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Removal of Reactive Blue 19 Dye from Textile Wastewater Using Fenton Oxidation Process: Case Study on Bahir Dar Textile Share Company

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SCHOOL OF GRADUATE STUDIES
FACULTY OF CHEMICAL AND FOOD ENGINEERING
MSc in Environmental Engineering

MSc thesis on:

**Removal of Reactive Blue 19 Dye from Textile Wastewater Using Fenton
Oxidation Process: Case Study on Bahir Dar Textile Share Company**

BY

Mulugeta Gedefaw

March,2022

Bahir Dar, Ethiopia



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Removal of Reactive Blue 19 Dye from Textile Wastewater Using Fenton
Oxidation Process: Case Study on Bahir Dar Textile Share Company

BY

Mulugeta Gedefaw

A thesis submitted in partial fulfillment of the requirements for the degree of
masters in Environmental Engineering.

Supervisor: Zenamarkos Bantie (PhD)

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March,2022

Bahir Dar, Ethiopia

DECLARATION

This is to certify that the thesis entitled “**Removal of Reactive Blue 19 Dye from Textile Wastewater Using Fenton Oxidation Process: Case Study on Bahir Dar Textile Share Company**”, submitted in partial fulfillment of the requirements for the degree of Master of Science in environmental engineering under chemical and food engineering, Bahir Dar Institute of Technology, is a record of original work carried out by me and has never been submitted to this or any other institution to get any other degree or certificates. The assistance and help I received during the course of this investigation have been duly acknowledged.

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Approval of thesis for defense result

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ABSTRACT

Textile industry is one of the industries that uses a lot of water during the manufacturing process and also releases a lot of effluents containing synthetic colors into the environment, causing health and environmental concerns. Textile companies use reactive blue 19 dye which is regarded major health risks due to its anthraquinone nature. The principal aim of this study is to remove reactive blue 19 dye with Fenton reagents. The main factors of experimental runs of this study are Fenton reagents (H_2O_2 and ferrous ion Fe^{2+}) and pH of solutions. Currently, the wastewater treatment methods of Bahir Dar textile Share Company are physical, chemical and biological methods for the removal of dyes from wastewater by focusing on aerobic biological processes followed by chemical coagulation. However, these treatment methods have not been effective in treating organic pollutants from textile wastewater due to the complicated aromatic structure and low biodegradability natures. Hence, to solve this environmental problem, this study investigates the potential use of Fenton advanced oxidation treatment methods for the removal of reactive blue 19 dye wastes from textile wastewater. Fenton reagent is a reaction between hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) in acidic media to produce hydroxyl radical, and be a strong oxidant capable of oxidizing various organic compounds. This process is oxidation process for the removal of color and chemical oxygen demand (COD) from textile wastewater containing dyes. Batch experiments were carried out in order to study the effect of various dose of Fenton reagents for removal efficiency of reactive blue 19 dye. The maximum removal efficiencies were 90.8% and 94.8% for color and COD respectively under the dosages of 20 mg/l of Fe^{2+} , 100mg/l of H_2O_2 and pH of 3.5. Fenton process is able to remove reactive blue 19 dye from textile wastewater with different dose of Fenton reagents in acidic media.

Keywords: Reactive blue19 dye, Fenton reagent, Fenton oxidation, ferrous ion, hydrogen peroxide, textile wastewater.

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List of Acronyms

| | |
|-------------------------------|------------------------------------|
| AOP | Advanced Oxidation Process |
| FOP | Fenton Oxidation Processes |
| RB19 | Reactive Blue 19 |
| COD | Chemical Oxygen Demand |
| BOD | Biological Oxygen Demand |
| $HO\cdot$ | Hydroxyl Radical |
| H ₂ O ₂ | Hydrogen Peroxide |
| FeSO ₄ | Iron Sulphate |
| EDTA | Ethylene Diamine Tetra Acetic acid |
| TDS | Total Dissolved Solids |
| TSS | Total Suspended Solids |
| CCD | Central Composite Design |
| RSM | Response Surface Methodology |
| ANOVA | Analysis of Variance |
| NA | Not Available |
| WW | Wastewater |
| EQW | Equivalent weight |

1. INTRODUCTION

1.1. Background

Water is an essential resource for life maintenance (Domingues *et al.*, 2018). It is vital to almost all life forms in existence and it is believed that the first life started in water (Review, 2014). Although more than 70% of earth surface is covered by water, majority of it is not apposite to sustain human life and only inadequate potable water resources are available. The extensive chemicals use in everyday life and growing industrialization led to unwanted contamination of existing natural resources by the release of diverse organic and inorganic pollutants into water systems (Patil and Raut, 2014c).

Dye is a visible pollutant that is found in industrial wastewaters and is considered to be one of the most important pollutants from an aesthetic standpoint. Dyes are widely utilized in the textile, paper, plastic, leather, cosmetics, and food companies to color their products.

It is usually had synthetic origin and complex aromatic molecular structures which makes them more stable and difficult for bio - removals. Also, frequently caused environmental issues in the form of colored effluents discarded into bodies of water (Buthiyappan *et al.*, 2015). Discharge of colored wastewater not only affects the aesthetic aspects of receiving waters, but also prevents the aquatic environments from access to sunlight, causes the loss of photosynthesis, and disrupts biological processes.

Textile company is a very diverse sector in terms of raw materials use, processes, products and equipment and has very complicated industrial chains. Emerging dye pollution and salts are extremely hazardous to the environment. Since, many textile industries generate huge quantities of highly polluted wastewaters containing dyes, inorganic salts such as (NaCl, Na₂SO₄), various types of surfactants, suspended solid particles, acids, alkalis, and other auxiliary chemicals (Tavangar *et al.*, 2019). The presence of such pollutants makes the water treatment difficult due to their chemical stability. Without any proper treatments, discharge of textile wastewaters would cause much concern to the environment (Tavangar *et al.*, 2019).

With the widespread use of synthetic dyes, dye containing wastewaters are extensively discharges to the environment from various industries including textiles, leathers, foods, drinks, pharmaceuticals, cosmetics, paper manufacturing and so on(Zou *et al.*, 2020). Effects on the environment by textile industries are recognized for a few times, both in terms of the discharge of pollutants and of the consumption of water & energy. Water is mostly used for dyeing and finishing processes, contributing ~80 % of the overall effluent containing high amounts of organics as well as dyestuff such as azo dyes, vat dyes, reactive dyes, acidic and basic dyes (Nakhate *et al.*, 2019).

In wastewater treatment, variety of physical, biological, and chemical methods are used. However, some pollutants in wastewater are resistant to typical treatment methods to some extent. Chemical oxidation process is transformations that could improve current treatment methods. Through oxidation and reduction reactions, oxidation and reduction processes destroy specific molecules and constituents. Chemical oxidation by hydroxyl radicals, which are highly reactive and short-lived oxidants known as advanced oxidation process. Before being discharged to the local public treatment facility, the color and COD of the wastewater from the facility needed to be lowered in concentration. Fenton process is among the most effective processes for the removal of organic pollutants due to the high oxidation power, rapid oxidation, reduced energy consumption for the presence of iron catalyst. Fenton reagent (Fe^{2+} and H_2O_2) used in the advanced Oxidation Process (AOP) aids in the removal of organic molecules found in polluted water (Patil and Raut *et al.*, 2014). In AOP, hydroxyl radicals ($\cdot\text{OH}$) are generated in solution and are responsible for oxidation of organic compounds. H_2O_2 is a multiuse oxidant for many systems(Gore *et al.*, 2014).

Reactive dyes represent nearly 30% of synthetic dyes worldwide. They contain functional group comprising molecular structures, chromophore group, and covalent bonds with cellulose fibers. Reactive Blue 19 (RB19) dye is an anthraquinone-based dye utilized in textile industries and is more resistant to biological removal due to attached aromatic structures compared to azo-based dyes (Akyol, 2020). It is a harmful dye and may damage aquatic life and also vegetative life if the contaminated water is used for irrigation(Profile, 2018).

1.2. Statement of the Problem

Textile industries use different dyes such reactive dyes, vat dyes, basic and acidic dyes, and sulphur dyes. These organic pollutants are usually discharged toward receiving water bodies and caused damages to aquatic ecosystems. Among the various classes of dyes, reactive dyes are the brightest class of soluble dyes utilized by the textile industry as their coloring value is extremely high.

Pollution of water by organic matter could be a major risk to water quality because it often poses problems for treatment. This pollution is worse because of the numerous organic contents, low biodegradability, and high discoloration nature due to its high covalent bonds. The occurrence of very small amounts of dyes in water (less than 1ppm for some dyes) is highly visible and undesirable. Consequently, such wastewater disposals may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at large. Therefore, the removal of such colored agents from effluents is essential for environmental aspects.

Bahir Dar textile share company is one of the biggest economic sectors in Ethiopia, which discharges colored wastewater into Abay River. These colored effluents give undesirable view to the water streams and possess toxic, carcinogenic and mutagenic effects. Dyes also prevent light penetration and reduce photosynthetic activities of water streams and disturb aquatic equilibrium. Currently, the company used several wastewater treatment methods like physical, chemical and biological methods for the removal of dyes from wastewaters by focusing on aerobic biological processes followed by chemical coagulation. However, removal efficiency of reactive dyes with biological processes followed by chemical coagulation is low compared to advanced oxidation process because reactive dyes resist against microbial removal due to their complicated structures. Hence, the purpose of this study is the removal of RB 19 dye from textile wastewater by using advanced oxidation process (AOP) through Fenton reagents and to provide research-based recommendations for Bahir Dar textile share company about the less efficient performance of current treatment methods.

1.3. Objective

1.3.1. General Objective

The main objective of this research is to study the removal efficiency of reactive blue 19(RB19) dye from textile wastewater by applying advanced oxidation processes using Fenton reagents.

1.3.2. Specific Objectives

The specific objectives of this thesis are: -

- To prepare and characterize wastewater from distilled water and RB19 dye
- To analyze the effects of pH, Fe^{2+} and H_2O_2 dosage on the removal efficiency of reactive 19 dye.
- To determine the optimum conditions for removal of reactive blue 19 dye

1.4. Significant of the Study

Dyes are soluble organic compounds, especially those classified as reactive, direct, basic and acidic dyes. They exhibit high solubility in water, and it is difficult to get rid of them easily. The color related to textile dyes not only causes visual damage to the water bodies, but also prevents the penetration of sunshine through water. The textile dyes act as toxic, mutagenic and carcinogenic agents. However, the significance of this study is to eradicate RB 19 dye from textile industry effluent by Fenton advanced oxidation processes to maintain aquatic fauna and flora. And also, enhance environmental problems and health risks. Effective success of this research able to play a great role for reducing environmental pollution of textile wastewater problems by advanced Fenton oxidation process before discharge the receiving water bodies. This research provides information for company about effective wastewater treatment methods.

1.5. Scope of the Study

This thesis focuses on textile wastewater treatments by advanced oxidation process (Fenton oxidation process) to RB19 dye using Fenton reagents. In textile industry, reactive dyes play an important role for dyeing. However, because of their complicated aromatic molecular structures can pose major environmental problems. Once the reactive dye being withdraw to the environment without destructive treatment, these water-soluble dyes can

remain for long time and alter the quality of water bodies. Among technologies for organic pollutant treatment is advanced oxidation processes (Fenton oxidation process) have mandatory due to their high efficiency and ability to thoroughly remove pollutants from wastewater effluents. This study shows that is treatment of wastewater containing RB19 dye from Bahir Dar textile share company wastewater effluents by using advanced Fenton oxidation processes before discharging the Aby River. Since, the scope of this study is preparation of wastewater from distilled water and reactive blue 19 dye and determination of its removal by Fenton oxidation process.

2. LITERATURE REVIEW

2.1. Wastewater Treatment

Wastewater treatment is a process used to remove contaminants from wastewater before discharged back into the environment. Wastewater treatment system is a collection of unit operations and processes that work together to remove contaminants to a safe level. One major challenge for any industry is treating industrial wastewater mainly organic waste which may cause significant health and environmental risks(Mehari, Gebremedhin, and Ayele, 2015). Environmentalists, and scientists are look for ways of eliminating organic pollutants from discharged sources into the environment. In an attempt to solve these problems various treatment technologies starting from physical and biological remediation to advanced chemical techniques are being explored for effective removal of those organic compounds from effluents, sludge, soils, and other industrial discharges(Silva *et al.*, 2020).

