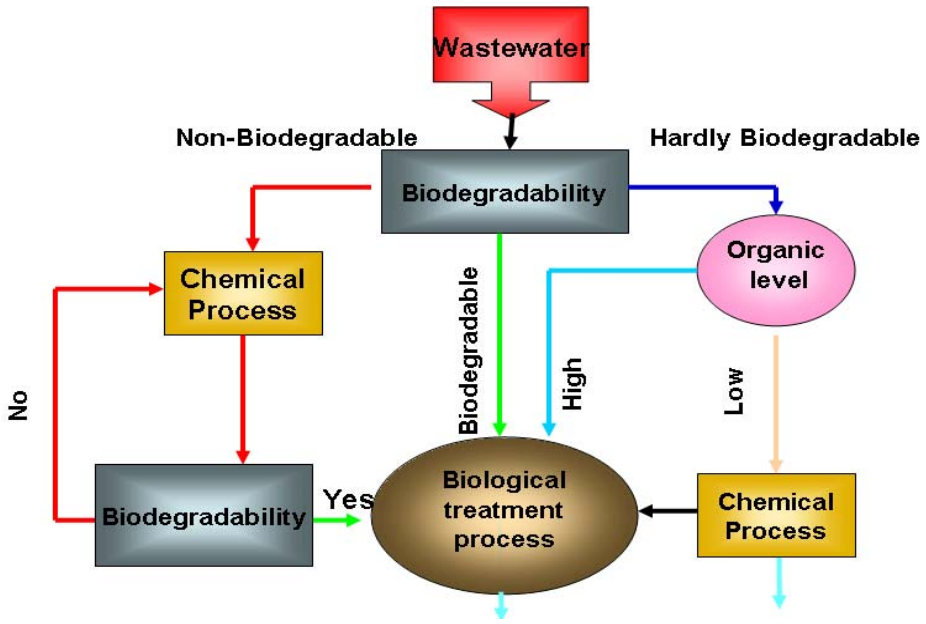


Figure 2.2: Strategies for the choice of appropriate treatment processes **[28]**

2.4.5 Advanced oxidation processes (AOPs)

A wide range of organic compounds is detected in industrial and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in biological treatment systems due to their resistance to biodegradation or/and toxic effects on microbial processes. As a result, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. Among them, advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals. Moreover, they have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes [29].

The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and nonselectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions comparing to conventional oxidants such asH_2O_2 or $KMnO_4$ [30].

The goal of any AOPs design is to generate and use hydroxyl free radical (HO·) as strong oxidant to destroy compound that can not be oxidized by conventional oxidant. Table shows the relative oxidation potentials of several chemical oxidizers. Advanced oxidation processes are characterized by production of OH• radicals and selectivity of attack which is a useful attribute for an oxidant [31].

Table 2.4: Oxidizing potential for conventional oxidizing agents [31].

Oxidizing agent	Electrochemical oxidation potential (EOP),V	EOP relative to chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen molecular	1.23	0.90

The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH• radicals. A list of the different possibilities offered by AOP is given in Table2.4. Generation of HO· is commonly accelerated by combining O_3, H_2O_2, TiO_2, UV radiation, electron-beam irradiation and ultrasound. Of these, O_3/ H_2O_2, O_3/UV and H_2O_2 /UV hold the greatest promise to oxidize textile wastewater [31]. *Basic types of* Advanced oxidation processes are listed in the following table (2.5).

Table 2.5: Types of advanced oxidation process [31]

number	Types of advanced oxidation process
1	H_2O_2/UV/Fe^{2+}(photo assisted Fenton)
2	H_2O_2/Fe^{2+}(Fenton)
3	Ozone/ H_2O_2
4	Ozone/UV/ H_2O_2
5	Ozone/TiO_2/Electron-beam irradiation
6	Ozone/UV(also applicable in the gas phase)
7	Ozone/TiO_2/ H_2O_2
8	Ozone+ Electron-beam irradiation
9	Ozone/ultra sonoics
10	H_2O_2/UV

2.4.6 Combination of Advanced Oxidation Processes and biological treatments

Appropriate techniques must be combined to provide technically and economically feasible options. The performance of an AOP treatment could be enhanced in several ways. The first possibilities are to position the AOP in a sequence of physical, chemical and biological treatments. Such a treatment approach often involves at least one AOP step and one biological treatment step. Whether the AOP or the biological process is first in the treatment line, the overall purpose of reducing costs will be nearly the same as minimizing AOP treatment and maximizing the biological stage, because of the wide difference in the cost of the two treatments. Individual treatment, such as the chemical oxidant to be used (photo-Fenton or Fenton reagent, O_3/ H_2O_2, O_3/UV, H_2O_2 /UV, TiO_2/ UV, etc. [32] . Measurement of the combined process efficiency depends on the purpose of the treatment, but normally requires the independent optimization of each chemical and biological step. For example, the extent of mineralization of the organic compounds may be a measure of efficiency if highly pure water is needed or an effluent with a specific dissolved organic carbon limit. The main purpose of other treatments may be reduction of toxicity or elimination of a specific pollutant. Determining the target is an

essential step in combination studies since it helps define process efficiency and provides a basis for comparing the different operating conditions and optimizing the process [32]

2.5 Fenton Chemistry

Though the history of the Fenton chemistry extends over more than a century, basic questions about its mechanism and the nature of the active intermediate still remain controversial. There are basically two alternative models which have been proposed in the literature: in the first mechanism, introduced by Haber and Weiss and subsequently modified by Barb et al., the oxidative intermediate is identified with the free hydroxyl radical formed by the metal-catalyzed decomposition of the hydrogen peroxide; the second mechanism involves the formation of a highly reactive, high-valent iron complex, such as the ferryl-oxo complex first proposed by Bray and Gorin [**33].**

The Fenton reagent, a mixture of ferrous ions and hydrogen peroxide in water, has great relevance for the chemical industry in view of its powerful oxidizing properties. Indeed, Fenton reagents are used in the hydroxylation of aromatic substrates (e.g., production of phenol with benzene as a substrate), for the treatment of contaminated waters containing non biodegradable organic compounds. Moreover, the oxidative reactions of the Fenton chemistry show analogies with fundamental processes in biology which are involved in the etiology of diseases. Therefore, an understanding of the microscopic mechanisms of the Fenton chemistry is of fundamental importance and may have an impact on very different fields and applications **[32].**

2.5.1 Applications of the Fenton's Chemistry

This process can be used to the treatment of wastewater which is contaminated with soils and sludge’s with the following actions:

- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD/COD removal
- Odor and color removal

- Destruction of resin in radioactive contaminated sludge

2.6 Fenton Oxidation Process

The Fenton reaction (reaction of hydrogen peroxide with Fe (II) ion) has been proven to be an effective method for treating organic pollutants in wastewater. Many investigations have been performed on the kinetics of the Fenton and Fenton-like reactions.

Reactions	Rate constant ($M^{-1}S^{-1}$)	
$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH\cdot+OH^-$	$K_1=58M^{-1}S^{-1}$	(2.1)
$Fe^{3+}+ H_2O_2 \rightarrow Fe^{2+}+HO_2\cdot+H^+$	$K_2=0.02\ M^{-1}S^{-1}$	(2.2)
$Fe^{2+}+ OH\cdot \rightarrow Fe^{3+} + OH^-$		(2.3)
$Fe^{3+}+ HO_2\cdot \rightarrow Fe^{2+}+O_2+ H^+$		(2.4)
$OH\cdot+ H_2O_2 \rightarrow HO_2\cdot+H_2O$		(2.5)

During reaction (2.2), Fe(III) ions are formed that can react with H_2O_2 and $HO_2\cdot$ to reproduce Fe(II) ions. The reaction of hydrogen peroxide with Fe(III) ions is referred to as a Fenton-like reaction. Transformation of Fe(II) to Fe(III) ions, and vice versa, proceeds via reactions (2.1) and (2.2), which continually produce the active radicals ·OH and $HO_2\cdot$. The slow step of the above-mentioned mechanism.

[Reaction (2.2)] is the rate-determining step of this process. One of the important advantages of a Fenton like reaction, in comparison to the Fenton reaction, is that the cost of Fe(III) salts is lower than that of Fe(II) salts. Any reaction capable of promoting the transformation of Fe(III) to Fe(II) ions would help accelerate the Fenton reaction. It has been reported that many kinds of inorganic and organic compounds can interact with Fe(III) or Fe(II) ions and, hence, considerably influence the kinetics of the Fenton reaction.

Inorganic materials, such as Cl^{-1}, $H_2PO_4^{-1}$ and organic aromatic derivatives, such as hydroquinone and hydroquinone-like compounds, are promising candidate materials. Considering that aromatic derivatives are the main pollutants in most dye-contaminated wastewater, a comprehensive study on their effect on the Fenton reaction could generate important data [32].

Fenton's reagent is particularly attractive because of the low costs, the lack of toxicity of the reagents (i.e.,Fe^{2+} and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology required . As a result, Fenton's process has been widely used to treat recalcitrant wastewater such as industrial effluents, landfill leachates, etc. Furthermore, because of its widespread application, the effectiveness of the Fenton's process has been extensively investigated [33].

The method of ferrous hydrogen peroxide oxidation is also known as Fenton's reagent method. Hydrogen peroxide reacts with ferrous ion in water and generates the hydroxyl free radical (HO:), which is one of the most active oxidants, (and) whose oxidation ability is only next to F_2 among the known oxidants Fenton's reagent method is very efficient to degrade the refractory organic substances in phenol [34].More recent research has demonstrated that the oxidation mechanism by Fenton's reagent was due to the reactive hydroxyl radical generated in an acidic solution by the catalytic decomposition of hydrogen peroxide. Its mechanism is as follows: [35].

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH\cdot +OH^- \quad (2.6)$$

$$RH + OH\cdot \rightarrow R. + H_2O \quad (2.7)$$

$$R. + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad (2.8)$$

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^- \quad (2.9)$$

As shown in the above reactions, hydrogen per- oxide is used for the oxidation of organic substances and ferrous iron. It acts as a reluctant when reacting with a strong oxidizing agent such as potassium dichromate, and generates the free oxygen with decomposition by itself.

Consequently, the mechanism of these reactions with respect to hydrogen peroxide is very complex and may change with conditions of the reaction and the type of catalyst. Generally, Fenton's oxidation process was composed of four stages, which are: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. So, the organic substances are removed at two stages of the oxidation and the coagulation. In the literature, the overall COD removal efficiency of Fenton's oxidation process has been investigated. mentioned that the COD removal efficiency by coagulation with formation of the ferric hydroxo complexes is higher than that by oxidation reacted with hydrogen per- oxide [35].

Several methods are being used to decolorize dye wastewater, but individually these methods are ineffective for dealing with treating wastewater containing soluble and insoluble dyes. For example, the ozonation oxidation process can effectively decolorize wastewater containing soluble dyes, such as reactive dyes . However, ozonation oxidation cannot decolorize insoluble dyes, such as disperse dyes. Insoluble dyes can be effectively decolorized by coagulation, but coagulation is ineffective for soluble dyes. Finally, Fenton's reagent that has been demonstrable effectively in decolorizing both soluble and insoluble dyes [36]. The current development of the Fenton process comes out with three types namely, dark Fenton, photo Fenton and solar Fenton. The following section explain different types of Fenton process.

2.6.1 Dark Fenton (thermal Fenton)

Dark Fenton is a conventional method that involves the decomposition of H_2O_2 by Fe^{2+} in acidic solution in the dark. It is also referred to us thermal Fenton reaction ,it means the energy is driven from the surrounding rather than photo chemical energy [37]. The Fenton's reactions at acidic pH lead to the production of ferric ion and of the hydroxyl radical [38]. The efficiency of the Fenton reaction depends mainly on H_2O_2concentration, Fe^{2+}/ H_2O_2 ratio, pH and reaction time. The initial concentration of the pollutant and its character as well as temperature, also have a substantial influence on the final efficiency. Moreover, there is wide spread experience in the practical use of Fenton reagent for degradation of organic substrates in wastewater and other wastes [38].

To mitigate the degradation of environmental quality, many physico-chemical processes have been applied to treating parathion in the environment. The classic Fenton processes initiated by the hydroxyl radical were found very effective in contaminant treatment compared to many conventional treatment processes The hydroxyl radical is a highly active agent capable of oxidizing various organic contaminants almost without selectivity. In this process, H_2O_2 decomposed with Fe^{2+} catalysis, resulting in the formation of the hydroxyl radical (.OH). The following sequence of reactions show Fenton process without the presence of organic contaminants. Beside .OH, the per hydroxyl radical ($.HO_2$) and superoxide anion ($.O_2^-$) are formed as well in this process. They may react with one another or with other species, resulting in the high complexity of Fenton reaction mechanism [39].