Among the numerous chemical techniques that are applied to removal of organic pollutant are oxidation processes, specifically advanced Fenton oxidation process(Serrano Martinez *et al.*, 2020). Fenton oxidation process was discovered in 1894 by a British chemist, Henry J.H. Fenton. He observed that copper and iron catalyze the oxygen transfer processes, thus increasing the capacity of peroxide to act as an oxidant. Fenton oxidation process is predicated on the reaction between hydrogen peroxide and iron salt leading to the generation of a highly reactive and strongly oxidizing potential radicals for the elimination of organic pollutants in water(Using and Oxidation, 2015).

2.1.1. Wastewater Treatment Methods

Pollution by organic chemicals including dyes is one of the most serious environmental problems facing life on environment(Bhatt and Patel, 2021). Several sources of water pollutions with dyes and pigments are leather tanning, paper, rubber, food technology, and textile industries (Shiyong *et al.*, 2009). Dyes have a variety of complex organic compounds and toxic substances which cause carcinogenic effects. The resistance of these organic compounds for removal is due to the complex chemical structure of synthetic pigments in dyes(Scholz, 2019). Different studies have looked into chemical, physical, and biological methods to remove colors from wastewaters including adsorption, chemical precipitation,

electro-chemical oxidation, chemical oxidation, and aerobic and anaerobic biological processes (Garrido-cardenas and Agüera, 2020).

2.1.2. Classification of Wastewater Treatment Methods

Wastewater treatment methods can be classified depending on the nature of pollutants and the level of desired removals.

2.1.2.1. Biological Treatment Method

Biological treatment involves the conversion or destruction of contaminants with the help of microorganisms. It is relatively economical method compared to other physical and chemical processes. Bio removal methods such as dye decolorization, microbial removal, adsorption (living or dead) microbial biomass, and bioremediation systems are frequently used to treat industrial wastewater by utilizing microorganisms such as bacteria, yeasts, algae and fungi to accumulate and remove various pollutants. Biological treatment methods are utilized to breakdown numerous organic pollutants but due to the complicated chemical bonds and synthetic organic origin bio removal technologies are unable to achieve adequate color removals.

2.1.2.2. Physical Treatment Methods

Physical treatment involves removal of pollutants from wastewater by using sedimentation, screening, filtration, membrane – filtration processes (nanofiltration, reverse osmosis) and adsorption techniques. Physical treatments methods mainly used for removal of suspended solids(Engineering, 2020).

2.1.2.3. Chemical Methods

Chemical treatment involves the addition of chemicals for conversion or destruction of contaminants through chemical reactions. Coagulation or flocculation mixed with flotation and filtration, electro flotation, electro kinetic coagulation, traditional oxidation procedures using oxidizing chemicals, irradiation, or electrochemical processes are examples of chemical approaches (Engineeringin 2020)and(Assefa and Sahu, 2016).

2.1.2.3.1. Coagulation

One of most common wastewater treatment methods especially in the traditional treatment process is coagulation or flocculation. The surface electrical charges of colloids can be

eliminated with adding water electrolytic products such as aluminum sulphate, ferric sulphate and ferric-chloride. Textile wastewater treatment is carried out through tank with mild shaking, where the finely separated suspended solids come together to form bigger particles to settle out. The amount and grade of chemicals used have an effect on the degree of clarity obtained. 80-90 % of total suspended matter, 40-70 % of BOD, 30-60 % of COD and 80-90 % of bacteria eliminated using coagulation procedures(Assefa and Sahu, 2016). However, in simple sedimentation only 50-70% of the total suspended matter and 30-40% of the organic matter settles out(Assefa and Sahu, 2016). The extreme removal of disperse and reactive dyes were 75% and 46% respectively by Alcea rosea root mucilage coagulant from wastewater (Mahmoudabadi, Talebi, and Jalili, 2019). Maximum COD removal efficiency (%) of textile wastewater by Alum coagulation is 58%(Nawaz and Ahsan, 2014).

2.2.Reactive Dyes

In the textile industry, reactive dyes play an important role. However, because of their complicated aromatic molecular structures they can pose major environmental problems. If once being discharged to the environment without critical treatment, these water- soluble dyes can persist for a long time and alter the quality of water bodies by thwarting light penetration, and deterring photosynthesis and affects the ecosystems(Bich *et al.*, 2021). Reactive dyes are more resistant and difficult to remove completely using visual approaches (physical, biological and chemical coagulation) due their complex aromatic molecular structures. However, there are different new technologies used for the complete removal of organic pollutants from wastewater. Among new alternative technologies for wastewater treatment, one effective technique is Fenton oxidation processes (FOPs), which can be used to remove very complicated aromatic structures of dyes with short period of time (Javaid , 2019).

2.2.1. Toxic effects of Reactive Dyes

A dye is a colored organic compound with the ability to absorb visible light and bind strongly to fiber through chemical or physical bonding. Dyes are colored by chromophores, and their disposal into water not only affects the visual but also causes biotoxicity (GD and R, 2018). The observation of color is only formed when a molecule absorbs the specific wavelength of light in the visible region of the electromagnetic spectrum and transmits or

reflects the other wavelengths and also cause toxicity on health and environment (Lellis *et al.*, 2019) . Chromophores and auxochromes are main components of dye molecules. An unsaturated group that absorbs light and reflects it at a specified angle is known as a chromophore. Color is created by the presence of chromophores in the structure, while auxochromes serve as an additive, making the molecule soluble in water and allowing it to form a strong bond with fibers. Dyes can be classified based on their chemical structure as well as the existence of specific chromophores. Various kinds of reactive dyes are commonly used in industries, and classified as azo dyes, anthraquinone, triphenylmethane, phthalocyanine, indigo, and sulfur dyes. Chromophore are found in the following chemical structures:- -C=C- , -C=O , -N=N- , -NO_2 and -C=N (Javaid 2019). Anthraquinone is derived from anthracene or phthalic anhydride used in the manufacture of dyes (Lavanya, 2014).

2.2.2. Reactive Blue 19 Dye (Reactive Remazol brilliant blue R)

Reactive blue 19 dye is oxidized derivatives of aromatic compounds and often readily made from reactive aromatic compounds with electron-donating substituents such as phenols and catechol, which increase the nucleophilicity(high color) of the ring and contributes to the large redox potential(more difficult for oxidation) needed to break aromaticity(Ahmadi *et al.*, 2018). Reactive remazol brilliant blue R dyes have a very strong chemical bonds due to aromatic anthraquinone structures. Different physical, chemical and biological treatment strategies have been utilized for the treatment of these material effluents but it is not treat effectively (Haque *et al.*, 2020).

Reactive blue 19 dye with its chemical structure is normally resistant to chemical attack and has a small stabilization effect due to the competition between the formation of its reactive state (vinyl sulfone) and hydrolysis reactions (Değermenci and Akyol, 2020). It can pose a negative impact on the environment due to the reduction in light penetration and impairment of photosynthesis process. Reactive Blue 19 (RB19) also known as Remazol Brilliant blue is an anthraquinone dye used by the textile industries(Yi, Sun, and Dai ,2017). The removal of the dye from wastewaters is of great necessity. Removal of color is possible through various physical, chemical, biological methods or a combination of them. Several treatment methods have been proposed for the removal of RB19 from

contaminated waters, which include photodecomposition, electro-coagulation, adsorption, dissolved air flotation, biodegradation, and other processes (Ahmadi, Mohammadi, Igwegbe, *et al.*, 2018). The mentioned methods cause problems such as their control, injection of chemicals and production of high volumes of sludge with attendant problems of filtration and sludge disposal (Mahmoudabadi, Talebi, and Jalili, 2019). Advanced oxidation process (AOP) is highly effective in the removal of RB19 dye because of its high efficiency and high oxidation potential (Ahmadi, Mohammadi, Igwegbe, *et al.*, 2018).

Reactive Blue 19 (RB19) is an anthraquinone dye, and because it is highly stabilized by resonance and it is very resistant to chemical oxidation. There are many studies about the removal of RB19 dye like photocatalytic degradation of RB19 by different bismuth compounds used as photocatalyst. Relative to the previous techniques adsorption is considered to be less efficient and relatively expensive to remove RB19 dye (Najdanović *et al.*, 2020).

RB19 dye removal mechanism has been established by X-ray diffraction, Uv- spectroscopy and IR spectroscopy analysis. The removal of RB19 dye from textile effluents has involved in the last few years, not only because of their toxicity, but also mainly due to their visibility. In recent years, many investigations have focused on several adsorbents. In the field of textile, special attention was paid to these industries by developing research to identify cost-effective methods of treatment of their releases colored and meet required standards (Elkhatabi *et al.*, 2013).

RB19 dye is remove with Fenton processes for wastewater reuse and to control aquatic effects with H_2O_2 and Fe^{2+} reagents in acidic media (Siddique, Farooq, and Price, 2014). Various methods for treatment of industrial sewages have been proposed in recent years, includes aerobic digestion, anaerobic digestion, coagulation, advanced oxidation, chemical and biochemical combinations, adsorption, and membrane filtrations, all of which have different benefits and drawbacks, as well as removal efficiency (Moghadam and Kohbanan, 2018).

Table 2.1 Properties of the RB19 dyes

| Properties | |
|--|--|
| Molecular formula | $C_{22}H_{16}N_2Na_2O_{11}S_3$ |
| Molecular weight | 626.533 g/mol |
| Maximum absorption (λ_{max}) | 594 nm |
| Common name | Remazol Brilliant Blue R |
| Functional group | Anthraquinone |
| Ionization | Reactive |
| Aqueous solubility in water | Soluble |
| Chemical name | Disodium -1-amino-9,10-dioxo-4 [3 - (2sulfonatoxyethylsulfonyl) anilino] anthracene -2-sulfonate |

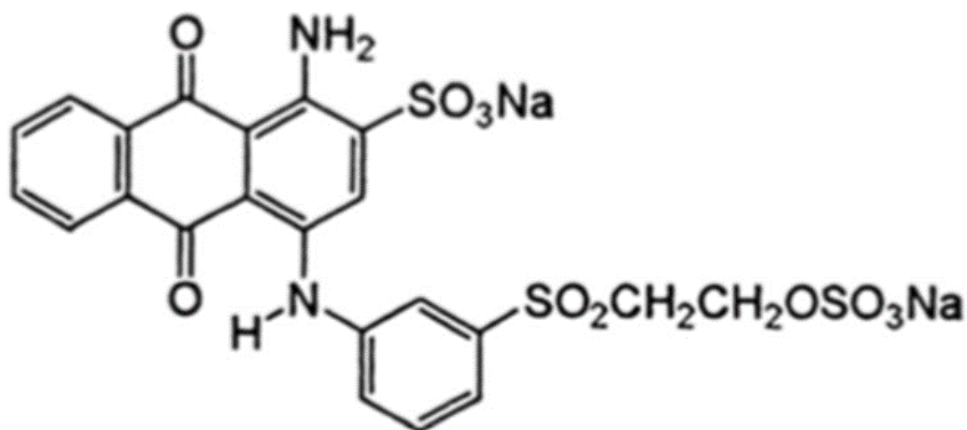


Figure 2.1 Molecular structure of RB19 dye (Haque *et al.*, 2020).

Table 2.2 Classification of dyes based on application methods

| Dye Classes | Main application | General description | Chemical type |
|-------------|---|---|--|
| Reactive | Used for all cellulosic goods (knitted) | Easy application; moderate price, good fastness, anionic compounds, and highly water soluble. | Azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic |

| | | | |
|----------|--|--|--|
| | fabric), wool,silk,and nylon | | |
| Direct | Cellulosic,fibers,rayon, silk,and wool | Simple application,cheap,moderate,colourfastness,anionic compounds, and highly water soluble | azo,phthalocyanine, stilbene,nitro, and,benzodifuranone |
| Disperse | Polyester, acetate,nylon , and acrylic | Require skill in application (by carrier or high temperature), good fastness, and limited solubility in water. | azo,anthraquinone, nitro,and benzodifuranone |
| Acidic | Wool,silk, paperink, nylon,and leather | Easy application, poor fastness, anionic compounds, and highly water soluble. | Azo(including premetallized),anthraquinone,azine, triphenylmethane, xanthene, nitro and nitroso |
| Basic | Acrylic, polyester,wool,and leather | Careful application required to prevent unlevel dyeing and adverse effect in hand feel, cationic, and highly water soluble | Cyanine,azo,azine, hemicyanine, diazahemicyanine, triarylmethane, xanthen, acridine, oxazine, and anthraquinone. |
| Vat | Cotton,wool, and rayon | Difficult to apply, expensive, good fastnessexcept indigo and sulphurised vat species, and insoluble in water. | Anthraquinone (including polycyclic quinones) and indigoids. |
| Sulphur | Usedfor heavy cellulose goodsin darkshades,a nd rayon | Difficulttoapply,cheap, poorfastness, and insoluble in water. | Indeterminate structures |

Source :- https://www.brainkart.com/article/Classification-of-Dyes_1851/

2.3. Dye Removal Methods

Removal is the process by which a chemical substance is broken down to smaller molecules by biotic means (biodegradability) or abiotic means (hydrolysis, photolysis or oxidization).

Adsorption: is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a solid surface is known as adsorption. This procedure forms an adsorbate coating on the adsorbent's surface. Adsorption is a surface phenomenon, whereas absorption affects the entire volume of the substance, but adsorption frequently occurs before absorption.

Biosorption: is the binding of ions from aqueous solutions to functional groups on the surface of biomass in a fast and reversible process. This method is unaffected by cellular metabolism. It is also a key process in environmental protection. The passive adsorption of harmful chemicals by dead, inactive, or biologically generated materials is known as biosorption

Activated carbon Filtration: is a widely utilized method that involves the adsorption of pollutants onto the filter surface. This process removes some organics such as unpleasant taste, aroma and micropollutants, chlorine, and fluorine from drinking water or wastewater.

Chemical Coagulation: is a significant unit procedure in water treatment. It is utilized to remove turbidity. The water treatment process next to coagulations are sedimentation and filtration process.

Electro-Coagulation: (electro meaning to apply an electrical charge to water and coagulation meaning the process of modifying the particle surface charge, allowing suspended particles to form an agglomeration) is a sophisticated and cost-effective water treatment method.

The most common electrochemical water treatment methods are electrochemical oxidation, which is used for mineralization of organic pollutants, water disinfection, and removal of cyanides and sulfides, electrochemical reduction, which is used for metals recovery and transformation of persistent organic compounds to fewer toxic forms.

Ion exchange: is water treatment process in which one or more harmful ionic contaminants are eliminated from water by exchanging them with a less harmful ionic materials. The process of water softening, which aims to lower calcium and magnesium ions by sodium ions is a good example of ion exchanges.

Membrane separation: is a method of separating components in a solution by rejecting undesired elements and allowing the remaining chemicals to flow through the membrane. The membrane duty also includes changing the composition of a solution based on relative penetration rates.

Bio-removal: is the process by which living microorganisms break down organic molecules into smaller one. It is the process of treating wastewater using microorganisms after growing micro-organisms in suitable environments.

Chemical oxidation: the transfer of electrons from an oxidizing reagent to the chemical species being oxidized is known as chemical oxidation. Chemical oxidation is used in water and wastewater engineering to transform dangerous pollutants into harmless or stable products.

Advanced oxidation Processes: in a broad sense, advanced oxidation processes (AOPs) are a set of chemical treatment methods that use hydroxyl radicals ($\bullet\text{OH}$) to oxidize organic (and sometimes inorganic) compounds in water and wastewater.

Photolysis: is a chemical reaction in which chemical bonds between organic and inorganic wastewater contaminants are broken as a result of the passage of light energy to these bonds.

Sonolysis: is the process of utilization of ultrasonic irradiation without the presence of catalysts to produce $\bullet\text{OH}$ in aqueous media. It is one of the successful systems utilized for the removal of organic pollutants in water.

Ozonation: is a wastewater treatment method based on the use of ozone in wastewaters. Ozone is composed of three oxygen atoms (O_3) which is one of the most powerful oxidants.

Fenton Processes: is an effective advanced treatment process. The hydroxyl radical ($\bullet\text{OH}$) is formed when aqueous ferrous ions combine with hydrogen peroxide (H_2O_2), and it has the ability to remove refractory and harmful organic contaminants in wastewater. Among the different removal strategies, advanced oxidation processes (AOPs) have recently gained a lot of attention for their efficacy in dye removal. The formation of extremely reactive oxidants, primarily hydroxyl radical ($\bullet\text{OH}$) is the heart of these reactions and most potent oxidizing agents(Nidheesh *et al.*, 2018).

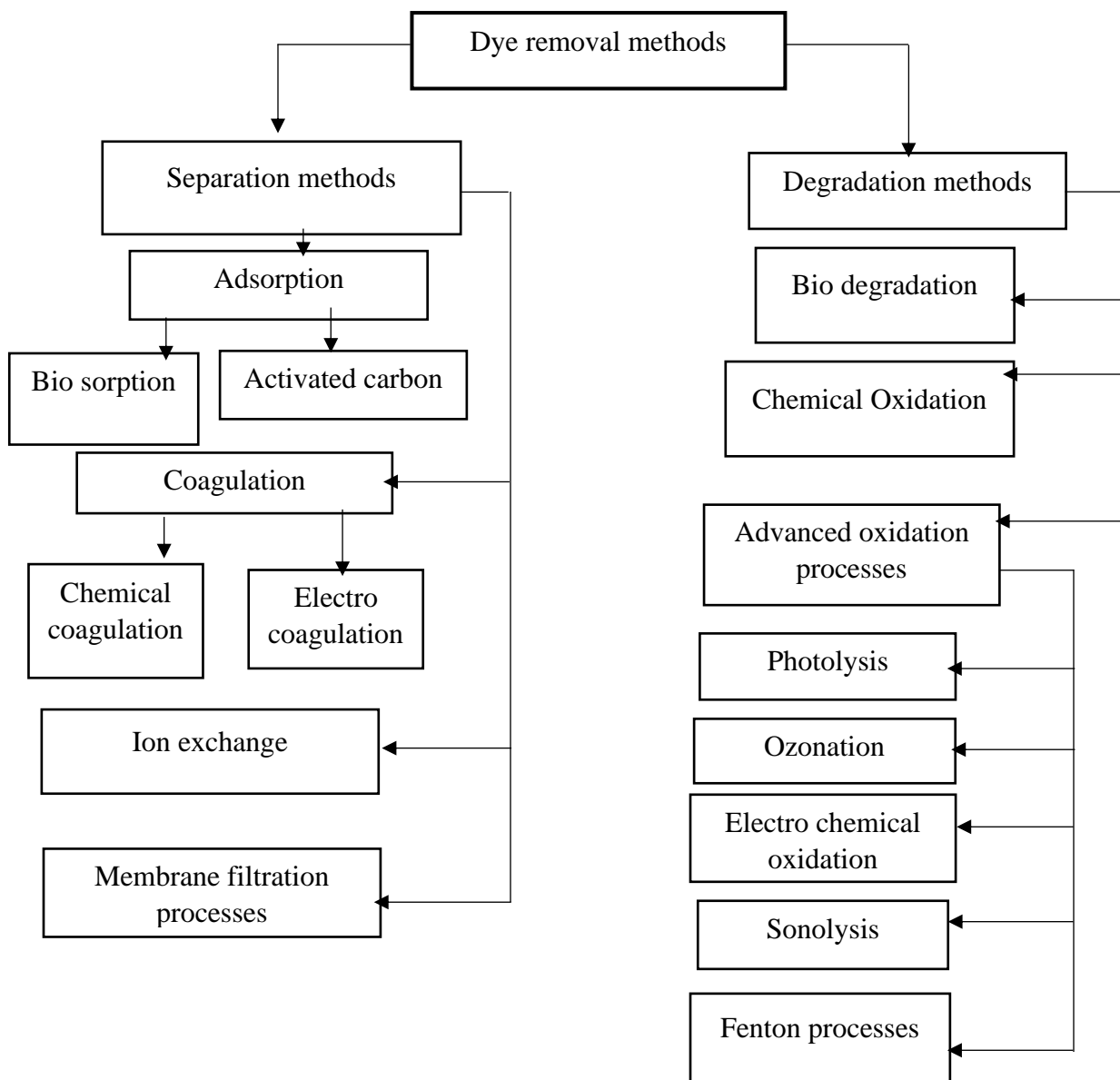


Figure 2.2 Schematic representation of methods used in dye removal from wastewater (Nidheesh *et al.*, 2018).

2.4. Advanced Oxidation Process

Advanced oxidation process (AOP) is a chemical process that is characterized by the use of highly reactive hydroxyl radicals generated in a solution to remove organic pollutants in drinking water and industrial effluents(Shiying *et al.*, 2009). This highly reactive radicals able to attack organic pollutants in wastewaters to decompose them into stable inorganic compounds such as carbon dioxide, and water(Ullah *et al.*, 2019). Advanced oxidation process is an alternative treatment method to the conventional treatment techniques. The

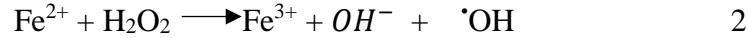
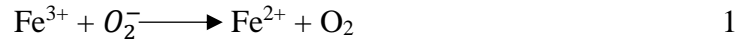
conventional treatment techniques are based on, the physico - chemical, and biological methods involve combination of coagulation, filtration, sedimentation, and disinfection of wastewaters (Racyte and Rimeika ,2015).

The process is applied to remove solids, organic matter, and microbial contaminants from wastewater(Kalantary, Esrafil, and Gholami, 2013). Treatment of wastewaters with a high biochemical oxygen demand (BOD) to chemical oxygen demand (COD) ratio has proven successful using conventional treatment methods(Matavos-aramyan and Moussavi ,2017). The terms biochemical oxygen demand and chemical oxygen demand are used to describe how much organic matter is present in water. BOD involves the use of microorganisms or bacteria in the removal of organic matter. It is a measurement of how much oxygen requires by microorganisms. COD on the other hand, involves the application of chemical oxidants for degrading both organic and inorganic matter in the wastewater. It is a measure of the amount of total oxygen required to oxidize pollutants into carbon dioxide and water. COD measurement can be done within a few hours (about 2 hours) whereas BOD measurements take up to five days. AOPs involve the use of ozone (O_3), hydrogen peroxide (H_2O_2), UV radiation, electron-beam irradiation, ultrasound, and specific catalysts to generate and use free hydroxyl radical ($\cdot OH$) as a strong oxidant to break down compounds that are not easily oxidized by conventional treatment mechanisms(Barrera-salgado *et al.*, 2016). AOP is applied to in wastewater treatment with the aim of reducing chemical contamination and toxicity levels to clean wastewater(Qi *et al.*, 2016). AOPs also are applied in treating wastewater from different industries such as petrochemical and plastics, pulp and paper, textile and dyes, chemical, oil refining, metal and metal plating, food processing, and pharmaceuticals(Barbusiński, 2005).

2.4.1. Hydroxyl Radical and its Reaction

The Hydroxyl radical ($\cdot OH$) is an extraordinarily reactive chemical species. It is a strong and nonspecific oxidant that reacts with organic substances as well as biological molecules. Hydroxyl radicals and superoxide radicals ($O_2\cdot$) are two major reactive species of living organisms that are formed continuously in the reduction process of oxygen in water. In the Haber-Weiss process, hydroxyl radicals are formed in the second step through the reaction

of hydrogen peroxide and iron ions (Fenton reaction). The first step involves the reduction of ferric ion into ferrous ion.