Reactions	Rate Constants ($M^{-1}S^{-1}$)	
$Fe^{2+}+H_2O_2 \rightarrow .OH + OH^{-1} + Fe^{3+}$	63	(2.10)
$H_2O_2+Fe^{3+} \rightarrow .HO_2 + H^+ + Fe^{2+}$	0.01	(2.11)
$H_2O_2+.OH \rightarrow H_2O+.HO_2$	2.7×10^{7}	(2.12)
$Fe^{2+}+.OH \rightarrow OH^- + Fe^{3+}$	3.2×10^{8}	(2.13)
$.HO_2 \rightarrow H^+ + .O_2^-$	1.58×10^{-5}	(2.14)
$.HO_2 + Fe^{2+} + H^- \rightarrow H_2O_2 + + Fe^{3+}$	1.2×10^{6}	(2.15)
$.HO_2 + Fe^{3+\ -} \rightarrow O_2 + H^+ + Fe^{2}$	3.1×10^{5}	(2.16)
$.O_2^- + H^+ \rightarrow .HO_2$	1.0×10^{10}	(2.17)
$.O_2^- + Fe^{2+} + 2H^- \rightarrow H_2O_2 + + Fe^{3+}$	1.0×10^{7}	(2.18)
$.O_2^- + Fe^{3} \rightarrow O_2 + Fe^{2+}$	5.0×10^{7}	(2.29)
$.OH + .OH \rightarrow H_2O_2$	4.2×10^{9}	(2.20)
$.HO_2 + .HO_2 \rightarrow H_2O_2 + O_2$	8.3×10^{5}	(2.21)
$.OH + .HO_2 \rightarrow H_2O + O_2$	1.0×10^{10}	(2.22)
$.OH + .O_2^- \rightarrow O_2 + .OH$	1.0×10^{10}	(2.23)
$.HO_2 + .O_2^- + (H^+) \rightarrow H_2O_2 + O_2$	9.7×10^{7}	(2.24)

2.6.2 Electro Fenton oxidation

Recently, a new advanced oxidation process induced by electrochemistry, electro-Fenton has attracted much interest. This process consists of either adding Fe^{2+} or reducing Fe^{3+} electrochemically with the simultaneous production of H_2O_2 upon the reduction of O_2 on the electrodes such as graphite , mercury pool , carbon fiber or carbon poly tetra fluoro ethylene O_2-fed cathodes Compared with traditional Fenton's reagent oxidation, electro-Fenton can avoid the high cost of H_2O_2 , maintain an almost constant concentration of H_2O_2 and regenerate Fe^{2+} more effectively . Electro-Fenton can oxidize organic compounds quickly and economically. Many persistent pollutants have successfully been been degraded by this method [40].

Electro- Fenton oxidation method as an indirect electrochemical advanced oxidation process was developed and widely applied for oxidation of various organic pollutants In this method, H_2O_2 is continuously generated by reduction of the dissolved molecular O_2 in mildly acidic aqueous medium there is no production of iron sludge in the reactor and consequently no subsequent disposal problems were found. On other side, the hydroxyl radicals (OH•) are non-selective very powerful oxidizing agent that react with organics yielding de hydrogenated or hydroxylated derivatives until their overall mineralization (conversion into CO_2 and H_2O) [41].

Various types of electrodes such as graphite , activated carbon fiber ,Pt –and boron doped diamond electrodes (BDD) have been studied but, in the last years, Dimensionally Stable Anodes (DSA) have arisen great interest as one of the promising electrodes. Currently, their use for the degradation of organic pollutants is an active area of research [42].

Thanks to the development of new electrode materials and more compact reactors, electrochemical technologies have reached a promising stage of development and can now also be effectively used for the destruction of toxic or bio refractory organic The electrochemical oxidation of organics for wastewater treatment can be obtained by direct electrolysis, where the pollutants are oxidized after adsorption on the anode surface without the involvement of any substances other than the electron, which is a ‘‘clean reagent Many studies have reported the application of H_2O_2, fed with pure oxygen, for the treatment of wastewater containing organic pollutants, especially in the presence of Fe^{2+} ions (electro-Fenton process) or with Fe^{2+} and

UVA irradiation (photoelectron- Fenton process In both processes, strong oxidizing OH. radicals are generated in the solution by the well-known Fenton's reaction between Fe^{2+} and electro generated H_2O_2 [44].

$$\mathbf{Fe^{2+}} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (2.25)$$

A relatively new chemical oxidation method that has not received much attention for OMW or other industrial wastewater treatment is the electro- Fenton method . This method represents a combination of the electrochemical process and the Fenton oxidation. It is based on the fact that hydrogen peroxide (H_2O_2) can be used as an oxidant in advanced Oxidation processes to decompose refractory or toxic wastewaters [44].

Electro-Fenton is an advanced electrochemical oxidation process based on the continuous supply of H_2O_2 generated from reaction (2.26) to a contaminated acid solution containing Fe^{2+} or Fe^{3+} as

catalyst) . OH is then produced in the medium by the Fenton's reaction between ferrous ion and hydrogen peroxide.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2.26)$$

$$Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + OH^- \quad (2.27)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH\cdot \quad (2.28)$$

This catalytic reaction is propagated from Fe^{2+} regeneration, which mainly takes place by the reduction of Fe^{3+} at the cathode. Since .OH production does not involve the use of harmful chemicals which can be hazardous for the environment, this process is environmentally friendly for wastewater treatment and seems to be promising for the purification of water polluted by persistent and/or toxic organic pollutants [44].

2.6.3 Photo Fenton

Fenton's reaction cannot completely mineralize organic pollutants since normally less than 50% of the organic carbon can be converted to CO_2. Furthermore, the biggest disadvantage of this

methodology is the sludge generation due to iron and pollutant molecules flocculation. When the process uses ultraviolet (UV) radiation, visible light or a combination of both, the process is known as the photo-Fenton process. The photo-Fenton process has several advantages, mainly an increase of the degradation rate and no sludge generation [45].

Photochemical oxidation methods such as the photo-Fenton have been given considerable attention in recent years for the treatment of recalcitrant wastewaters. Fenton reagent was reported to be effective for degradation of the refractory organic contaminants such as chlorophenols, chlorobenzene nitrophenols and dye pollutants]. Fenton reagent can completely decolorize and partially mineralize the textile dyes rather rapidly [47]. The photo-Fenton process starts with the combination of H_2O_2 with Fe^{2+} (Equation. (2.29))

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + OH\cdot \qquad (2.29)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (2.30)$$

When irradiation is involved, the Fe^{3+} generated by Fenton's reaction (Equation (2.29)) is continuously reduced to Fe^{2+}: The reaction process starts again (Equation (2.32)) using photo generated Fe^{2+}. In particular for dye degradation, visible radiation can increase the reaction rate through the generation of free radicals by means of the Fe^{2+} regeneration as previously proposed and showed in Equations. (2.31) and (2.32).

$$Dye + h\nu \rightarrow Dye^* \qquad (2.31)$$

$$Dye^* + Fe^{3+} \rightarrow Dye^+ + Fe^2 \qquad (2.32$$

Applying UV irradiation to Fenton's reaction can enhance the oxidation rate of organic compounds by the photo reduction of produced ferric ions (Fe^{3+}) and ferric complexes. Ferrous ions are recycled continuously by irradiation, and so they are not depleted during the course of the oxidation reaction, as shown in .Moreover, the production of hydroxyl radicals is limited only by the availability of UV/vis radiationand H_2O_2. This route facilitates the formation of hydroxyl radicals and promotes the degradation rates of organic compounds [48]. The

mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals and other reactive species that attack the organic molecules [49].

Photo–Fenton process produces more hydroxyl radicals in comparison to the conventional Fenton method (Fe (II) with hydrogen peroxide) or the photolysis, thus promoting the rates of degradation of organic pollutants. It should be also noted here that the exact mechanism and the role of Fe(II) and Fe(III) ions; identifying the exact equilibrium concentration of the two species is very complicated and not understood in detail up to now. Figure 2.4 shows the reaction pathways for the process starting with the primary photo-reduction of the dissolved Fe(III) complexes to Fe(II) ions followed by the Fenton's reaction and the subsequent oxidation of organic compounds. Additional hydroxyl radicals generated in the first step also take part in the oxidation reaction [50].

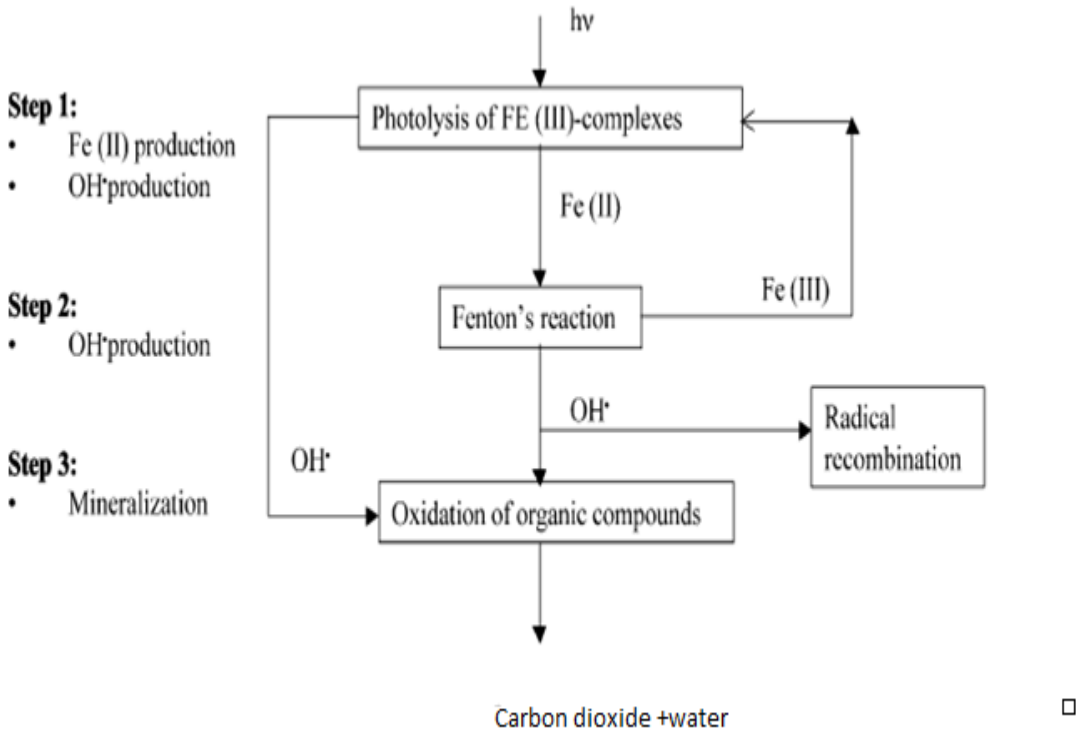


Figure 2.3: Reaction pathways of the Photo-Fenton process [51].

2.6.5 Solar Fenton

As one of the chemical methods of wastewater treatment, AOPs (Advanced Oxidation Processes) being effectively used to detoxify noxious and recalcitrant pollutants in industrial wastewater, there is the photo-Fenton process which consists of a combination of the Fenton reagents (Fe^{2+}/H_2O_2) and light energy. The photo-Fenton process consists of two reactions .Solar light has been expected to be available for photo-Fenton processes instead of costly and hazardous artificial UV light. The use of sunlight being an abundant natural energy source can significantly reduce the costs of the color removal process [51].

Photo-Fenton process possesses several advantages, mainly the increase of reaction rate and the possibility of use a cheap, non-contaminant and widely distributed energy source; solar radiation [52]. Photo degradation of pollutants using H_2O_2 with solar light can make it an economically viable process since solar energy is an abundant while these compounds are highly recalcitrant to biodegradation, they can be destroyed by solar catalytic oxidation within hours. Furthermore, during the anaerobic digestion stage of the conventional biological treatment process, the dyes can be readily transformed to other intermediates which are usually more toxic than the parental dyes. Solar catalytic oxidation, on the contrary, can oxidize these dyes efficiently to CO_2 & mineral ions [52].

The Fenton reagent consists in a mixture of iron(II) salts and hydrogen peroxide. Although its mechanism of action has not yet been completely elucidated it may involve decomposition of hydrogen peroxide into hydroxyl radical, catalyzed by the metal cation The process can be accelerated by irradiation of the solution; although wavelengths corresponding to the UV-range are the most commonly employed, sunlight can also be used, with important environmental and economical advantages [53].

3. Material and Methods

3.1 Materials

3.1.1 Dye Stuff

Water soluble C.I. 11105 dye, basic blue 41, were used in this study. The characteristics of the dyes are shown in Table 3.1.

Table 3.1: General Characteristic of Basic Blue 41

Chemical Name	Synonyms	λmax	Class	Color	Form	Molecular Formula	Molecular weight
Basic Blue 41	CI 11105;BASIC BLUE 41;Catonic Blue GRL	617nm	Azo	Deep blue	Powder	$C_{20}H_{26}N_4O_6S_2$	482.57g/mol

The Structural formula of Basic Blue 41 is shown below

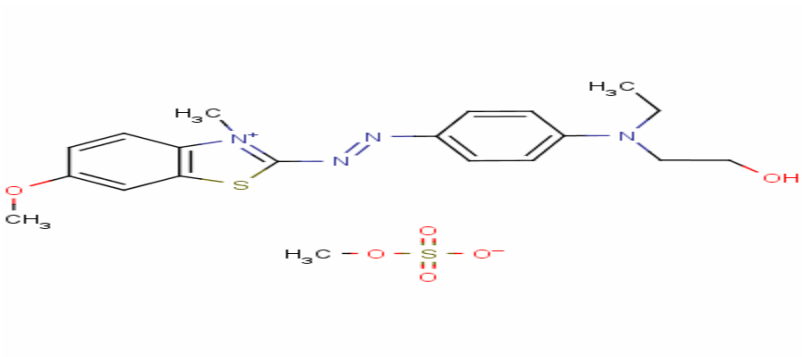


Figure 3.1: Structural Formula of Basic Blue 41

3.1.2 Dye House Waste water Sample

For this experiment wastewater is brought from dyeing unit of K.K Textile Factory. Where all of the dye house wastewater is discharge from the dyeing process.