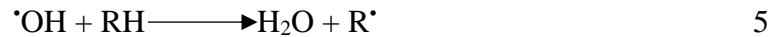
The net reaction is given as



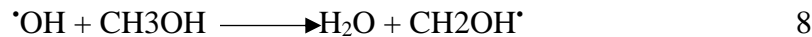
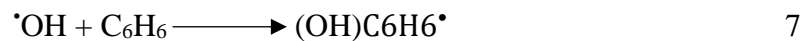
Fenton reaction is the generation of hydroxyl radical catalyzed by ferric ions without the addition of another redox agents. The reaction involves the transfer of an electron from the hydroxyl group to the ferric ion, resulting in the formation of iron (+2) and hydroxyl radical.



Reaction of $\cdot\text{OH}$: the hydroxyl radical reacts with volatile organic compounds to produce water and an alkyl radical eq (5). The alkyl radical then reacts with oxygen to produce peroxy radical in eq (6).



Hydroxyl radical is added to an unsaturated compound to form a free radical product as described in equation (7). It removes hydrogen from organic compound for the formation of a free organic radicals and water (equation 8).



2.4.2. Advantages and Disadvantages of the AOPS

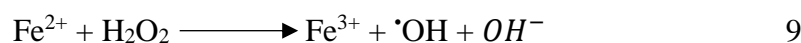
Advantages of AOPs over biological or physical treatments include the generation of the free hydroxyl radical and high degree of flexibility as they can be used individually or combined depending on the problem to be solved (Kothai *et al.*, 2020). Another advantage of the AOPs is its applicability under mild conditions (room temperature and ambient atmospheric pressure). They are also used in cleaning up biologically toxic, refractory or non-biodegradable materials such as volatile organic compounds, petroleum constituents,

aromatic, and pesticides in wastewaters. The process produces little or no sludge waste and it has the ability of handling fluctuating flow rates and composition. It does not require a biological process and does not require long processing time as typically required by the biological treatment methods. AOPs do not introduce any hazardous substance into the water because the complete reduction of the hydroxyl radical is water. However, AOPs have variety of advantages as treatment technique, they also have some drawbacks which include high cost for most photocatalysis materials like TiO_2 is used as photocatalyst which is expensive and also the application of ozone requires ozone gas which is expensive.

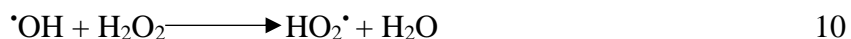
2.4.3. Fenton Oxidation Process

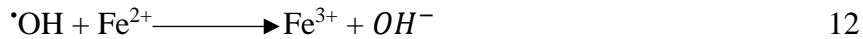
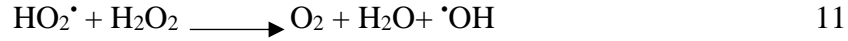
Fenton oxidation process is an advanced oxidation process that removes organic compound from wastewater by hydrogen peroxide and ferrous ion reagents (Network *et al.*, 2016.). It is an iron-catalyzed hydrogen peroxide process that involves the reaction of ferrous ions with hydrogen peroxide in acidic media to generate hydroxyl radicals in solution (Dutta *et al.*, 2015). The Fenton reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is one of the most effective ways for the removal organic pollutants among the many AOPs. It is also affordable and capable of achieving total destruction (mineralization) of pollutants to less damaging by products because it is rapid and requires no energy input (Yazdanbakhsh *et al.*, 2009).

Fentons reagent has been utilized as a chemical treatment method for a wide range of wastewater treatments, either alone or in combination with other treatment methods (Chen *et al.*, 2020). It is a process that has been applied to treatment of toxicity in industrial wastewaters, treatment of petroleum extraction wastewaters, treatment of landfill leachate and treatment of dye wastewaters and oily wastewater treatments (Mokhbi, Korichi, and Akchiche, 2019). It is also used as a post treatment technique for improving the efficiency of wastewater treatments (Buthiyappan *et al.*, 2015). Fenton reaction produce the hydroxyl radical and the ferric ion intermediate as shown in equation (9) (Barbusinski, 2016).

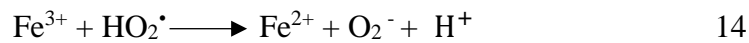


Haber, Weiss and Will sitter (1934) planned the involvement of hydroxyl radicals in the catalytic decomposition of hydrogen peroxide by iron salt, some years after Fenton death in 1929. The proposed reaction proceeds from eq (10) described by Fenton.





Equation (10) is considered as the chain initiation reaction. Reaction of the iron salt with hydrogen peroxide is referred to as Fenton chemistry and the mixture is termed Fenton reagent. Equation (11) and (12) are the radical reactions proposed by Haber and Will siter. Equation (13) describes the process of broken chains. The ferric ion produced in the Fenton initial reaction shown above can react with Hydrogen peroxide and the hydroperoxyl radical, resulting in the production of ferrous ion (Fe^{2+}) as given in reaction (13) and (14).



The generations of HO_2^\bullet and O_2^- uses to oxidize as well as reduce available iron catalysts.

2.4.3.1. Operating Parameters of Fenton Oxidation Process

Removal efficiency of organic pollutants from different wastewater sources are influenced by different doses of oxidants, pH values, reaction time , concentration of pollutants and reaction temperatures but in Fenton oxidation process main factors of the process for treatments of wastewaters are its Fenton reagent and pH values because Fenton oxidation process are effective in ambient conditions (Günes *et al.*, 2021) with short period of time from 5- 30 min(Moghadam and Nori Kohbanan, 2018).

2.4.3.1.1. Effect of pH

PH is a vital parameter that affects the efficiency of wastewater treatments. The oxidizing potential of the hydroxyl radical is pH-dependent and is effective in acidic pH ranges. The removal of pollutants is significantly affected by the operating pH value in a solution. The optimum pH value occurs between the ranges of 2 and 5 in Fenton reaction(Perkowski and Kos ,2002). Reactions with pH less than 2 have been shown the formation of complex iron species and oxonium ion $[\text{H}_3\text{O}_2]^+$ which is attributed to the transition of iron from the hydrated form to a colloidal ferric species(Wang *et al.*, 2014). PH values above 6 could cause iron to precipitate as iron (III) hydroxide ($\text{Fe}(\text{OH})_3$) and also catalytically decompose hydrogen peroxide to oxygen and water without forming hydroxyl radicals. In the Fenton

reaction there is a shift in pH from the initial pH of the wastewater to a lower pH (Shiyong *et al.*, 2009).

2.4.3.1.2. Effect of Iron sulfate Catalyst

Iron is essential for a wide variety of industrial processes for the production of many metallic substances due to its low cost and high strength. It is not only important and useful in its metal form but also important in the form of chemical compounds for industrial uses (Senthilkumar and Muthukumar, 2007). The combination of iron with other elements produces a wide variety of products. These include iron chlorides, sulfates of iron, and oxides of iron. For example, iron chlorides, such as ferrous chloride (FeCl_2), and ferric chloride (FeCl_3), are important chemical compounds used for water and wastewater treatment. Ferrous sulphate (FeSO_4) also serves as a reducing agent in sewage treatment system, and also it act as catalyst in wastewater treatment system (Taylor, Wang, and Xu, 2011). Iron sulphate is the catalysis for the production of hydroxyl radicals from hydrogen peroxide. Optimal dosage range of iron sulphate is varied depend on nature of wastewaters. Mostly ferrous ion concentration range is 10 to 80 mg/l in textile wastewater treatment methods (K. Meerbergen, 2018). Ferrous ion is used to catalyze Fentons reaction to remove hazardous organic compounds by generating hydroxyl radicals (Yonar, 2014).

2.4.3.1.3. Hydrogen peroxide (H_2O_2)

Hydrogen peroxide is a hydride of oxygen. It is a colorless liquid with a pungent odor. It can be produced industrially by the catalytic oxidation of 2-ethylanthraquinone. It can act both as an oxidizing and reducing agent depending on the pH of the solution (Oturán *et al.*, 2008). If pH value is in acidic media, it acts as oxidizing agent and in basic media act as reducing agent. Hydrogen peroxide is a strong oxidizing agent. It reacts with transition metals such as iron or copper which acts as catalyst. Different researchers have been used different doses of hydrogen peroxide to determine the optimum removal of COD in wastewater treatment of textile industry using a Fenton oxidation process from 100 to 400 mg/l (Ajmal, Majeed, and Malik, 2014).

2.4.3.1.3.1. Uses and risks of Hydrogen peroxide

Hydrogen peroxide is used in pulp and paper for bleaching and other applications are for water treatment methods. It is useful in numerous applications but can pose several risks if not properly handled. When in contact with organic compounds or other readily oxidized materials, it forms an explosive mixture. High concentration of hydrogen peroxide is considered as hazardous. The household strength solution of hydrogen peroxide (3 - 9%) can cause irritation to the skin and eyes. Inhalation of concentration higher than 10% can result in severe pulmonary irritation. Ingestion of a dilute solution may lead to vomiting, mild gastrointestinal irritation and gastrointestinal erosion, which is the blockage of blood vessels by air bubbles. If someone consumed H_2O_2 , the stomach releases large amount of gas which can result in internal bleeding and also when in contact with skin, it results temporary bleaching of the skin and hair in addition to irritation(Yazdanbakhsh *et al.*, 2009).

2.4.3.2. Advantages and Disadvantages of Fenton Oxidation Process

2.4.3.2.1. Advantages of Fenton Oxidation Process over other AOPs

Fenton process has a short reaction time. The major materials for the Fenton process are iron salt and hydrogen peroxides which are inexpensive and highly efficient. They are non-toxic and require less energy because the catalyst and the overall process are easily run and controlled when compared to the electrochemical coagulation process. Fenton process can be applied to achieve both oxidation and coagulation. Hydrogen peroxide is a stronger oxidizer compared to the oxygen or ozone used in other operations. The process shows complete mineralization and production of non-toxic compounds in to water and carbon dioxide by-products(Using and Oxidation ,2015).

2.4.3.2.2. Disadvantages of Fenton Oxidation Process

There are some drawbacks of Fenton process which include the requirement of pH lower than 6 unlike ozonation which is effective at a higher pH (>8). Furthermore, Fenton process is producing iron sludge ($Fe(OH)_3$) in higher pH values. In order to overcome this drawback knowledge of the residue characteristics of the treatment process is important so as to design a successful waste management plan that may guarantee the viability of the applied treatment method for the wastewater treatment(Using and Oxidation, 2015).

3. MATERIAL AND METHODS

3.1. Chemicals

All required chemicals of this study were obtained from three institutions. Chemicals like, Hcl with standard grade (supplied by Traders and Scientific Company, India), NaOH with analytical grade of (supplied by Alphax chemical industry, India), Distilled water and 30 % of H₂O₂ were obtained from Bahir Dar institute of technology, school of chemical and food engineering organic chemistry laboratory, and also chemicals like, all BOD reagents, reactive blue 19 dye and total hardness reagents were obtained from Bahir Dar textile Share Company chemical laboratory. However, COD reagents were obtained from Bahir Dar textile Share Company chemical laboratory and Abay Bassine authority institutions. All required chemicals were taken from the two institutions are H₂SO₄, MnSO₄, Sodium thiosulphates, K₂Cr₂O₇, Ferrous ammonium Sulphates, Mercuric sulphates, EDTA, FeSO₄ and Ag₂SO₄, Phosphate buffer, Ammonia buffer solution, calcium chloride, iron indicator, Eriochrome Black T indicator, and ferric chlorides.

3.2. Equipment

Equipment was used in this experimental works are glass beaker, Whatman filter paper, Uv- spectrometer, COD analyzer, ever flow BOD incubator, pH meter, analytical balance, spatula, volumetric flask, conical flask, cuvette, magnetic stirrer, burette, burette stand, oven, dropper, aluminum foil paper, crucible, digital nephelo meter, conductivity meter and petri dish.

3.3. Experimental Method

The performance of advanced Fenton oxidation processes for wastewater treatment was evaluated in lab scale. Most advanced oxidation processes take place in a conical flask. First, all necessary chemicals and equipment were collected, and then all equipment were cleaned. Then, 20mg of reactive blue 19 dye, 1g NaOH, 10g of Na₂CO₃ were measured with analytical balance and mixed with 1000 ml of distilled water in flask. Next, the pH of the solution was adjusted by using 0.1 M of Hcl and NaOH with a pH meter to 2.5, 3.5 and 4.5 pH values separately for each experiment. Then, iron catalyst (Fe²⁺) (15mg, 20mg, and 25mg) was added, and then hydrogen peroxide (75 mg, 100mg and 125mg) is slowly added separately in each experiment. The solution of each sample was mixed with magnetic

stirrer for 18 min, reaction time of Fenton oxidation ranging from 5- 30 min (Moghadam and Nori Kohbanan, 2018), so that a reaction time of 18 min is taken from the interval, a value just higher than mean value. Then, it is left for only 30 min to settle since less sludge exist in Fenton oxidation process (D. Patil and Raut, 2014) . After settling, filtration was done with Whatman filter paper. Finally, filtrate sample was taken for color and COD analyses. All experiments were done at room temperature.

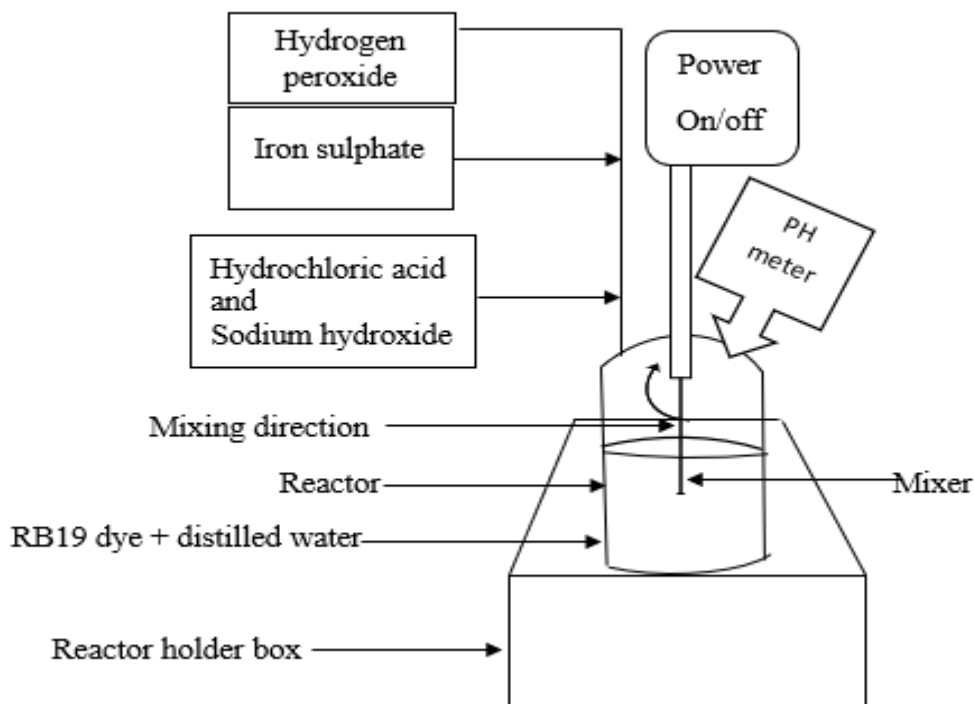


Figure 3.1 Fenton processes experimental Setup

3.3.1. Experimental Solution Preparation

The wastewater samples were prepared from distilled water and reactive blue 19 dye after measuring the reactive blue19 dye powder with analytical balance. The use of high-purity water is for accurate, cost effective and reliable laboratory works. In laboratory, it is important to use high purify water because contaminants in raw water could interfere with ingredients of required chemicals to treat and cause to decrease effectiveness of treatment methods of process. In distilled water there is less impurities other than oxygen and hydrogen. Hence, in this laboratory work distilled water was used to analyze the detail removal efficiency of reactive blue 19 dye with Fenton reagents. Sodium hydroxide is used for pH adjustment of reactive dyes for dyeing purpose in basic media and sodium carbonate

uses for increasing brightness of reactive dyes during dyeing process. Accordingly, in this laboratory work wastewaters samples were prepared from distilled water and reactive blue 19 dye is similar with wastewaters that discharges from only dyeing machine except the type of water, interaction effects of cotton during dyeing and amounts of wastewaters that discharge from this machine.

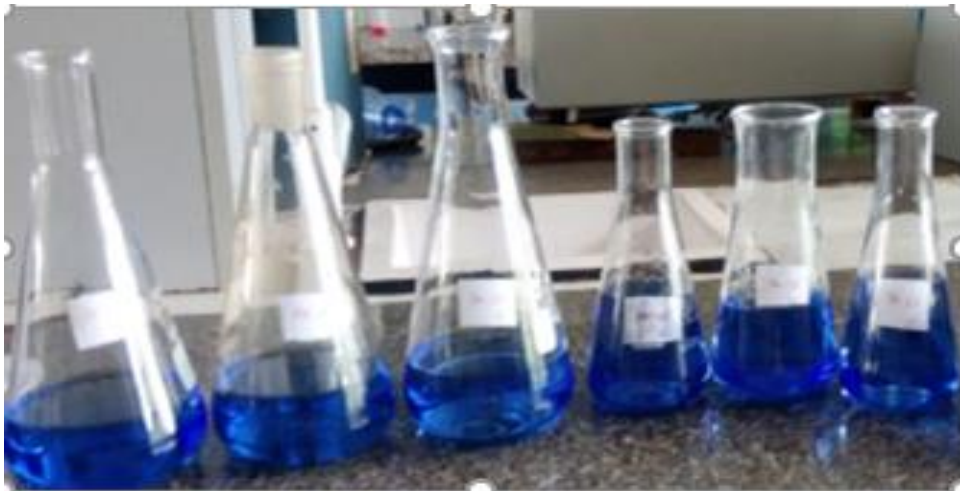


Figure 3.2 Experimental sample preparation

3.3.2. Solution pH adjustment

Adjustment of pH is used to indicate treatments of wastewaters from different sources are difference due to nature of wastewaters and treatment methods. In this study the pHs of wastewater samples were adjusted with 0.1M of HCl and NaOH to 2.5,3.5 And 4.5 values. Since, Fenton oxidation treatment methods only functional in acidic media.

3.3.3. Mixing process

Mixing process is the process of homogenizing the given wastewater sample for uniform distribution of catalyst and oxidant in all reactor. Magnetic stirrers use a stir bar in liquid samples for mixing process. The movement of this stir bar mixes the sample thoroughly with rapid movement and agitation. Iron sulphate and H_2O_2 were mixed in magnetic stirrer for the generation of hydroxyl radicals.

3.3.4. Filtration Process

Filtration process is the process of separating solid and liquids from the solution using filter medium. Solid particles in a liquid were removed by what man filter papers that permits the fluid to pass through but retains the solid particles.

3.4. Characterization of Prepared Wastewater

Characterization of wastewater is vital to assess the characteristics of wastewater. Textile industries play significant role as domestic and national economy in the country. Chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), pH, and total suspended solids (TSS) values indicate that textile factory effluents contains a large amount both of organic and inorganic pollutants(Tesfahun,2019). Thus, wastewater characteristics play an important role in the choice of the treatment methods of wastewater. The following textile wastewater characteristics (pH, turbidity, TDS, TSS, conductivity, total hardness, color, BOD₅ and COD) were analyzed separately as shown below.

3.4.1. pH

PH of wastewater was determined using pH meter which has been initially standardized by using buffer solutions of known value before analysis. Determination of pH is one of the most important and frequently used in water analysis. It used to indicate the wastewater characteristics whether it is acidic or basic nature.

3.4.2. Total Hardness by EDTA Method

Total hardness is the total of calcium and magnesium concentrations, both reported in milligrams per liter (mg/l) as calcium carbonate. EDTA react with calcium and magnesium to form a soluble chelated complex calcium and magnesium ion and develop wine red color with Eriochrome black T. EDTA was added as titrant. 50 ml wastewater was taken in 250ml conical flask and 2ml of buffer solution was added to wastewater and Pinch of Eriochrome Black T indicator was added. Then wastewater was titrated by 0.02 N of EDTA solution. The titration was continued up to end point was observed when wine red was changed to steel blue color.

$$\text{Total Hardness(mg/l)} = \frac{\text{Titration value} \times \text{Eqw of CaCo}_3 \times \text{N of EDTA}}{\text{volume of waste water taken}} \dots \dots \dots (3.1)$$

(Wara, Local, and Region 2014).

Where, titration value is total volume of EDTA taken as titration, Eqw is equivalent weight of CaCO₃, N is normality of EDTA.

3.4.3. Total Dissolved Solids (TDS)

A total dissolved solid (TDS) is a measure of the combined total of organic and inorganic substances contained in a liquid. This includes minerals, salts, and organic matters. These solids are primarily the general indicator of wastewater characteristics. Total dissolved solids (TDS) refer to the total number of mobile charged ions dissolved in a particular volume of water, measured in milligrams per liter (mg/l). The porcelain dish was taken and dried in the oven at 180°c for 1 hr., and the initial weight of the dish (W₁) was measured. 50ml filtered wastewater was taken in the dish. The filtered one was completely dried in water bath. Then it was kept in the oven for 1hr at 180°c. Finally, the dish was kept in desiccator and cooled. The final weight was taken as (W₂) in g.

$$\text{Total Dissolved solids (TDS) mg/l} = \frac{(W_2 - W_1) \times 1000 \times 1000}{V} \dots \dots \dots (3.2)$$

(Meride and Ayenew, 2016).

Where,

W₁, initial weight of the porcelain dish (g)

W₂, Final weight of the porcelain dish(g)

V, Volume of waste water (ml)

3.4.4. Total Suspended Solids (TSS)

Total suspended solids are particles that are larger than 2µm found in water. Total suspended solids in wastewater were determined by gravimetric method. Gooch crucible dried in oven at 105°c for 1 hr., and the initial weight of the crucible was measured (W₁). 50 ml of wastewater was taken, well shacked and filtered through crucible. It was dried in oven for 1hr at 105°c. Then it was kept in a desiccator and cooled. The final weight (W₂) was taken in g.

$$\text{Total suspended solids (TSS) mg/l} = \frac{(W_2 - W_1) \times 1000 \times 1000}{V} \dots \dots (3.3)$$

(Meride and Ayenew, 2016).

Where,

W_1 = Initial weight of the crucible (g)

W_2 = Final weight of the crucible (g)

V = Volume of wastewater (ml)

3.4.5. Conductivity

Conductivity is a measurement of the ability of an aqueous solution to transfer an electrical current. The current is carried by ions, and therefore the conductivity increases with the concentration of ions present in solution. The conductivity of wastewater is determined by Conductivity meter (ELICOCM180). Conductivity was expressed by milli Siemens/meter/ or micro- Siemen/cm.

3.4.6. Turbidity

Turbidity is the measure of relative clarity of a liquid. Clay, silt, extremely small inorganic and organic materials, algae, dissolved colored organic compounds, plankton, and other microscopic organisms all contribute to the turbidity of water. Turbidity was determined with digital nephelo meter (model of 341). Depending on the measuring method, turbidity is commonly expressed in nephelometric turbidity units (NTU) or Jackson turbidity units (JTU).

3.4.7. Biochemical Oxygen Demand (BOD) by Azide modification method

Bio chemical oxygen demand was defined as the amount of oxygen required by microorganisms while stabilizing biologically decomposable organic matter in a waste under aerobic conditions. Since the test was primarily a bioassay process that involved measuring the amount of oxygen consumed by bacteria while stabilizing organic materials in aerobic conditions. It was important to establish standard nutrient supply conditions. Strong wastes were constantly diluted to ensure that demand did not exceed available oxygen due to the limited solubility of O_2 in water. The wastewater was seeded artificially and the temperature was controlled at $27^\circ C$ and the test was conducted for 5 days. Two BOD bottles were filled with dilution water (blank) without creating air bubbles stopper and marked them as initial and final. The wastewater was neutralized to pH 6.5 using NaOH/ H_2SO_4 . Then 5 ml of wastewater was diluted by distilled water and marked them as sample bottles and 2ml of $MnSO_4$ was added, and followed by 2 ml of alkali iodide Azide

reagent. The solution was mixed well and the stopper was removed and 2 ml of concentrated H₂SO₄ was added. 200 ml of the sample was taken from BOD bottles and titrated against 0.025N Sodium thiosulphates solutions (Na₂S₂O₃). The titration was repeated for the samples and blanks after 5 days to obtain the final value (Assefa and Sahu 2016b).

$$\text{BOD (mg/l)} = \frac{[(A-B)-(C-D)] * \text{EQW of Oxygen} * N \text{ of Sodium thio sulphates} * D.F}{\text{Volume taken as titration}} \dots \dots (3.4)$$

Where,

A, Initial volume of sample (ml)

B, Final volume of sample (ml)

C, Initial volume of blank (ml)

D, Final volume of blank (ml).