3.1.3 Analytical instruments

UV/Visible spectrophotometer was used to detect the color of the wastewater, digital PH meter was used for PH measurement, Oxi-Direct BOD measuring instrument and some reagents were used to measure BOD of the wastewater samples and the permeate of the real wastewater. HANNA COD reactor, multi-parameter bench photometer, and reagents were used for COD measurement. To measure total solids (TS) crucible, oven, desiccators and weighing balance were used. Turbidity was measured using HACH 2100N turbidimeter

3.1.4 Chemicals

1. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) used as source of Fe^{2+} was analytical grade
2. Hydrogen peroxide solution (30%, w/w) in stable form
3. The pH of aqueous solutions was adjusted using either dilute NaOH or H_2SO_4

3.2 Methods

3.2.1 Characterizing the waste water sample

The characteristics of the dye house wastewaters (i.e. their BOD, COD, TS, turbidity, pH and color) will be determined using the analytical instruments so as to know the degree which the dye-house wastewater is far from the from the standard discharge limits.

BOD determination: First the pH of the solution will be adjusted to a neutral value. Then based on the BOD rang of the wastewater sample 400ml (for lower range), 157ml (for medium rang) or 27ml (higher range) sample will be taken using overflow measuring flask. The samples will be introduced in to the bottles of BOD measuring unit with the help of funnel, in which magnetic stirrer is put. Then we will add some drops of nitrification inhibitor based on the sample type. The bottle then first be sealed with a rubber seal gasket in which three or four drops of KOH is added to react with the CO_2 evolved during the process; and then screwed with a cover which consists of pressure sensor and can be fit to electronic system ready for the measurement. Finally the bottle will be placed in the bottle rack and then the entire unit will be kept in a thermostat

under constant temperature of 20^{o}C. The data will be recorded every 24 hours automatically. The value obtained at the fifth day is called BOD_5, which is mostly referred.

COD determination: here also the COD range of the sample should be determined first. Then for lower and medium range 2ml, and for higher range 0.2ml sample is added to the respective reagent vial then inverting each vial up and down a couple of times, the reagent will be mixed with the sample. A blank will also be prepared based on our COD range by mixing equal amount of distilled water with the respective reagent. In the mean time the HANNA reactor will be warmed up until it reaches up to 150^{o}C. Then the sample and the blank will be fed in to the reactor and stayed there for two hours at that temperature. After two hours the reactor will be off and waiting for some time, until the system cools down to reasonable temperature, the sample and the blank will be taken out and put in to a rack until it cools down to room temperature. Finally a bench photo meter will be calibrated using the blank and after that the sample will be inserted in the photo meter for reading.

TS determination: a dry crucible, after being inserted in a desiccators for a recorded amount of time, will be weighed and the result will be recorded. Then the crucible with 100ml well mixed sample will be weighed and the result will be recorded. The crucible with the sample will then be put into an oven at 150^{o}C for 24 hours after that it will be weighed, after being in a desiccator for the same amount of time as the previous. The difference between the two weights will be the amount of TS per 100ml of sample.

Turbidity determination: first the turbid meter will be calibrated using the standards. Then the sample will be introduced and the reading will be obtained.

pH determination: first make sure that the digital pH meter is calibrated by introducing the meter in to distilled water and checking whether the reading is 7 or not. If it is calibrated, insert the pH meter in sample and read the value.

3.2.2.1 Experimental procedures to determine color of real dye house waste water

1. Initially the pH of the real dye waste water were adjusted to 7.6.
2. The blank (deionised water) was filtered using membrane flitter paper.
3. The instrument was Calibrated using deionized water.
4. The program was being started
5. 10 ml of the unknown sample was Finally measured and then inserted in to the cell holder.

3.2.2 Constituting wastewater sample

Synthetic dye solutions had been used by most researchers in their investigation of treatment technologies since synthetic solutions was useful in obtaining information on how individual dyes react to different types of treatment. Apart from this, constant composition of a synthetic solution enables the specific study of treatment efficiency on a particular treatment technology. The wastewater was prepared using distilled water and Basic Blue 41dye of different concentrations (based on the concentrations of the real dye house wastewater).

3.2.3 Dye solution preparation

1. An accurately weighted quantity of the dye (Basic Blue 41) was dissolved in distilled water to prepare stock solution (1000mg/l).
2. Experimental solutions of the desired concentration were obtained by successive dilutions.
3. The pH of each experimental were maintained with the use of 1M H_2SO_4& 1M NaOH Solutions.

3.2.4 Experimental Design and optimization of process variables

So as to determine the effect of main parameter on the removal of the Basic Blue 41 dye as well as to optimize all the affecting parameters collectively by statistical experimental design, Response surface methodology is used in this work. Box–Behnken statistical experiment design (BBD) of the RSM, consisting of a three-factor and three-level pattern was used to conduct the

experiment. The result of the experimental design were studied and interpreted by Design expert 8.0.5 statistical software to estimate the response of the dependent variable

i) Selection of response variable

- %COD removal &%color removal

ii) Choice of factors, levels and range

- Factors:

The potential design factors that have prime effect on the oxidation of the dye house waste water are:

1. Initial dye concentration
2. concentration of Fe^{2+}
3. concentrations of H_2O_2

Table 3.2: Experimental range and levels of independent variables

Factor	Unit	Coded values		
		low	medium	high
		-1	0	+1
[dye stuff]	mg/L	12	132	252
$[H_2O_2]$	mg/L	95	1045	1995
	ml	0.12	1.34	2.56
$[Fe^{2+}]$	mg/L	0	52	102
	mg	0	129.1	253.2

The initial dye concentration selected for batch experiments is within the range recommended in the actual textile effluent. The $[Fe^{2+}]$ &$[H_2O_2]$ is based on most literature values.

Design comprised of 17 runs in random order; all points in coded factor levels. The centre point (0, 0, 0) was replicated five times. The combination of the three factors (initial dye

concentration, $[Fe^{2+}]$ &$[H_2O_2]$) studied in the response surface experiment and optimization was based on the +1 and -1 variable levels of the experimental design.

Table 3.3: Three- Factor, Three level Box-Behenken statistical experimental design

Run	Factor 1 A:[dye stuff] mg/L	Factor 2 B:$[Fe^{2+}]$ mg/L	Factor 3 C:$[H_2O_2]$ mg/L	Response 1 Color removal %	Response 2 COD removal %
1	0	1	-1		
2	-1	0	1		
3	0	0	0		
4	0	1	1		
5	0	-1	-1		
6	0	-1	1		
7	1	0	-1		
8	1	0	1		
9	0	0	0		
10	-1	0	- 1		
11	-1	1	0		
12	0	0	0		
13	1	1	0		
14	0	0	0		
15	0	0	0		
16	-1	-1	0		
17	1	-1	0		

3.2.5 Experimental procedures

The experiments were carried out in the presence of solar irradiation. The experiments were at laboratory scale.

3.2.5.1 Fenton experiment procedures

1. 500ml of required concentration of dye solution was added to 1000ml beaker.
2. Next the PH was adjusted to 3 then stoichiometric amount of iron sulphate was added .when the iron is dissolved sample is taken and tested at time=o.
3. Stoichiometric amount of hydrogen peroxide was added.

4. After 60 minute the PH was increased to 7 using sodium hydroxide &the process allow to continue for additional 5 minutes.
5. The stirrer speed was reduced and the process was proceed for 15 minutes &allow to settle for 30 minutes then immediately the filtrate analyzed.

All of the experiments conducted by exposing the reaction mixture to solar radiation.

3.2.6 Calibration Curves

Concerning dye concentration detection, for all cases, using samples of known Dye concentration (10-255 mg/L) and based on Lambert Beer's law, calibration curves are made. From the curves by interpolation or extrapolation, depending on the sample, the unknown concentrations are obtained. The following diagram shows the calibrations curve obtained from sample of known concentration.

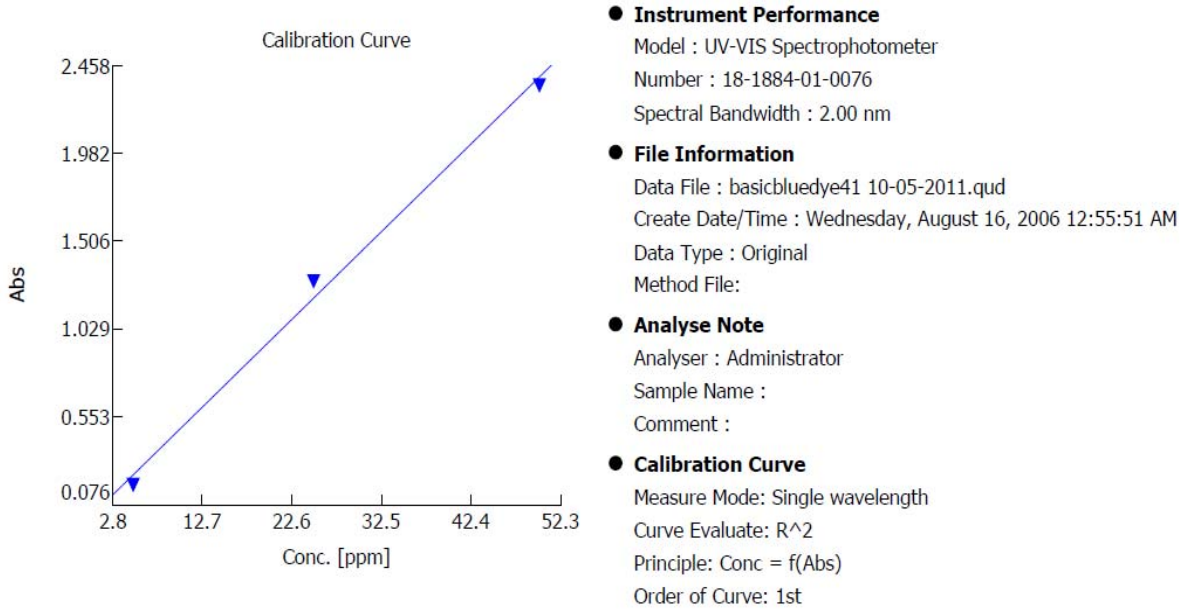


Figure 3.2 : Calibrations curve

3.2.7 Experimental Approach

So as to determine the effect of main parameter on the removal of the Basic Blue 41 dye as well as to optimize all the affecting parameters collectively by statistical experimental design, Response surface methodology is used in this work. Box–Behnken statistical experiment design and the RSM, consisting of a three-factor and three-level pattern was used to conduct the experiment. The result of the experimental design were studied and interpreted by DESIGN EXPERT 8.0.2.0 statistical software to estimate the response of the dependent variable. in addition to this each experiment is done three times to insure the reproducibility of the result.

4. Result and discussion

The real dye house wastewater after it has been analyzed using the analytical instruments mentioned earlier shows the following characteristics

Table 4.1**:** Characteristics of the wastewater sample

Sample type	pH	COD(mg/L)	BOD(mg/L)	TS(mg/L)	Turbidity (NTU)	Color in Pt-Co unit
Waste water from the dyeing section	6.0±0.1	709.8	163	0.17	162	60

The values in Table 4.1 shows that the dye house wastewaters are highly colored which can be hazardous to the environment if it is disposed untreated. The COD values are also much higher and are very far from the free discharge limit shown in Table 2.2. Though the BOD values are relatively low as compared to other wastewater types, they are still above the free discharge limit. Turbidity and color of the wastewater are extremely higher than the free discharge limit. Especially the color, even the low concentration wastewater is highly colored but the discharge regulation says wastewater to be discharged should be colorless. Generally the result of the characterization shows that dye house wastewaters are hazardous and have to be treated before discharge.

Table 4.2: experimental result of the treated real dye House waste water using Fenton reagents

Run number	$[Fe^{2+}]$ (mg)	$[H_2O_2]$ (ml)	%color removal	%COD removal
1	0.124	0.14	99.652	76.13
2	0.253	1.57	95.316	83.53
3	0	1.57	20	12
4	0.372	0.14	97.642	8543
5	0.506	3ml	98.16	86.17
6	0.253	0.14	99.100	79.19

The results in table 4.2 tell us that the method of treatment of dye house waste water using Fenton reagents are effective to remove the color and also the COD can be reduced to greater amount. So by applying AOP it is possible to change harmful organic compounds in to harm less inorganic species such as CO_2 &H_2O. As a result of this latest approach it is possible to protect the environment & safe the people around the factory.

Table 4.3: Results of the constituted wastewater by Box–Behnken design (BBD) of experiments

Run	Factor 1 A:[dye stuff] mg/L	Factor 2 B:$[Fe^{2+}]$ mg/L	Factor 3 C:$[H_2O_2]$ mg/L	Response 1 % Color removal	Response 2 %COD removal
1	0	1	-1	99.60	87
2	-1	0	1	95.43	63
3	0	0	0	99.51	88.92
4	0	1	1	94.78	88.92
5	0	-1	-1	18.34	2.3
6	0	-1	1	40.14	8.00
7	1	0	-1	95.20	80
8	1	0	1	99.78	79.9
9	0	0	0	99.51	88.92
10	-1	0	-1	98.76	32
11	-1	1	0	98.04	43.25
12	0	0	0	99.51	88.92
13	1	1	0	99.62	80.02
14	0	0	0	99.51	88.92
15	0	0	0	99.51	88.92
16	-1	-1	0	45	11
17	1	-1	0	20	17

The values of the dependent and independent variables and the experimental data are presented in Table 4.3 for every experiment. The center point (0, 0, 0) was repeated five times and nearly the same results were obtained indicating the reproducibility of the data.

4.1 The response function coefficients

The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function Y_1 (*%dye removal)* &Y_2(COD *removal*) and the independent variables *A([dye stuff]),B([Fe^{2+}])&C*([H_2O_2]) can be approximated by a quadratic polynomial equation as follows:

$$Y= b_o+b_1A+b_2B+b_3C+b_{12}AB+b_{13}AC+b_{23}BC+b_{11}A^2+b_{22}B^2+b_{33}C^2 \quad (4.1)$$

The coefficients of the response functions for different dependent variables were determined correlating the experimental results with the response functions by using a Stat-Ease Design Expert 8.0.5 regression program. The response functions with the determined coefficients for percent color (Y_1) and COD (Y_2) removals are presented by Equations (4.2) and (4.3).

$$Y_{1=} +99.51000 -2.82875A +33.57000B+2.27875C+6.64500AB +1.97750 AC- 6.65500 BC +0.11625A^2 \_33.96125B^2 \_2.3375C^{2.} \quad (R^2=0.99) \quad (4.2)$$

$$Y_2=+88.9200+14.20875A+34.58625B+4.7900C+6.19250AB-7.77500XAC-0.99500BC-18.94125A^2-36.16125B^2-6.25375C^2 \quad (R^2=0.99) \quad (4.3)$$

On the basis of the coefficients in Equations. (4.2) and (4.3), it can be said that percent color removal decreases with the dyestuff concentration (A) while increasing with peroxide (C) and Fe(II) (B) doses. Fe(II) dose has a more profound effect on decolorization as compared to peroxide. COD removal increases with the dyestuff, peroxide and Fe(II) doses with a more profound effect by the Fe(II) dose.

4.2 Color removal

4.2.1 Analysis of variance for Color removal of the surface Quadratic Model

The model F- value of 106.40 implies the model is significant .There is only a0.01% chance that a "model F-value " this large could occur due to noise. Values of "Prob >F" less than0.0500 indicates model terms are significant in this B,AB,BC,B^2 are significant model terms. Values greater than 0.1000 indicates the model terms are not significant. If there are many in significant model terms (not counting those required to support hierarchy).model reduction may improve the model.

Table 4.4: Analysis of variance Table for color removal

Source	Sum of square	df	Mean square	F value	P-value Prob>F
Model	14433.02	9	1603.76	106.40	<0.0001
A=[Dyestuff]	64.01	1	64.01	4.25	0.0783
B=[Fe^{2+}]	9015.56	1	9015.56	590.15	<0.0001
C=[H_2O_2]	41.54	1	41.54	2.76	0.1408
AB	176.62	1	176.62	11.72	0.0111
AC	15.64	1	15.64	1.04	0.3422
BC	177.16	1	177.16	11.75	0.0110
A^2	0.057	1	0.057	3.775E_0.003	0.9527
B^2	4856.28	1	4858.28	322.20	<0.0001
C^2	22.93	1	22.93	1.52	0.2572
Residual	105.51	7	15.07		
Lack of fit	105.51	3	35.17		
Pure error	0.000	4	0.000		
C or total	14539.93	16			

Color removal is related to removal of color imparting functional groups from the dyestuff (i.e., removal of azo-groups), but not necessarily complete degradation or mineralization of the dyestuff. Response functions with determined coefficients were used to estimate variations of color removals with the independent variables under different conditions.

Percent color removal decreased with increasing dyestuff concentrations at all H_2O_2 concentration due to limitations by H_2O_2doses at high dyestuff concentrations. At an H_2O_2 concentration of 95mg/L, percent color removal was nearly 99.6% when dyestuff was 12mg/L which decreased to 95.2% as dyestuff concentrations increased to 252mg/L.

4.2.2 Effect of Fe^{2+} dose on the color removal

The following Figure (4.1) tells that effect of ferrous ion concentration on color removal, the removal efficiency of color increased with increased ferrous ion concentration, because more ferrous ions can react with hydrogen peroxide and produce hydroxyl radicals. Moreover, in the presence of Solar radiation the ferrous ions will be regenerated during the Fenton process at faster rate. However, too many ferrous ions inhibit color removal due to the fact that the use of high catalyst doses inhibited the removal of color by forming radical scavengers .Moreover it is observed that Fenton's Oxidation in the absence of Fe^{2+} or with only hydrogen peroxide treatment color removal were very low .For example if we consider (run 5)at negligible iron concentration percent color removal is (18.34%), indicating the importance of Fe^{2+} in the Solar Fenton treatment.

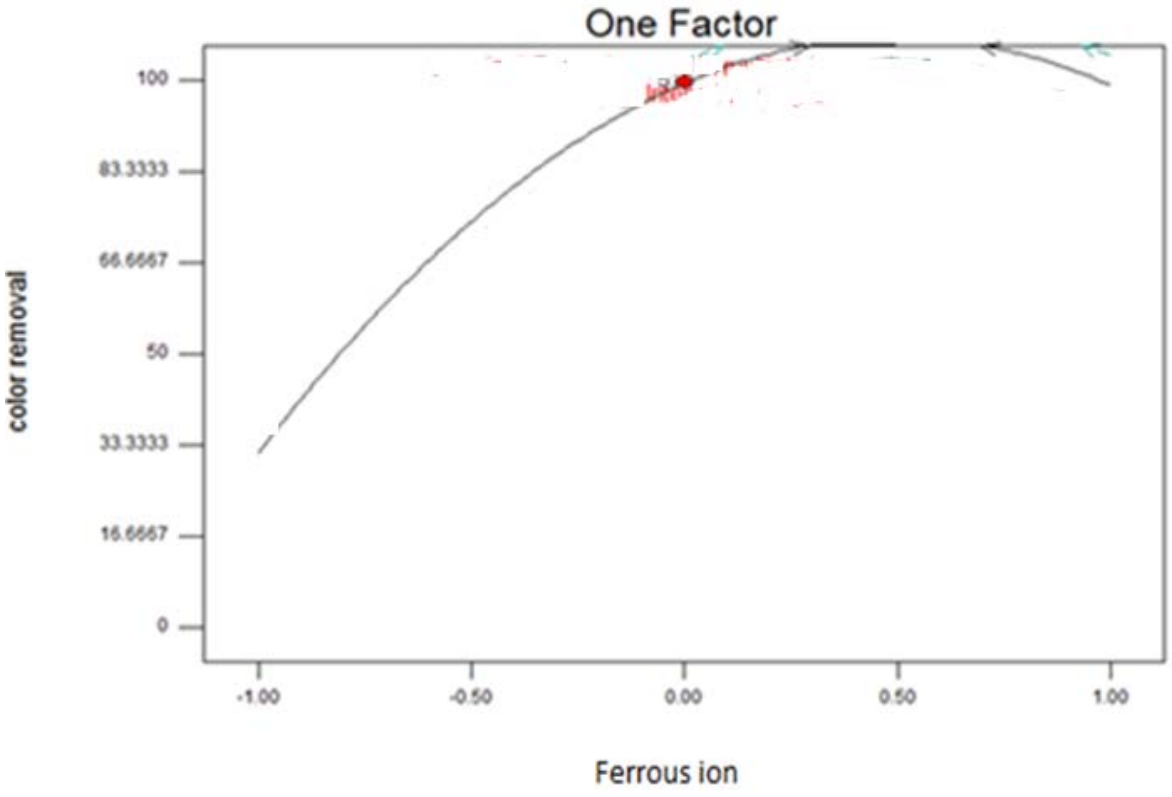


Figure 4.1: The effect of Fe^{2+} on color removal

4.2.3 Effect of H_2O_2 dose on Percent color removal

Figure 4.2 describe about the effect of H_2O_2 on the percent color removal.

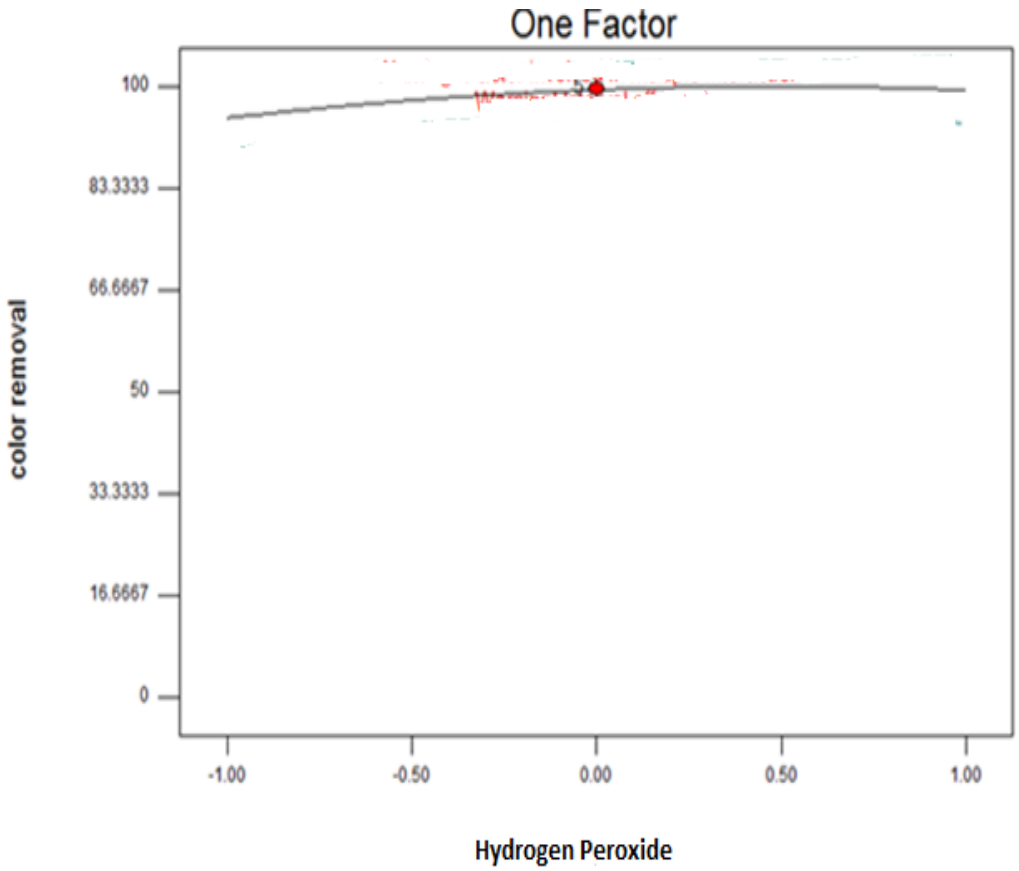


Figure 4.2: the effect of H_2O_2 on the color removal

In Figure 4.2 Percent color removal increased with increasing initial hydrogen peroxide concentration at all dyestuff concentrations. However, at low dyestuff concentrations12mg/L, color removal slightly decreased with increasing H_2O_2.Forexample in this experiments if Run-2 is compared with run -10, at the lowest dye concentration, run-10 with the least H_2O_2 concentration has greater color removal. the possible reason for this is due to to hydroxyl scavenging effect of high concentrations of H_2O_2 & auto decomposition of H_2O_2 to O_2 and water.

Results shown in Figure 4 .3 & 4.4 describe the effect of initial dye concentration,[Fe^{2+}] and [H_2O_2] on the percent color removal during experiments. In Figure 4.1, as the initial dye

concentration is getting increased, the percent dye removal will decrease. It shows that removal of dye is dependent upon the concentration of dye in a solution and as a whole the percentage removal decreases with the increase in dye concentration as observed in the plot. And also in the in the same plot as the [Fe^{2+}] is increased within the levels, the percent removal increases.

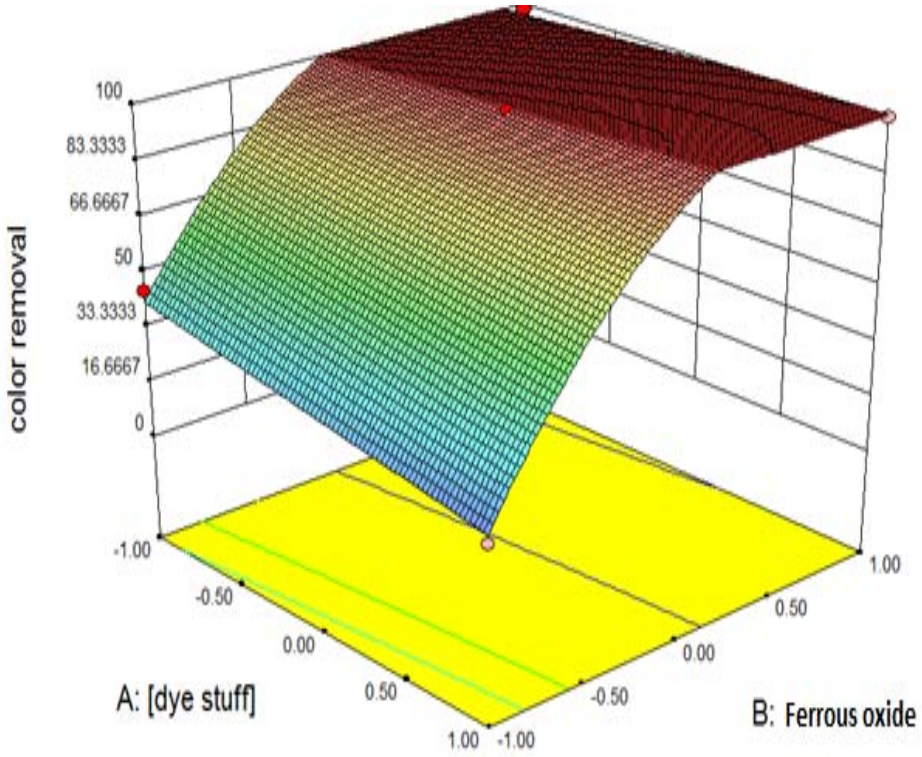


Figure 4.3: 3D surface drawing showing the effect of [Fe^{2+}] &[dye stuff] on color removal