DF, Dilution factor

$$\text{Dilution factor} = \frac{\text{Total voluem taken as BOD bottle}}{\text{Unit volume}} \dots \dots \dots (3.5)$$

3.4.8. Chemical oxygen Demand (COD) Determination by Open Reflux Method

COD were determined by dichromate oxidation. In the COD digester, potassium dichromate, silver sulfate, and mercury sulfate totally oxidize organic matter in the presence of sulfuric acid solution at reflux temperature to create CO₂ and H₂O. Using ferroin as an indicator, the known amount of potassium dichromate in the sulfuric acid medium and the excess dichromate were titrated with standard ferrous ammonium sulfate. The amount of dichromate used by the sample corresponds to the amount of oxygen needed to oxidize the organic matter. 10 ml of wastewater was taken to reflux and diluted by 5 ml of distilled water. 0.2g of Mercuric sulphates was added to this reflux flask and 5 ml of K₂Cr₂O₇ was added to the solution. 15 ml of H₂SO₄ containing Ag₂SO₄ was slowly added and mixed well. The flask was connected to the condenser and the content was mixed before heated improper mixing. The reflux was kept for 2hr at 150°C. The solution was cooled and washed down the condenser with 50 ml of distilled water. Then excess K₂Cr₂O₇ was titrated by 0.1N of ferrous ammonium sulphates using ferrous indicator. The reflux blank in the same manner used distilled water instead of wastewater.

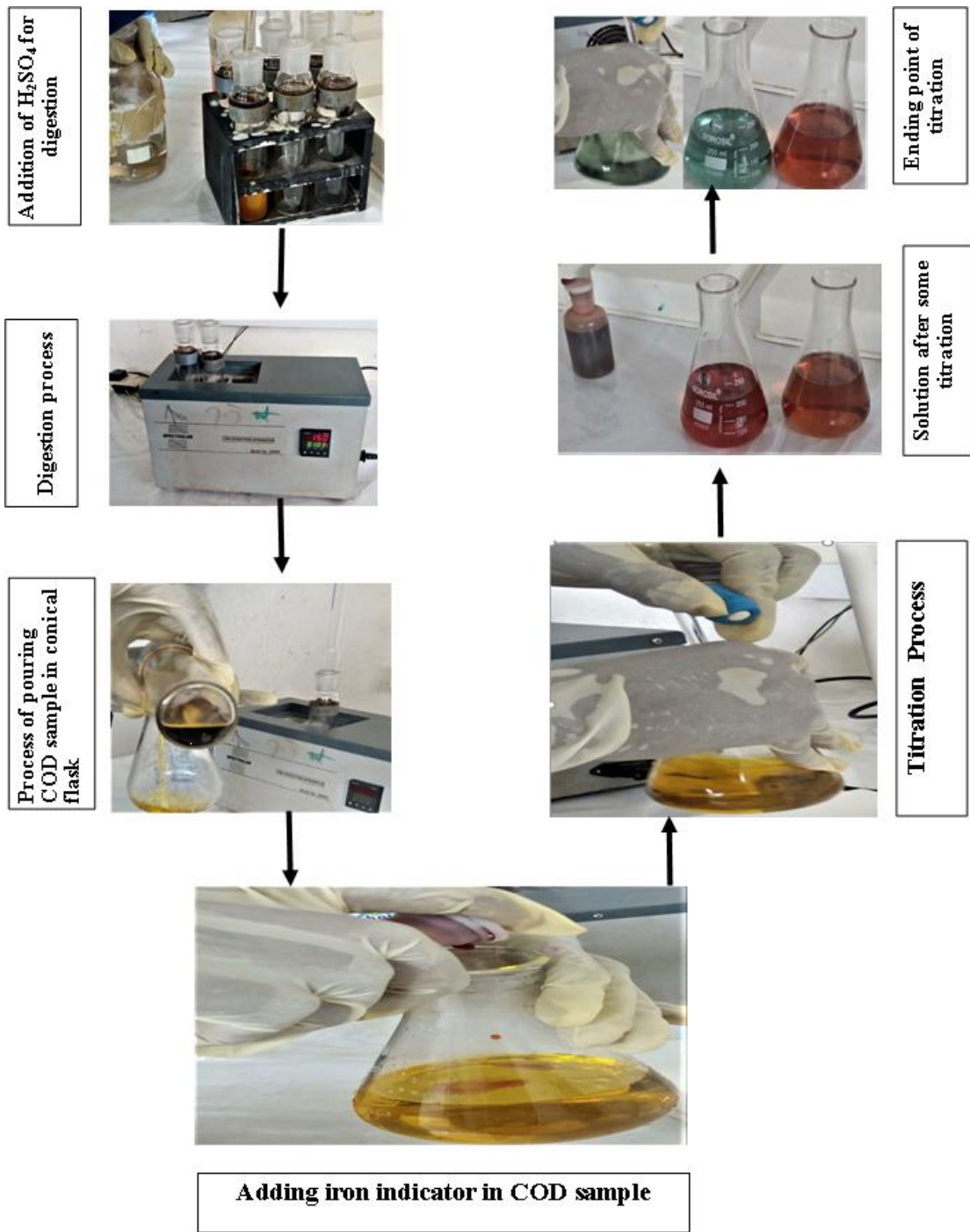


Figure 3.3 Overall COD removal process

$$\text{COD (mg/l)} = \frac{(A-B) * N * \text{Eqw of oxygen}}{V} \dots \dots \dots (3.6)$$

Where: -

COD is chemical oxygen demand in mg/l

A is volume of blank (ml of ferrous ammonium sulphates used for blank) which is volume of ferrous ammonium sulphates used for titration from blue green to reddish-brown color.

B is Volume of sample (ml of ferrous ammonium sulphates) used for wastewater of titration from blue green to reddish-brown color.

N is normality of ammonium sulphate used for both in blank and sample titration.

V is volume of wastewater taken for COD analysis

3.4.9. Determination of Color Absorbance

Spectrophotometry is a method used to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution. Processes of absorbance determinations are first wastewater samples were prepared and put in cuvettes. Next, ON power of Uv-spectrophotometer and waiting for at least 5-10 mins. Next to that, the apparatus was opened and adjusted with blank sample to display as 0 absorbance with a given wavelength and samples were added. Finally, all absorbance values were recorded. The absorbance of RB19 dye solutions were determined with wavelength of 594 nm from Uv- spectrophotometer using cuvettes (Ahmadi *et al.*, 2018).

3.5. Removal Efficiency Determination

The efficiency of Fenton oxidation processes was determined to know the removal efficiency of textile wastewater. Fenton oxidation methods provide the removal of organics pollutants. Various combinations of Fenton reagents (Fe^{2+} , H_2O_2) and pH were provided efficient treatment of textile wastewater depending upon the characteristics of wastewater to be treated.

$$\text{I. Color removal efficiency (\%)} = \left(\frac{A_{bi} - A_{bf}}{A_{bi}} \right) * 100 \dots \dots \dots (3.7)$$

$$\text{II. COD removal efficiency (\%)} = \left(\frac{C_i - C_f}{C_i} \right) * 100 \dots \dots \dots (3.8)$$

Where,

A_{bi} , Initial absorbance of the sample before treatment from Uv -spectrophotometer

Abf, Final absorbance of the sample from Uv -spectrophotometer

Ci, Initial concentration of COD analyzer before treatment in (mg/l).

Cf, Final concentration of COD analyzer after treatment in (mg/l)

3.6. Experimental Design

The Design-Expert software was used to design the number of experiments to be conducted and to evaluate the experimental results. The response surface methodology (RSM) method was used on the basis of different designs including (CCD, Box–Behnken design (BBD), one-factor design, d-optimal design), etc. The optimization technique entails analyzing the response of statistically generated functions and estimating the coefficients using experimental data. In this study, the CCD was applied to evaluate the effects of pH, H₂O₂, and Fe²⁺ on RB19 dye removal process. The CCD also applied using Design Expert software (dx7.0 trial version). To optimize the chosen variables, three factors at three levels of full factorial CCD based on RSM were utilized, yields a total of 20 experiments (14 factorial point and 6 repetition at the center points)(Sadri Moghaddam, Alavi Moghaddam, and Arami ,2010).

Table 3.1 Factors that affect the removal of reactive blue 19 dye

| Factors | Units | Minimum | Maximum |
|---------------------------------------|-------|---------|---------|
| Dose of Fe ²⁺ | mg/l | 15 | 25 |
| Dose of H ₂ O ₂ | mg/l | 75 | 125 |
| PH | | 2.5 | 4.5 |

Table 3.2 total number of experiments from Design expert software

| No of Run | Factor 1 Dose of Fe ²⁺ | Factor 2 Dose of H ₂ O ₂ | Factor 3 pH value | Removal efficiency of COD in % | Removal efficiency of Color in % |
|-----------|--------------------------------------|---|----------------------|--------------------------------|----------------------------------|
| 1 | 25.00 | 100.00 | 3.50 | | |
| 2 | 20.00 | 100.00 | 3.50 | | |
| 3 | 25.00 | 75.00 | 2.50 | | |
| 4 | 20.00 | 100.00 | 3.50 | | |
| 5 | 20.00 | 100.00 | 2.50 | | |
| 6 | 15.00 | 125.00 | 4.50 | | |

| | | | | | |
|----|-------|--------|------|--|--|
| 7 | 25.00 | 125.00 | 2.50 | | |
| 8 | 15.00 | 75.00 | 2.50 | | |
| 9 | 20.00 | 100.00 | 3.50 | | |
| 10 | 15.00 | 75.00 | 4.50 | | |
| 11 | 20.00 | 100.00 | 3.50 | | |
| 12 | 15.00 | 125.00 | 2.50 | | |
| 13 | 20.00 | 125.00 | 3.50 | | |
| 14 | 15.00 | 100.00 | 3.50 | | |
| 15 | 20.00 | 75.00 | 3.50 | | |
| 16 | 25.00 | 125.00 | 4.50 | | |
| 17 | 25.00 | 75.00 | 4.50 | | |
| 18 | 20.00 | 100.00 | 3.50 | | |
| 19 | 20.00 | 100.00 | 4.50 | | |
| 20 | 20.00 | 100.00 | 3.50 | | |

4. RESULTS AND DISCUSSION

4.1. Characterization of Prepared Wastewater Sample

Characterizations of prepared wastewater sample were provided basic information about wastewater characteristics. These are physical, chemical and biological characteristics. The pre-treatment experimental results of prepared wastewater sample are presented in table 4.1.

Table 4.1 Wastewater pre-treatment experimental results

| Parameter | Experimental Results | Real textile WW Results | Reference | Standard Results | Reference |
|---------------------------|----------------------|-------------------------|-------------------------------|------------------|---------------------------------------|
| PH | 11.38 | 12.3 | (Bidu, Rwiza, and Njau ,2021) | 6.5- 8.5 | (Bhatia <i>et al.</i> , 2018) |
| Hardness(mg/l) | 126 | NA | | NA | (Mehari, Gebremedhin, andAyele, 2015) |
| Turbidity (NTU) | 24.3 | 450 | (Bidu, Rwiza, and Njau ,2021) | 12.5-16.6 | (Scholz, 2019) |
| Conductivity(μ S/cm) | 2046.8 | 13460 | (Bidu, Rwiza, and Njau ,2021) | \leq 1200 | (Mostafa, 2020) |
| TDS in mg/l | 8073 | 12000 | (Yaseen and Scholz ,2018) | \leq 2000 | (Rabbi <i>et al.</i> , 2018) |
| TSS in mg/l | 264 | 8000 | (Ghaly <i>et al.</i> , 2017) | \leq 100 | (Sci <i>et al.</i> , 2014) |
| COD in mg/l | 1600 | 30000 | (Yaseen and Scholz ,2018) | \leq 200 | (Rabbi <i>et al.</i> , 2018) |
| BOD ₅ in mg/l | 231.8 | 6000 | (Kehinde and Aziz ,2014) | \leq 40 | (Bakar <i>et al.</i> , 2020) |
| Color absorbance | 0.559 | NA | | | |

NA: not available

The standard results of textile effluent parameters are almost constant in every company. Since, taken as an example the effluent of pH from any company is recommended in range of 6.5 to 8.5. Likewise other parameters are also recommended within given ranges. However, the typical textile wastewater characteristics of the above parameters are varied from time to time and day today due variation of dyes used for dyeing purpose and other chemicals used for other purpose due to the interest of the customers in textile company. The dye effluent is characterized by a strong color, high pH, high total suspended solid, high dissolved solids, high biochemical oxygen demand, high chemical oxygen demand and have different metals ions.

4.2. Analysis of Experimental Results

After conducting experiments, the removal efficiency of both color and COD from textile wastewater were analyzed. The percentage of color and COD removal in each run are shows in table 4.2.

Table 4.2 Experimental results of color and COD removal efficiency

| No of Run | Factor1 Dose of Fe ²⁺ (mg/l) | Factor 2 Dose of H ₂ O ₂ (mg/l) | Factor 3 PH value | Removal efficiency of Color % | Removal efficiency of COD in % |
|-----------|---|--|----------------------|-------------------------------------|--------------------------------------|
| 1 | 25.00 | 100.00 | 3.50 | 73.3 | 81.3 |
| 2 | 20.00 | 100.00 | 3.50 | 87.7 | 92.6 |
| 3 | 25.00 | 75.00 | 2.50 | 60.6 | 73 |
| 4 | 20.00 | 100.00 | 3.50 | 88.8 | 91.8 |
| 5 | 20.00 | 100.00 | 2.50 | 78.4 | 82 |
| 6 | 15.00 | 125.00 | 4.50 | 61 | 73.6 |
| 7 | 25.00 | 125.00 | 2.50 | 55.7 | 65.6 |
| 8 | 15.00 | 75.00 | 2.50 | 65.1 | 66.8 |
| 9 | 20.00 | 100.00 | 3.50 | 87.2 | 93.4 |
| 10 | 15.00 | 75.00 | 4.50 | 69.3 | 80.2 |
| 11 | 20.00 | 100.00 | 3.50 | 88.3 | 90 |
| 12 | 15.00 | 125.00 | 2.50 | 80.6 | 83.6 |

| | | | | | |
|----|-------|--------|------|------|------|
| 13 | 20.00 | 125.00 | 3.50 | 81.8 | 82.8 |
| 14 | 15.00 | 100.00 | 3.50 | 82.2 | 86.5 |
| 15 | 20 | 75.00 | 3.50 | 81.9 | 87.2 |
| 16 | 25.00 | 125.00 | 4.50 | 45.5 | 36.8 |
| 17 | 25.00 | 75.00 | 4.50 | 72.9 | 78 |
| 18 | 20.00 | 100.00 | 3.50 | 89.9 | 94.8 |
| 19 | 20.00 | 100.00 | 4.50 | 71 | 82.6 |
| 20 | 20.00 | 100.00 | 3.50 | 90.8 | 93 |

From table 4.2 it is observed that the highest color and COD removal efficiencies are 90.8 and 94.8% respectively and were obtained at pH of 3.5, dose of Fe^{2+} (20mg/l), and dose of H_2O_2 (100mg/l) because 100mg/l dose of oxidant (hydrogen per oxide) generates high hydroxyl radicals with 20mg/l of ferrous ion catalyst at pH of 3.5 rather than generating ferric oxide sludge. While the minimum removal efficiencies were of color (45.5 %), and COD (36.8%) are obtained at run 16 because less hydroxyl radical is generated at run 16 due to generation of less ferric oxide sludges rather than generating of most hydroxyl radicals. Hence, performance of Fenton oxidation process is mostly depending on generated hydroxyl radicals due to this reason minimum removal efficiency is obtained with less generated hydroxyl values.

4.2.1. Analysis of Variance (ANOVA) for Color Removal Efficiency

The analysis of variance was carried out using a central composite design with three factors (dose of Fe^{2+} , dose of H_2O_2 and pH of solution). Statistical analysis was done to determine the correlation coefficients of the model as a function of the responses. The sequential model sum of squares for color removal efficiency is summarized in (table 4.3).

Table 4.3 The model summary statistics

| Source | Std Dev | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
|-----------|-------------|---------------|--------------------|---------------------|---------------|------------------|
| Linear | 13.16 | 0.1145 | -0.0516 | -0.6392 | 5131.46 | |
| 2FI | 13.22 | 0.2746 | -0.0602 | -4.1153 | 16012.89 | |
| Quadratic | <u>2.33</u> | <u>0.9827</u> | <u>0.9671</u> | <u>0.9090</u> | <u>285.01</u> | <u>Suggested</u> |

| | | | | | | |
|-------|------|--------|--------|---------|----------|---------|
| Cubic | 2.28 | 0.9900 | 0.9684 | -7.6479 | 27071.59 | Aliased |
|-------|------|--------|--------|---------|----------|---------|

From table 4.3 the quadratic model is suggested due to the highest value of the "Predicted R-Squared" and the model is not aliased in cubic model due to negative "Predicted R-Squared" values and also the design summary for color removal efficiency under design software is shown in table 4.4

Table 4.4 Design summary of color removal efficiency

| Design summary of design expert software | |
|--|-------------------|
| Study type | Response surface |
| Initial design | Central composite |
| Design model | Quadratic |
| Run | 20 |
| Block | No block |

4.2.1.1.ANOVA for Response Surface Quadratic Model

To determine whether the Quadratic model is affected by the parameters listed in the design or not, ANOVA is carried out. In the ANOVA, probability values (P-values) were used to analyze significance of individual coefficients, interaction and quadratic model terms. Smaller the p-values are the bigger the consequence of the equivalent coefficient. Analysis of variance for the quadratic model of color removal efficiency is shown in table 4.5.

Table 4.5 Analysis of variance for the quadratic model of color removal efficiency

| ANOVA for Response Surface Quadratic Model | | | | | | |
|--|----------------|----|-------------|---------|----------------|-----------------|
| Source | Sum of Squares | Df | Mean Square | F Value | P-value Prob>F | Remark |
| Model | 3076.25 | 9 | 341.81 | 63.10 | < 0.0001 | Significant |
| A-Dose of Fe ²⁺ | 252.00 | 1 | 252.00 | 46.52 | < 0.0001 | |
| B-Dose of H ₂ O ₂ | 63.50 | 1 | 63.50 | 11.72 | 0.0065 | |
| C-PH | 42.85 | 1 | 42.85 | 7.91 | 0.0184 | |
| AB | 195.03 | 1 | 195.03 | 36.00 | 0.0001 | |
| AC | 38.28 | 1 | 38.28 | 7.07 | 0.0240 | |
| BC | 267.96 | 1 | 267.96 | 49.47 | < 0.0001 | |
| A ² | 196.36 | 1 | 196.36 | 36.25 | 0.0001 | |
| B ² | 52.04 | 1 | 52.04 | 9.61 | 0.0113 | |
| C ² | 363.69 | 1 | 363.69 | 67.14 | < 0.0001 | |
| Residual | 54.17 | 10 | 5.42 | | | |
| Lack of Fit | 44.94 | 5 | 8.99 | 4.87 | 0.0536 | not significant |
| Pure Error | 9.23 | 5 | 1.85 | | | |
| Cor Total | 3130.42 | 19 | | | | |

The Model F-value of 63.10 indicates the model is significant. There is only 0.01% of model F-value could occur due to noise. Values of probability less than 0.05 indicates model terms are significant. In this case, A, B, C, AB, AC, BC, A², B², C² are important model terms. The "Lack of Fit F-value" of 4.87 infers there is a 5.36% chance that a "Lack of Fit - value" could happen due to noise.

4.2.1.2. Model Adequacy Measures

The adequacy of the model was tested by analysis of variance. The model was found to be practically significant by determinations of correlation coefficients of R-Squared, adjusted R-Squared, predicted R-Squared and PRESS as shown in table 4.6.

Table 4.6 Model adequacy measure

| Lists | Value | Lists | Value |
|-----------|--------|----------------|--------|
| Std. Dev. | 2.33 | R-Squared | 0.9827 |
| Mean | 75.60 | Adj R-Squared | 0.9671 |
| C.V. % | 3.08 | Pred R-Squared | 0.9090 |
| PRESS | 285.01 | Adeq Precision | 25.792 |

The R^2 value (0.9827) is closer to 1.0 it indicates that the regression line perfectly fits the data and these results imply that the predicted values were found to be in good agreement with experimental values (R -Squared = 0.9827 and Adj- R -Squared = 0.9671), indicating the achievement of the response surface model. The model goodness of fit was checked by regression coefficient (R^2). In this case, the value of the coefficient ($R^2 = 0.9827$) from table 4.5 indicates that only 1.73% of variance was not explained by the developed regression model. The Predicted R^2 of 0.9090 is in reasonable agreement with the Adjusted R^2 of 0.9671. The adequacy precision measures signal to-noise ratio. A ratio greater than 4 is desirable. In this model, the ratio of 25.792 indicates an acceptable indication.

4.2.1.3. Development of regression model equation

A model equation is a mathematical expression in which the whole model was expressed in a single equation that helps to maximize response. The model equation that correlates the response (color removal efficiency) to the process variables in terms of coded and actual values after excluding the insignificant terms were shown in below equations. Estimated coefficient values for coded factor equation was shown in table 4.7.

Table 4.7 Estimated coefficient values for coded factor equation

| Factor | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|---|----------------------|----|----------------|------------|-------------|------|
| Intercept | 87.75 | 1 | 0.80 | 85.97 | 89.53 | |
| A-Dose of Fe ²⁺ | -5.02 | 1 | 0.74 | -6.66 | -3.38 | 1.00 |
| B-Dose of H ₂ O ₂ | -2.52 | 1 | 0.74 | -4.16 | -0.88 | 1.00 |
| C-PH | -2.07 | 1 | 0.74 | -3.71 | -0.43 | 1.00 |
| AB | -4.94 | 1 | 0.82 | -6.77 | -3.10 | 1.00 |
| AC | 2.19 | 1 | 0.82 | 0.35 | 4.02 | 1.00 |
| BC | -5.79 | 1 | 0.82 | -7.62 | -3.95 | 1.00 |
| A ² | -8.45 | 1 | 1.40 | -11.58 | -5.32 | 1.82 |
| B ² | -4.35 | 1 | 1.40 | -7.48 | -1.22 | 1.82 |
| C ² | -11.50 | 1 | 1.40 | -14.63 | -8.37 | 1.82 |

Final equation in terms of coded factors: for color removal efficiency

$$\eta(\%) = + 87.75 - 5.02 * A - 2.52 * B - 2.07 * C - 4.94 * A * B + 2.19 * A * C - 5.79 * B * C - 8.45 * A^2 - 4.35 * B^2 - 11.50 * C^2 \dots (4.1)$$

Where, η , color removal efficiency

A, dose of Fe²⁺

B, dose of H₂O₂

C, pH of the solution

The equation developed from the regression model in terms of coded factors represents the percentage of color removal efficiency. The efficiency is as response and affected by linear terms such as doses of Fe²⁺(A), dose of H₂O₂(B) and solution pH (C), and pure quadratics terms (A², B², and C²) and interaction quadratic terms (AB, AC, and BC). Based on the coefficients in (equation 4.1), it is clear doses of factors affect the percentage of color removal positively and negatively. Hence, all factors have a negative linear effect on color removal efficiency. Interaction doses of Fe²⁺ and pH (AC) has a positive quadratic effect on the response while the interaction doses of Fe²⁺ and dose of H₂O₂ (AB), and dose of

H₂O₂ and pH (BC), and also all quadratic terms have a negative effect on color removal efficiency.