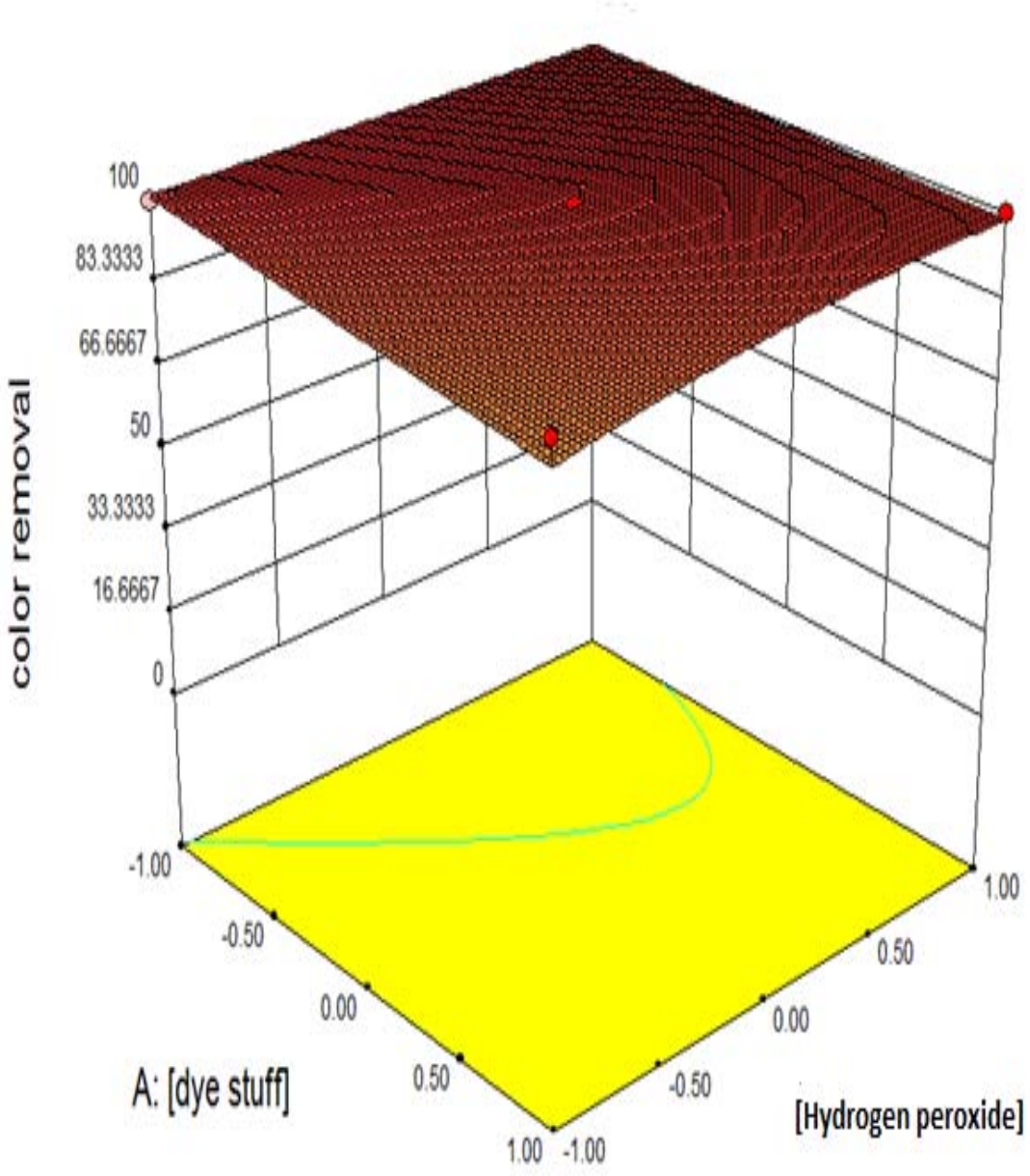


Figure 4.4: 3D surface drawing which indicate the effect of [H_2O_2] and [dye stuff] .

In Figure 4 .3 & 4.4 , Percent color removal decreased with increasing dyestuff concentrations at all H_2O_2 concentrations due to limitations by H_2O_2 doses at high dyestuff concentrations. At an H_2O_2concentration of 95mg L−1, percent color removal was nearly 99.60% when dyestuff was 132mg/L which decreased to 95.20% as dyestuff concentrations increased to 252mg/L.

4.3 Chemical Oxygen demand (COD) removal

Table 4.5: Analysis of variance table for percent COD removal

Source	Sum of square	df	Mean square	F Value	P-value Prob>F
Model	19475.33	9	2163.93	32.37	<0.001
A=[dye stuff]	1615.11	1	1615.11	24.16	0.0017
B=[Fe^{2+}]	9569.67	1	9569.67	143.15	<0.0001
C=[H_2O_2]	183.55	1	183.55	2.75	0.1415
AB	153.39	1	153.39	2.29	0.1736
AC	241.80	1	241.80	3.62	0.0989
BC	3.96	1	3.96	0.059	0.8147
A^2	1510.61	1	1510.61	22.60	0.0021
B^2	5505.84	1	5505.84	82.36	<0.0001
C^2	164.67	1	164.67	2.46	0.1605
Residual	467.96	7	66.85		
LacK of fit	467.96	3	155.99		
Pure Error	0.000	4	0.000		
C or Total	19943.30	16			

The Model F-value of 32.37 implies the model is significant . There is only a 0.01% chance that a Model F value .Values of "Prob>F" less than 0.0500 indicates model terms are significant. in this case A,B,A^2 &B^2 are significant terms . Values greater than 0.1000 indicates the model terms are not significant.

Decolorization of the dyestuff does not always result incomplete degradation to CO_2 and H_2O. Some colorless reaction intermediates may be formed during degradation of dyestuffs. Therefore, it is important to know the degree of mineralization or COD removal during decolorization of dyes. In this study, mineralization of the dyestuff was achieved after decolorization was occur. The difference between percent color and COD removals is a measure of formation of colorless organic intermediates contributing to COD, but not to color measurements. Equation (4.3) tells us that initial dye concentration has a great role in the % COD removal efficiency.

4.3.1 Effect of Fe^{2+} dose on percent COD removal

The Following Figure (Figure 4.5) illustrates the effect of Fe^{2+} on COD removal.

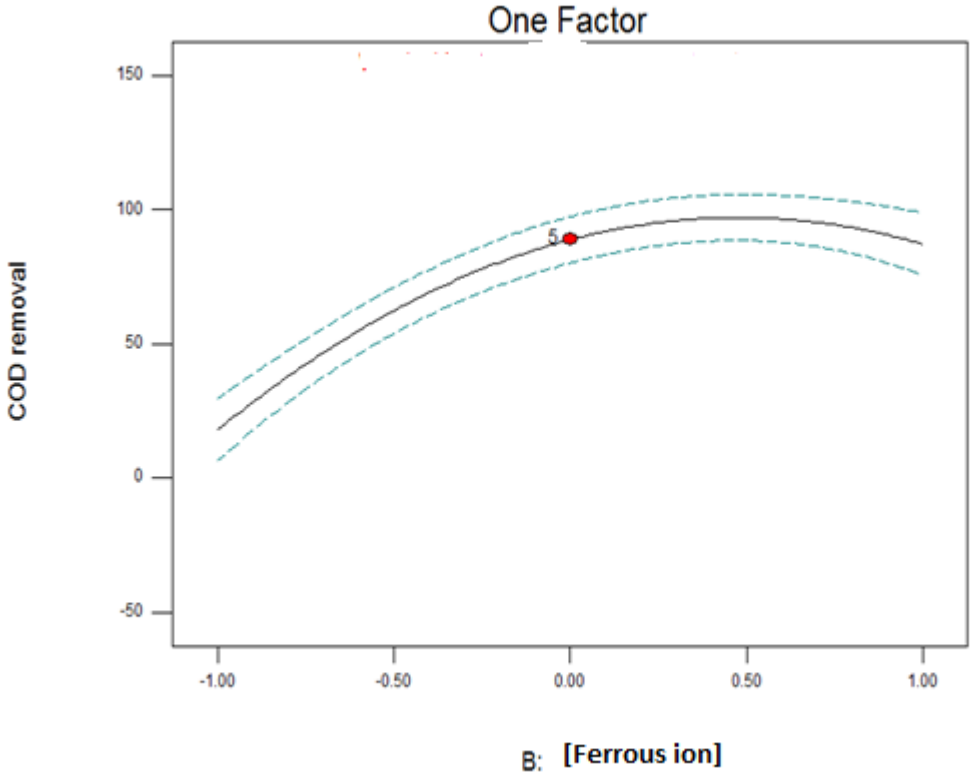


Figure 4.5: Effect of Fe^{2+}on COD removal

Figure4.5 tells us that Percent COD removal increased with increasing Fe^{2+} doses up to nearly 52mgL−1 due to limitations by the Fe^{2+} ions and then decreased with further increases in Fe^{2+} due to adverse effects of high Fe^{2+} doses yielding an optimal Fe^{2+} dose under the specified experimental conditions. Excessive ferrous ions in the system resulted in decreases in mineralization yield due to radical scavenging effects of high Fe^{2+} doses.

Figure 4.5 indicates Percent COD removal increased with increasing Fe^{2+} doses up to nearly Certain levels due to limitations by the Fe^{2+} ions and then decreased with further increases in Fe^{2+} due to adverse effects of high Fe^{2+} doses yielding an optimal Fe^{2+} dose. Excessive ferrous ions in the system resulted in decreases in mineralization yield due to radical scavenging effects of high Fe^{2+} doses.

4.3.2 Effect of dye dose on the percent COD removal

In order to visualize the effect of dye stuff on on COD removal, consider Figure 4.6.

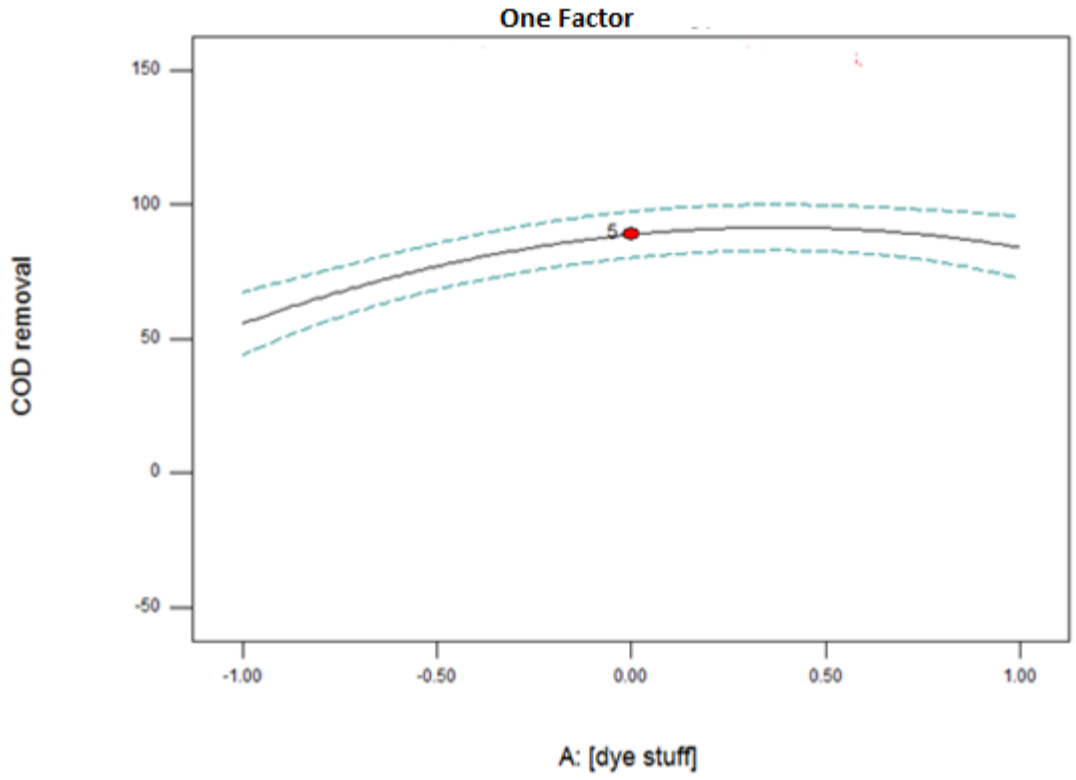


Figure 4.6: Effect of dye dose on COD removal

COD removal steadily increased with increasing dyestuff concentrations up to 132mg/L due to limitations by low dyestuff concentrations while the peroxide and Fe(II) doses were high. Decrease in percent COD removal for dyestuff concentrations above 132mg /L is due to limitations by the peroxide and Fe^{2+} which were probably below the required levels.

4.3.3 Effect of H_2O_2 on percent COD removal

Figure 4.7 describes about the effect of H_2O_2up on COD removal.

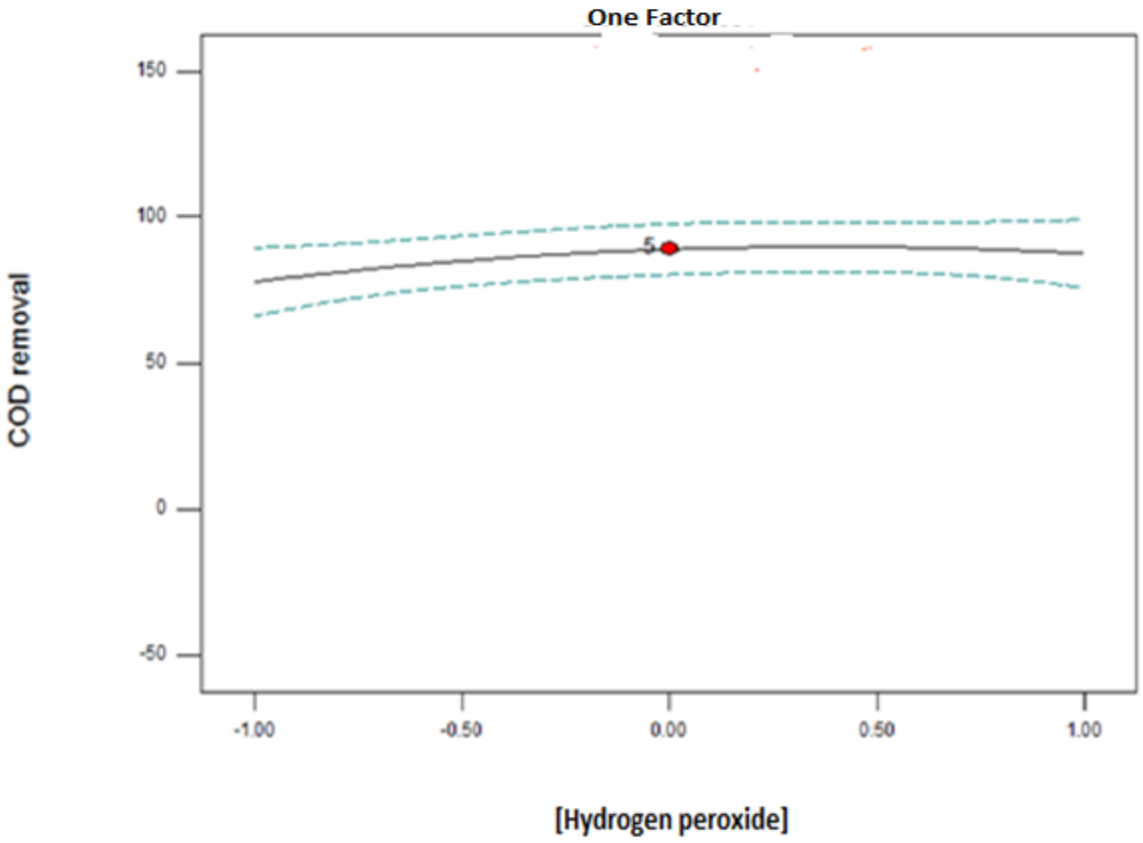


Figure 4.7: effect of H_2O_2 on COD removal

COD removal increased with H_2O_2 dose to nearly 1045mg /L indicating limitations by H_2O_2 concentration. COD removal decreased with further increases in H_2O_2 dose due to hydroxyl radical scavenging effect of high H_2O_2doses. At high hydrogen peroxide concentrations,H_2O_2 serve as a free-radical scavenger reducing the hydroxyl radical concentration.

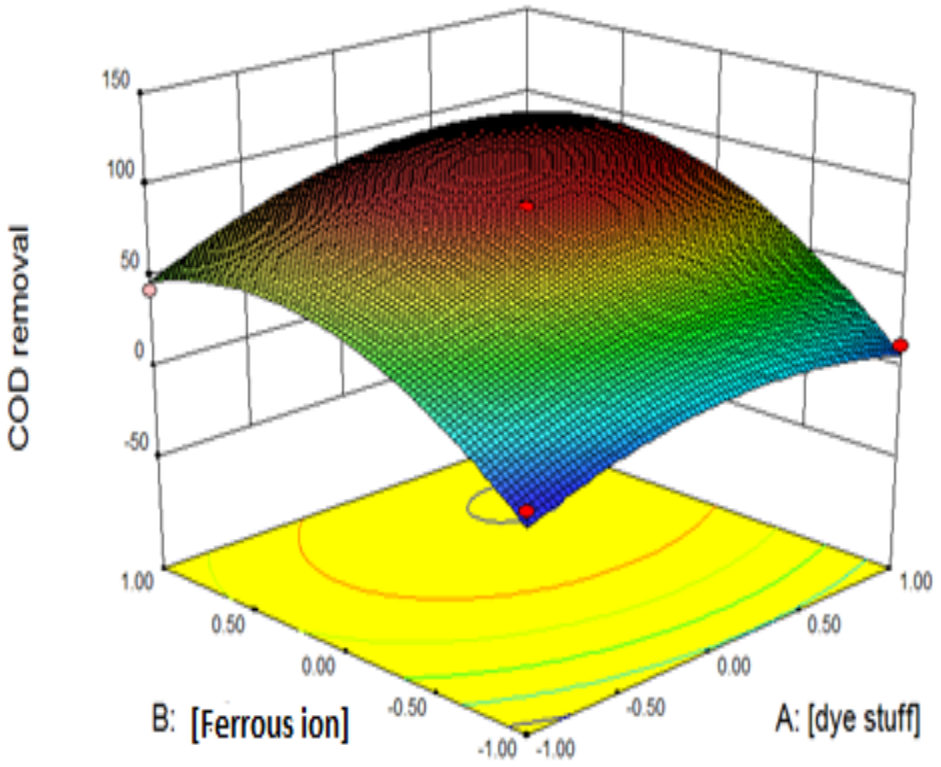


Figure 4.8: 3D surface drawing which shows the effect of Fe^{2+} &H_2O_2 on COD removal

In Figure 4.8 both the Fe^{2+} &Dye stuff increase also increase in the percent COD removal until some range and this is the same with result with the above mentioned one dimensional Figures (4.6 &4.7)

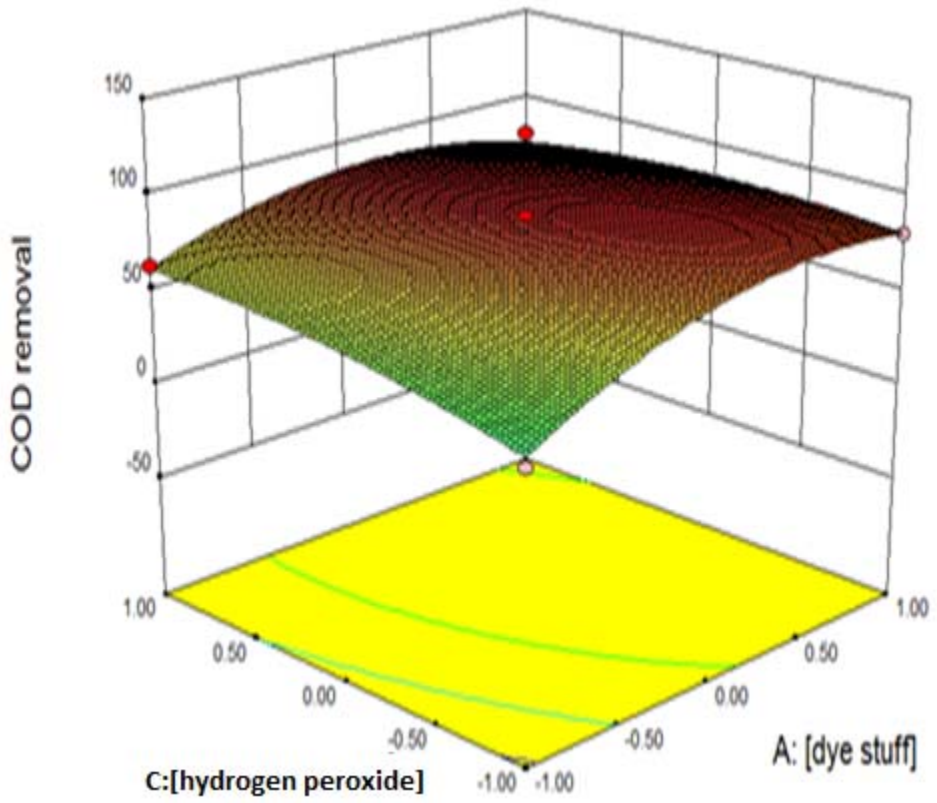


Figure 4.9: 3D surface drawing indicating the effect of [H_2 O_2] &[dye stuff] on percent COD removal

According to Figure 4.9 When both the dye stuff &[H_2O_2] increase the percent COD removal also proportionally increase and this graph also tells the same result with that of the one dimensional graph we observed in Figure (4.6 &4.7).

4.4 Optimization of process parameters

The Conditions of optimum process can be determined by both Numerical Optimization and Graphical Optimization technique by using response surface methodology. In order to determine the optimum processing conditions, the two optimization technique should arrive in the same result. Therefore, in Numerical Optimization, I tried to maximize the responses for the percentage dye removal and COD removal by setting the criteria in Table 4.6.

4.4.1 Numerical Optimization

Table 4.6: Optimization Criteria table

Name	Goal	Lower Limit	Upper Limit
[dye stuff]	minimize	-1	+1
[Fe^{2+}]	In the range	-1	+1
[H_2O_2]	In the range	-1	+1
%dye removal	Maximize	60	99.78
%COD removal	Maximize	70	88.92

Table 4.7: Solution for the numerical optimization

Number	[dye stuff]	[Fe^{2+}]	[H_2O_2]	Color removal	COD removal	Desirability
1	-0.09	0.00	-0.00	99.5627	87.5627	0.842

Desirability range from zero to one for any given response. The program combines individual desirability into a single number and then searches for the greatest overall desirability. A value of one represents the ideal case. A zero indicates that one or more responses fall outside desirable limits. In this numerical optimization is 0.842 which is nearer to the ideal case &indicates both responses falls in the desirable limit.

4.4.2 Graphical optimization

The bar graph (Figure 4.10) shows how well each variable satisfies the criteria. All values near one indicate that the variables are nearly fulfilling the criteria that are previously assigned.

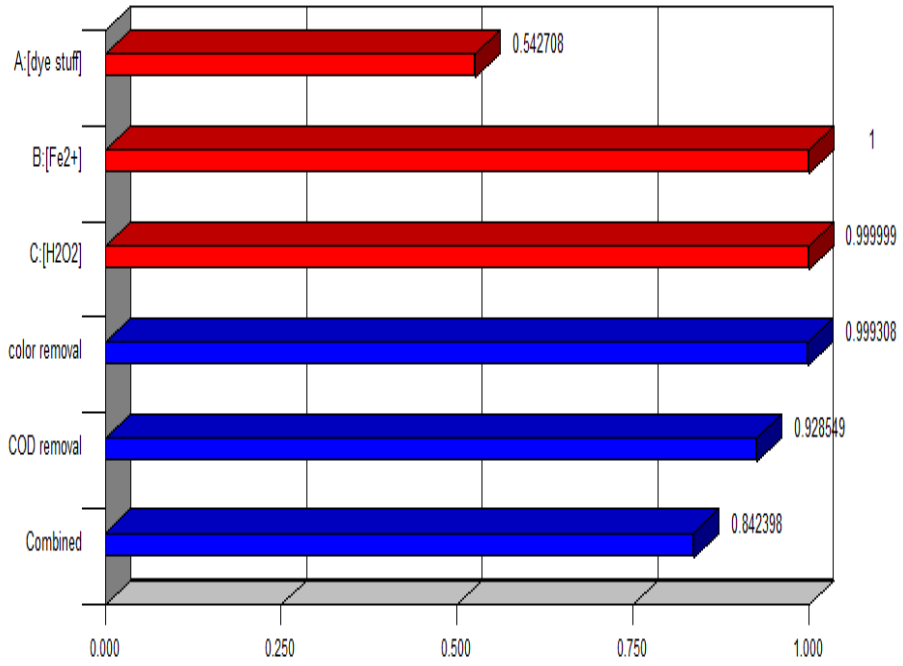


Figure 4.10: Bar graphs which shows desirability

In case of Graphical Optimization, the procedure was repeated with most importance assigned to maximize the response, the percent removal. The present study (Figure 4.11) indicated the optimum factor variable levels and responses using over lay plot. Therefore, the optimum Color removal were 99.751 %&% COD removal were 87.576 which are identical to Numerical Optimization result.

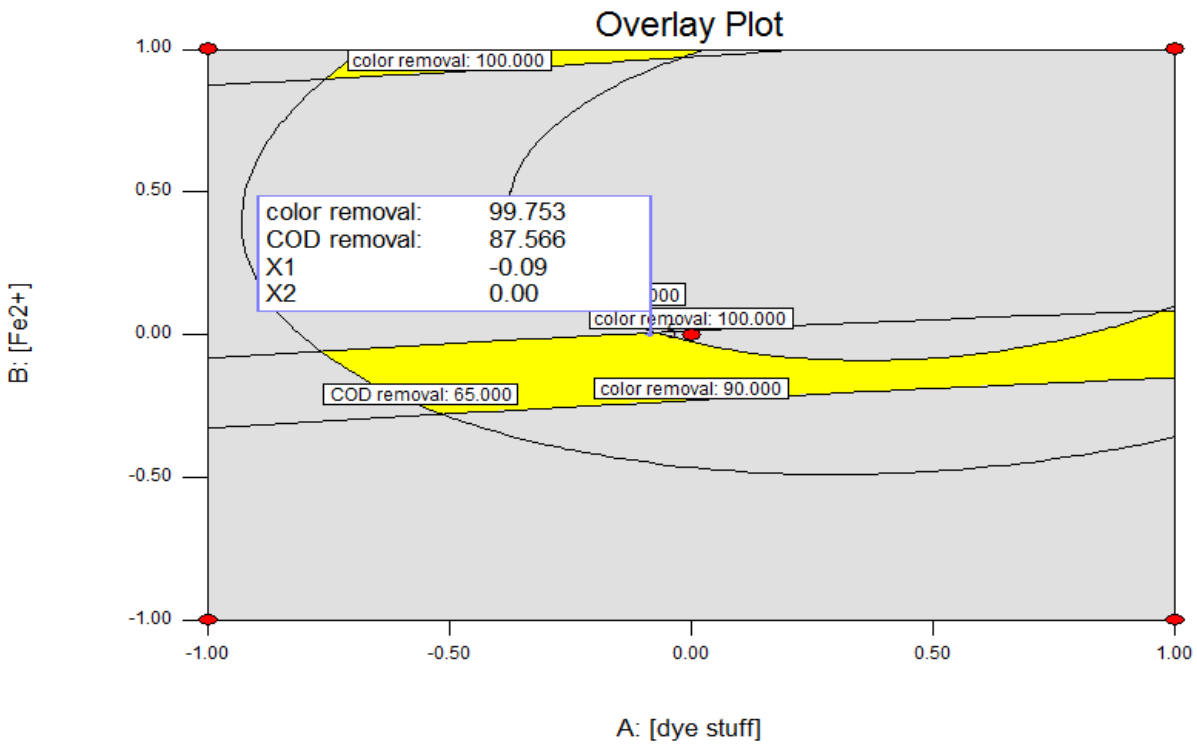
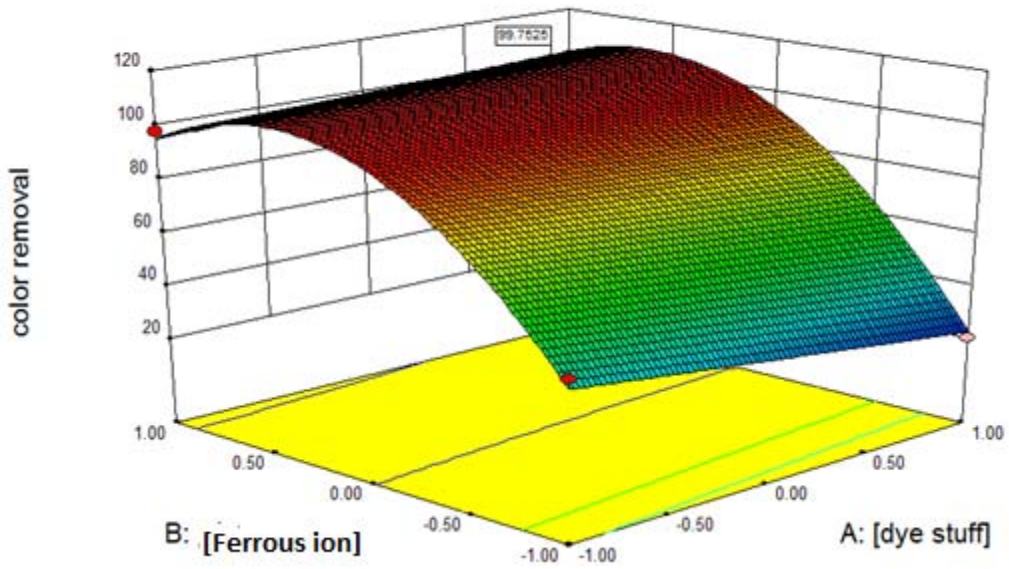


Figure 4.11: Overlay plot showing graphical Optimization

The above Figure 4.11 tells us that for the 99.751%color removal,87.576%COD removal the optimum amount of X_1($[Fe^{2+}]$) is "0" coded value (52mg/L)&that of [dye dose] is "-0.08" coded value(12mg/L).

The following figures, Figure 4.12 indicate the optimum percent color removal is 99.7534 and Figure 4-13 shows percent COD removal is 87.57. So one can conclude that it is possible to illustrate optimization using 3D surface graphical method for both responses as shown below. More over the result of optimum percent color removal &percent COD removal obtained are identical to the numerical value obtained in the previous section.



. Figure 4.12: 3D surface drawing showing the optimum color removal

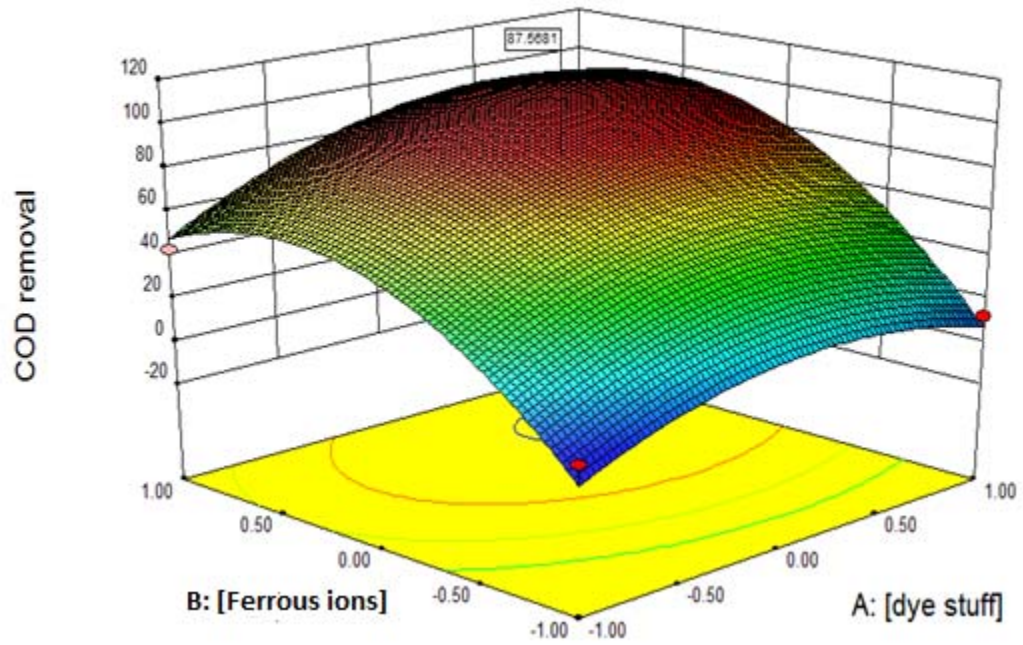


Figure 4.13: 3D surface drawing showing optimum COD removal

5. Conclusion and Recommendation

5.1 Conclusion

The characteristic of K.K Textile Factory dye house wastewater such as COD, BOD & color after laboratory analysis is found to be beyond the standard discharge limits. So it is mandatory to treat dye house wastewaters before discharge.

Box–Behnken statistical experiment design and the response surface methodology were proven to yield statistically reliable results for oxidation of dyestuffs by the solar Fenton treatment. The ferrous ion and hydrogen peroxide concentrations were found to be the most important factors in both color removal and COD removal efficiency. The results showed that the hydroxyl radical from Fenton's reaction was responsible for removing COD & color from dye house wastewater.

Percent color removals were higher than COD removals indicating formation of some colorless intermediates. At a constant dyestuff concentration percent color removal increased with increasing H_2O_2 and Fe^{2+}concentrations up to a certain level above which color removals decreased due to scavenging effects of both H_2O_2 and Fe^{2+} on hydroxyl radicals.

The optimal H_2O_2 / Fe^{2+} / dyestuff ratio resulting for the 99.75% color removal & 87.56% COD removal is concluded to be 1045mg/L / 52mg/L / 12mg/L (0, 0, - 0.09 coded value).

This investigation has demonstrated the potential of applying advanced oxidation process for the treatment of wastewater containing basic dye .Because commonly employed methods for color removal such as adsorption, coagulation–flocculation, oxidation and electrochemical methods are quite expensive and have operational problems.

In addition to numerous challenges in the treatment of dye house wastewater many of the synthetic dyestuffs are resistant to biological degradation due to the presence of large degree of aromatics, and hence color removal by bio processing is difficult and not complete as a result it is possible to conclude that AOP's using Fenton reagent is the efficient technology which entirely remove the COD and color of the textile wastewater.

5.2 Recommendation

Removal of basic dyes using Fenton reagent and solar energy has been utilized for the treatment of dye House waste water. The following recommendation should be carried out in order to improve the dye removal process.

Fenton AOP's is a very simple way of producing OH radicals neither special reactants nor special apparatus being required. In addition to this the reactants such as iron is very abundant and non toxic element and also Hydrogen peroxide is easy to handle and environmentally safe. So, if the treatment method is properly applied, it is the alternative recommended technology to remove efficiently non biodegradable organics in wastewater.

In Ethiopia solar energy is widely available so that among the AOPs solar Fenton is a recommended method of treatment because It can reduce the cost of the treatment technology.

Textile factories in Ethiopia, such as K.K Textile Factory, although they have biological treatment system, due to the fact that dyes are non bio degradable & toxic to the micro organisms as a result of the unique characteristics of this waste, the existing treatment method can't degrade & remove color of the wastewater. For instance, the color of the waste water in this factory is highly observable problem. So integrating the method of Solar Fenton with the biological method is a recommended approach.

5.2.1 Further study work suggestion

Additional research works is needed for effective and complete application of the dye house wastewater treatment process by using solar Fenton approach. The following are the main study issues recommended in future work to improve and complete Removal of basic dyes using solar Fenton AOP's

- The potential of recycling and reusing of the iron sludge would make the treatment process more attractive & reduce the cost of the catalyst so further study in this issue can complete the treatment process.

- Further studies at pilot- plant scale are needed to examine the potential of wastewater treatment by solar Fenton method.

- The Kinetics of solar Fenton oxidation reaction together with the design aspect should be considered.

6. **References**

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7. APPENDIXES

A. Sock Solution Calculation

Stock solution of hydrogen peroxide(H_2O_2)

Volume of H_2O_2 required for concentration 1045 mg/L is shown below.

Concentration of H_2O_2 (35%w/w)

$$\left(\frac{35gH_2O_2}{100gH_2O_2solution}\right)\times\left(1.11\times10^3\,gH_2O_2Solution\right)$$

=388.5g/L of H_2O_2solution

Volume required for 1045mg/L of H_2O_2 to prepare 500 ml of solution would be

$$\left(\frac{1045mgH_2O_2}{LH_2O_2}\right)\times\left(\frac{mlH_2O_2}{388.5mgH_2O_2}\right)\times\left(0.5Lofsolution\right)$$

=1.34ml of H_2O_2 required

Stock Solution of Ferrous ions (Fe^{2+})

Mass required for concentration of 52mg/L is shown below

Concentration of Fe^{2+}

$$=\left(\frac{52mgFe^{2+}}{L}\right)\times\left(\frac{mmolFe^{2+}}{56mgFe^{2+}}\right)$$

=0.93 mmol of Fe^{2+}/L

then, the mass of $Feso_4.7H_2O$ for 500ml solution

$$\left(\frac{278mgFeSO_4.7H_2O}{mmolFeSO_4.7H_2O}\right)\times\left(\frac{0.93mmolFe^{2+}}{L}\right)\times\left(0.5Lsolution\right)$$

=129mg of Fe^{2+}

B) Lists of Laboratory equipments used in the experimental work

a) Fenton reaction using magnetic stirrer

b) UV-VIS Spectrophotometer to determine color of the constituted waste water

c.1)supernatant solution of unknown Concenterations

c-

c.2)dye solution of known concentrations

d) HACH DR/2400 spectrophotometer to determine color of K.K waste water

e) COD digester

f) Back titeration equipement

C. Design Summery

Design Summary

Study Type	Response Surface	**Runs**	17
Design Type	Box-Behnken	**Blocks**	No Blocks
Design Mode	Quadratic	**Build Time (r**	54.72

Factor	Name	Units	Type	Subtype	Minimum	Maximum	Coded Values	Mean	Std. Dev.
A	[dye stuff]	mg/l	Numeric	Continuous	-1.00	1.00	-1.000=-1.00 1.000=1.00	0.00	0.69
B	[Fe2+]	mg/l	Numeric	Continuous	-1.00	1.00	-1.000=-1.00 1.000=1.00	0.00	0.69
C	[H2O2]	mg/l	Numeric	Continuous	-1.00	1.00	-1.000=-1.00 1.000=1.00	0.00	0.69

Response	Name	Units	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio	Trans	Model
Y1	color removal	%	17	Polynomial	18.34	99.78	82.4847	30.1448	5.44057	None	Quadratic
Y2	COD removal	%	17	Polynomial	0	88.92	60.0465	35.3052	N/A	None	Quadratic

D.Coefficient Table

Intercept	A	B	C	AB	AC	BC	A^2	B^2	C^2
99.51	-2.82875	33.57	2.27875	6.645	1.9775	-6.655	0.11625	-33.9613	-2.33375
	0.0783	< 0.0001	0.1408	0.0111	0.3422	0.0110	0.9527	< 0.0001	0.2572
88.92	14.2088	34.5863	4.79	6.1925	-7.775	-0.995	-18.9412	-36.1613	-6.25375
	0.0017	< 0.0001	0.1415	0.1736	0.0989	0.8147	0.0021	< 0.0001	0.1605
	p <.01	.01<= p <.05	.05<= p <.10	p >=.10					

E . Model Evaluation

999

3 Factors: A, B, C

Design Matrix Evaluation for Response Surface Quadratic Model

No aliases found for Quadratic Model

Aliases are calculated based on your response selection,
taking into account missing datapoints, if necessary.
Watch for aliases among terms you need to estimate.

Degrees of Freedom for Evaluation

Model	9
Residuals	7
Lack Of Fit	*3*
Pure Error	*4*
Corr Total	16

A recommendation is a minimum of 3 lack of fit df and 4 df for pure error.
This ensures a valid lack of fit test.
Fewer df will lead to a test that may not detect lack of fit.

				Power at 5 % alpha level to detect signal/noise		
Term	**StdErr****	**VIF**	**Ri-Squared**	**0.5 Std. Dev.**	**1 Std. Dev.**	**2 Std. Dev.**
A	0.35	1.00	0.0000	9.4 %	23.2 %	68.1 %
B	0.35	1.00	0.0000	9.4 %	23.2 %	68.1 %

B	0.35	1.00	0.0000	9.4 %	23.2 %	68.1 %
C	0.35	1.00	0.0000	9.4 %	23.2 %	68.1 %
AB	0.50	1.00	0.0000	7.2 %	14.0 %	40.8 %
AC	0.50	1.00	0.0000	7.2 %	14.0 %	40.8 %
BC	0.50	1.00	0.0000	7.2 %	14.0 %	40.8 %
A^2	0.49	1.01	0.0058	14.5 %	42.5 %	93.8 %
B^2	0.49	1.01	0.0058	14.5 %	42.5 %	93.8 %
C^2	0.49	1.01	0.0058	14.5 %	42.5 %	93.8 %

****Basis Std. Dev. = 1.0**

Standard errors should be similar within type of coefficient. Smaller is better.

Ideal VIF is 1.0. VIFs above 10 are cause for alarm,
indicating coefficients are poorly estimated due to multicollinearity.

Ideal Ri-squared is 0.0. High Ri-squared means terms are correlated with each other,
possibly leading to poor models.

If the design has multilinear constraints multicollinearity will exist to a greater degree,
thus increasing the VIFs and the Ri-squareds, rendering these statistics useless.
Use FDS instead.

Power is an inappropriate tool to evaluate response surface designs.
Use precision-based metrics provided in this program via fraction of design space (FDS) statistics.
Click on the Graphs button at the top of this screen, look for the [?] button on the FDS Tool
for detailed instructions

F.Fit Summery for Color Removal

Summary (detailed tables shown below)

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	0.0041		0.5413	0.3161	
2FI	0.8638		0.4444	-0.3845	
Quadratic	< 0.0001		0.9834	0.8839	Suggested
Cubic	< 0.0001		1.0000		Aliased

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	1.157E+005	1	1.157E+005			
Linear vs Mear	9121.12	3	3040.37	7.29	0.0041	
2FI vs Linear	369.42	3	123.14	0.24	0.8638	
Quadratic vs 2	4943.28	3	1647.76	109.32	< 0.0001	Suggest
Cubic vs Quad	105.51	3	35.17	6.366E+007	< 0.0001	Alias
Residual	0.000	4	0.000			
Total	1.302E+005	17	7658.98			

"Sequential Model Sum of Squares [Type I]": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Lack of Fit Tests

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Linear	5418.21	9	602.02		
2FI	5048.79	6	841.46		
Quadratic	105.51	3	35.17		
Cubic	0.000	0			
Pure Error	0.000	4	0.000		

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	20.42	0.6273	0.5413	0.3161	9944.06	
2FI	22.47	0.6527	0.4444	-0.3845	20129.49	
Quadratic	3.88	0.9927	0.9834	0.8839	1688.11	Suggested
Cubic	0.000	1.0000	1.0000		+	Aliased

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

G.Fit Summery for COD removal

Summary (detailed tables shown below)

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	0.0100		0.4708	0.3015	
2FI	0.9190		0.3441	-0.2683	
Quadratic	0.0001		0.9464	0.6246	Suggested
Cubic	< 0.0001		1.0000		Aliased

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	61294.84	1	61294.84			
Linear vs Mear	11368.33	3	3789.44	5.74	0.0100	
2FI vs Linear	399.15	3	133.05	0.16	0.9190	
Quadratic vs 2	7707.85	3	2569.28	38.43	0.0001	Sugge
Cubic vs Quad	467.96	3	155.99	6.366E+007	< 0.0001	Alia
Residual	0.000	4	0.000			
Total	81238.13	17	4778.71			

"Sequential Model Sum of Squares [Type I]": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Lack of Fit Tests

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Linear	8574.97	9	952.77		
2FI	8175.81	6	1362.64		
Quadratic	467.96	3	155.99		
Cubic	0.000	0			
Pure Error	0.000	4	0.000		

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	25.68	0.5700	0.4708	0.3015	13929.79	
2FI	28.59	0.5900	0.3441	-0.2683	25294.93	
Quadratic	8.18	0.9765	0.9464	0.6246	7487.42	Suggested
Cubic	0.000	1.0000	1.0000		+	Aliased

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

H.Solution for numerical Optimization

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:[dye stuff]	minimize	-1	1	1	1	3
B:[Fe2+]	is equal to 0.0(	-1	1	1	1	3
C:[H2O2]	is target = 0.0(	-1	1	1	1	3
color removal	maximize	60	99.78	1	1	3
COD removal	maximize	70	88.92	1	1	3

Solutions

Number	[dye stuff]	[Fe2+]	[H2O2]	color remova	COD removal	Desirability	
1	-0.09	0.00	-0.00	99.7521	87.5702	0.842	Selected

1 Solutions found

Number of Starting Points: 43

[dye stuff]	[Fe2+]	[H2O2]
0.00	-1.00	1.00
1.00	0.00	1.00
1.00	1.00	0.00
-1.00	-1.00	0.00
1.00	-1.00	0.00
0.00	0.00	0.00
0.00	-1.00	-1.00

-1.00	0.00	1.00
-1.00	1.00	0.00
0.00	1.00	-1.00
0.00	1.00	1.00
-1.00	0.00	-1.00
0.32	0.00	0.91
-0.56	0.00	0.13
-0.72	0.00	-0.37
-0.84	0.00	-0.06
0.54	0.00	0.42
0.14	0.00	0.58
0.09	0.00	0.65
0.39	0.00	-0.74
-0.40	0.00	0.78
0.44	0.00	0.71
-0.20	0.00	0.64
-0.49	0.00	0.22
0.86	0.00	0.75
0.67	0.00	0.52
0.09	0.00	-0.02
0.95	0.00	0.91
0.98	0.00	-0.42
0.55	0.00	0.71
0.18	0.00	0.99

I. ANOVA for color removal

Std. Dev.	3.88	R-Squared	0.9927
Mean	82.48	Adj R-Squared	0.9834
C.V. %	4.71	Pred R-Square	0.8839
PRESS	1688.11	Adeq Precisior	27.653

The "Pred R-Squared" of 0.8839 is in reasonable agreement with the "Adj R-Squared" of 0.9834.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 27.653 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	99.51	1	1.74	95.40	103.62	
A-[dye stuff]	-2.83	1	1.37	-6.07	0.42	1.00
B-[Fe2+]	33.57	1	1.37	30.32	36.82	1.00
C-[H2O2]	2.28	1	1.37	-0.97	5.52	1.00
AB	6.64	1	1.94	2.05	11.24	1.00
AC	1.98	1	1.94	-2.61	6.57	1.00
BC	-6.65	1	1.94	-11.25	-2.06	1.00
A^2	0.12	1	1.89	-4.36	4.59	1.01
B^2	-33.96	1	1.89	-38.44	-29.49	1.01
C^2	-2.33	1	1.89	-6.81	2.14	1.01

Final Equation in Terms of Coded Factors:

color removal =

+99.51

-2.83 * A

+33.57 * B

+2.28 * C

+6.64 * A * B

+1.98 * A * C

-6.65 * B * C

+0.12 * A^2

-33.96 * B^2

-2.33 * C^2

color removal =

+99.51000

-2.82875 * [dye stuff]

+33.57000 * [Fe2+]

+2.27875 * [H2O2]

+6.64500 * [dye stuff] * [Fe2+]

+1.97750 * [dye stuff] * [H2O2]

-6.65500 * [Fe2+] * [H2O2]

+0.11625 * [dye stuff]^2

-33.96125 * [Fe2+]^2

-2.33375 * [H2O2]^2

The Diagnostics Case Statistics Report has been moved to the Diagnostics Node.

In the Diagnostics Node, Select Case Statistics from the View Menu.

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

1) Normal probability plot of the studentized residuals to check for normality of residuals.

2) Studentized residuals versus predicted values to check for constant error.

3) Externally Studentized Residuals to look for outliers, i.e., influential values.

4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

J. ANOVA for COD removal

Std. Dev.	8.18	R-Squared	0.9765
Mean	60.05	Adj R-Squared	0.9464
C.V. %	13.62	Pred R-Square	0.6246
PRESS	7487.42	Adeq Precisior	15.581

The "Pred R-Squared" of 0.6246 is not as close to the "Adj R-Squared" of 0.9464 as one might normally expect. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 15.581 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	88.92	1	3.66	80.27	97.57	
A-[dye stuff]	14.21	1	2.89	7.37	21.04	1.00
B-[Fe2+]	34.59	1	2.89	27.75	41.42	1.00
C-[H2O2]	4.79	1	2.89	-2.05	11.63	1.00
AB	6.19	1	4.09	-3.47	15.86	1.00
AC	-7.77	1	4.09	-17.44	1.89	1.00
BC	-1.00	1	4.09	-10.66	8.67	1.00
A^2	-18.94	1	3.98	-28.36	-9.52	1.01
B^2	-36.16	1	3.98	-45.58	-26.74	1.01
C^2	-6.25	1	3.98	-15.68	3.17	1.01

Final Equation interms of coded variables For COD removal

Final Equation in Terms of Coded Factors:

COD removal =
+88.92
+14.21 * A
+34.59 * B
+4.79 * C
+6.19 * A * B
-7.77 * A * C
-1.00 * B * C
-18.94 * A^2
-36.16 * B^2
-6.25 * C^2

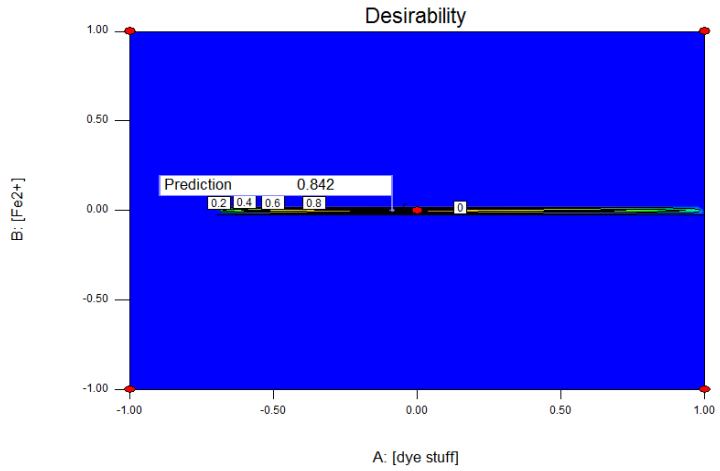
Final Equation in Terms of Actual Factors:

COD removal =
+88.92000
+14.20875 * [dye stuff]
+34.58625 * [Fe2+]
+4.79000 * [H2O2]
+6.19250 * [dye stuff] * [Fe2+]
-7.77500 * [dye stuff] * [H2O2]
-0.99500 * [Fe2+] * [H2O2]
-18.94125 * [dye stuff]^2
-36.16125 * [Fe2+]^2
-6.25375 * [H2O2]^2

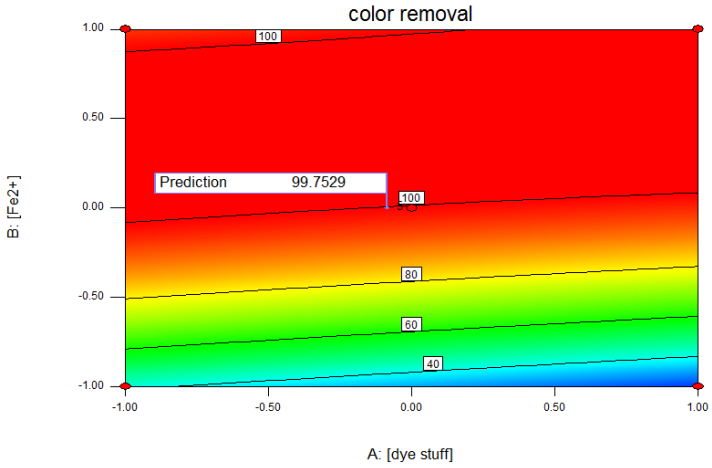
The Diagnostics Case Statistics Report has been moved to the Diagnostics Node.
In the Diagnostics Node, Select Case Statistics from the View Menu.

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:
1) Normal probability plot of the studentized residuals to check for normality of residuals.
2) Studentized residuals versus predicted values to check for constant error.
3) Externally Studentized Residuals to look for outliers, i.e., influential values.
4) Box-Cox plot for power transformations.

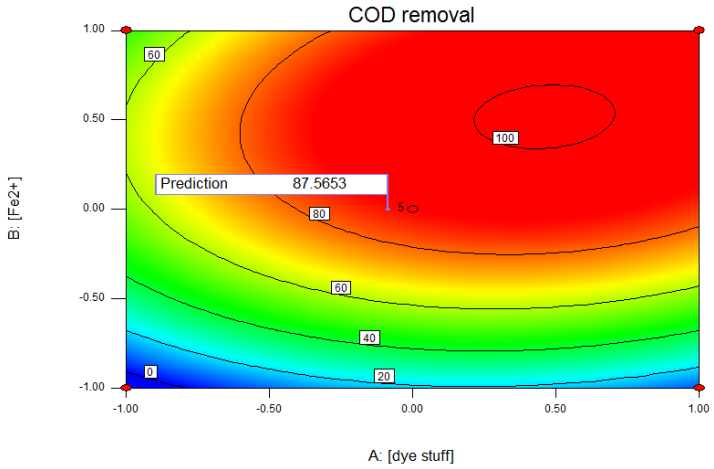
K. Graphical Optimization indicating Deseriability



L.Graphical Optimization for Color response



M . Graphical Optimization for COD response



Declaration

I, the undersigned, hereby declare that the work contained in this thesis entitled“ Removal of basic dyes from textile wastewater by applying advanced oxidation process using Fenton reagents” is my own Original work and it has not previously in its entirety or in part submitted it at any other University for degree. And that all source of materials used for the thesis have been duly acknowledged.

Desta Solomon _____ _____

Name **Signature** **Date**

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge.

Eng. Teshome Worku _____ _____

Advisor **Signature** **Date**