Final equation in terms of actual factors: for color removal efficiency

$$\begin{aligned} \eta (\%) = & -349.92 + 14.93 * \text{dose of } Fe^{2+} + 2.89 * \text{dose of H}_2\text{O}_2 + 92.83 * \text{pH} \\ & - 0.03 * \text{dose of } Fe^{2+} * \text{dose of H}_2\text{O}_2 + 0.44 * \text{dose of } Fe^{2+} * \text{pH} \\ & - 0.23 * \text{dose of H}_2\text{O}_2 * \text{pH} - 0.34 * (\text{dose of } Fe^{2+})^2 - 6.96E \\ & - 0.03 * \text{dose of H}_2\text{O}_2^2 - 11.50 * \text{pH}^2 \dots \dots \dots (4.2) \end{aligned}$$

Where, η is color removal efficiency

A , dose of Fe²⁺

B, dose of H₂O₂

C, pH of the solution

The regression model equation in terms of actual factors represent the percentage of color removal efficiency. The efficiency is affected by linear terms such as doses of Fe²⁺(A), dose of H₂O₂(B) and solution pH (C), and pure quadratics terms (A², B², and C²) and interaction quadratic terms (AB, AC, and BC). Based on the coefficients in (equation 4.2), it indicates that the dose of factors affects color removal percentages positively and negatively. Thus, all factors have a positive linear effect on color removal efficiency in actual factor equation. Interaction of dose of Fe²⁺ and pH (AC) has a positive quadratic effect on the response while the interaction of dose of Fe²⁺ and dose of H₂O₂ (AB), and dose of H₂O₂ and pH (BC), and also all quadratic terms have a negative effect on color removal efficiency in actual factor equation. Difference between coded factor and actual factor equation is due to the values of the intercept points. The intercept of coded factor equation is obtained from center points and for actual factor intercepts obtained away from center points.

4.2.1.4. Normal Probability plot

The normal probability plot in figure 4.1 indicates the residuals following by the normal % probability distribution, in the case of this experimental data, the points in the plots are in a good fit to the straight line, this shows that the quadratic polynomial model satisfies the analysis of the assumptions of variance (ANOVA) and error distribution is approximately normal. Since, the normality plot indicates distribution of data on a given line, and this

color removal results were distributed with and near the line of probability, so the data is normally distributed.

Design-Expert® Software
Color removal eff in %

Color points by value of
Color removal eff in %:

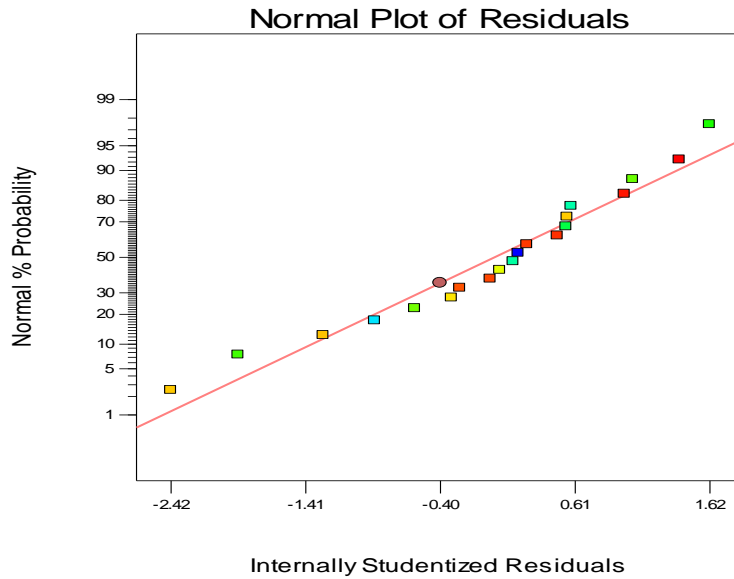


Figure 4.1 Normal probability plot of color removal efficiency

4.2.1.5. Residual versus Predicted Plot

If the model is correct and the assumptions are satisfied, the residuals should be less structured than the predicted response, and they should be unconnected to any other variables. Plotting the residuals against the fitted (predicted) values is a straightforward check. The assumption of constant variance is tested by plotting the residuals vs the expected response values in figure 4.2. The plot displays random scatter, indicates that no changes are required to reduce personal error.

Design-Expert® Software
Color removal eff in %

Color points by value of
Color removal eff in %:

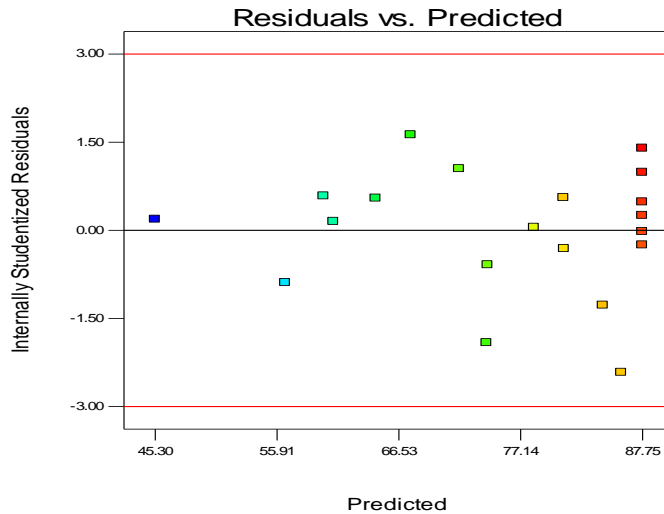


Figure 4.2 Residuals versus predicted values of color removal efficiency

4.2.2. Effects of Operating Variables on Color Removal Efficiency

Color removal efficiency was affected by different operating parameters. These parameters affecting the removal efficiencies of colors (solution pH, doses of catalyst, and doses of hydrogen peroxide) were discussed in the following sections.

4.2.2.1. Catalyst Doses on Color Removal Efficiency

The effects of Fe^{2+} catalyst doses on color removal efficiency from textile wastewater was shown in (figure 4.3). Iron catalyst acts as a catalyst to reduce hydrogen peroxide to hydroxyl radicals which oxidize organic molecules. Iron sulphate catalyst doses are crucial in any Fenton processes (Wali, 2015). As shown in figure 4.3, the removal efficiency of color increases with doses of ferrous ions up to optimum values and decreases when doses of ferrous ion increase above optimum values. Because maximum color removal efficiency is obtained with ferrous ion concentration of 20mg/l and this shows that there is high hydroxyl radical generation at 20mg/l of Fe^{2+} and also minimum color removal efficiency could be obtained at 15 and 25 mg/l of ferrous ion concentrations. Therefore, the obtained results show maximum at dose of 20mg/l of Fe^{2+} and this indicates that 20mg/l is optimum dose from a given range. Hence, high amount of hydroxyl radical value yields high results in color removal efficiency because color removal efficiency increases with the increase of hydroxyl radical (Moghadam and Kohbanan, 2018). Generation of hydroxyl

radicals depends on the concentration of ferrous ions and removal efficiency of color is low at lower ferrous ions concentration due low amount of hydroxyl radical at lower concentration of ferrous ions. Consequently, Fenton removal efficiency depends on amounts of ferrous ion (Zineb, 2018).

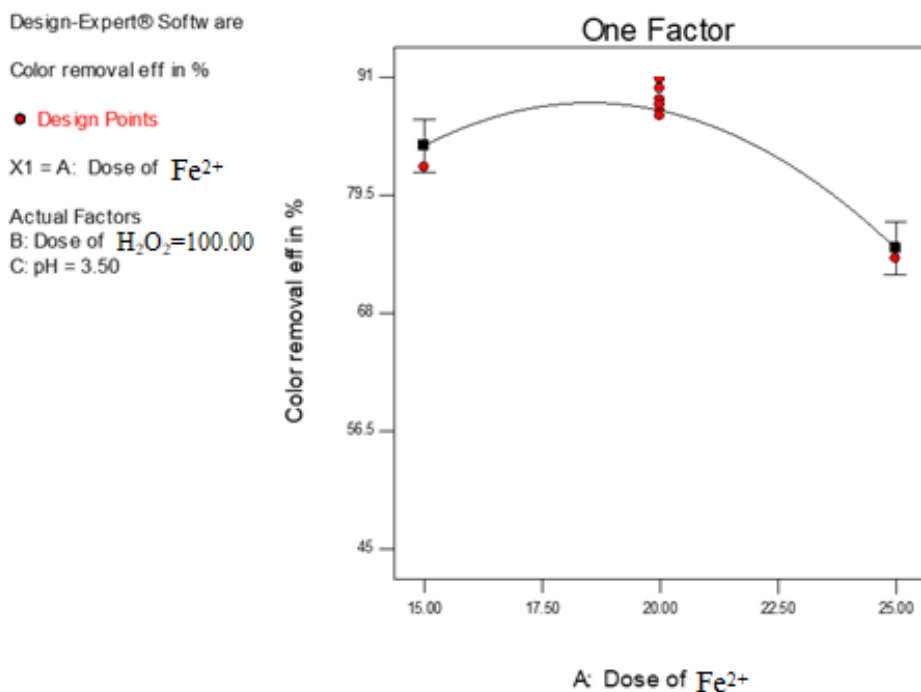


Figure 4.3 Effects of Fe²⁺ doses on color removal efficiency

4.2.2.2. Hydrogen peroxide Doses on Color Removal Efficiency

The concentration of the oxidant plays a vital role in the overall removal efficiency of dyes. The hydroxyl radicals depend on the concentration of H₂O₂ in the Fenton oxidation process (Jia *et al.*, 2014). It is observed that the removal efficiency of reactive blue 19 dye increases with an increase in the concentration of H₂O₂ up to its critical point while the concentration of H₂O₂ further increases the removal efficiency was decrease. Because the removal efficiency increased with the increasing doses of hydrogen peroxide until center point values of both pH (3.5) and catalyst (20mg/l) due the fact that further increase in dose of hydrogen per oxide results in decompose of H₂O₂ in to water and oxygen (Moghadam and Kohbanan, 2018). In this study, the removal efficiency was low at low dose of oxidant and increase as the doses increases, because as the dose of H₂O₂ up to 100mg/l and •OH formed

increase, the removal efficiency increases. Effects of hydrogen peroxide on color removal efficiency is shown in figure 4.4.

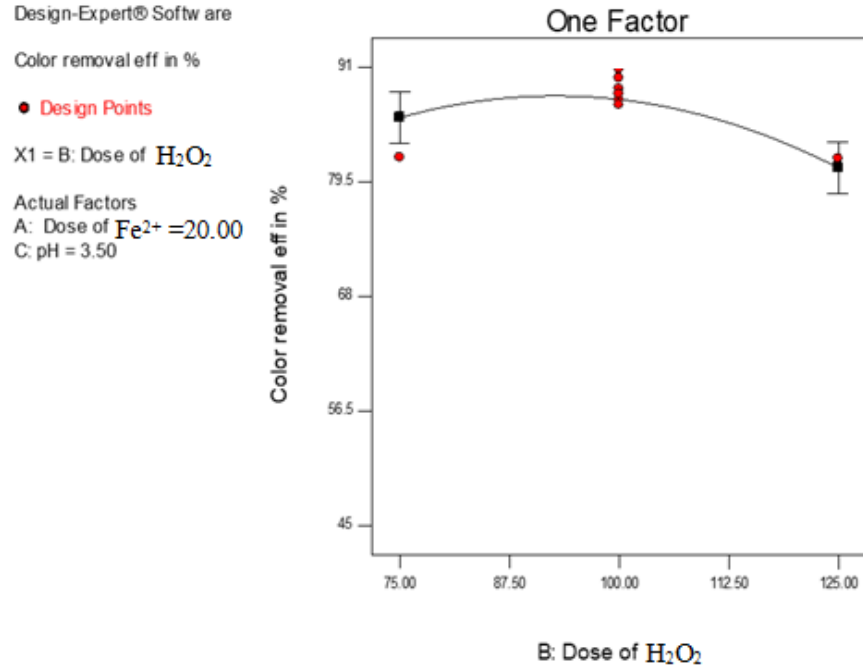


Figure 4.4 Effects of hydrogen peroxide doses on color removal efficiency

4.2.2.3. Solution pH on Color Removal Efficiency

The effect of pH, as shown in figure 4.5 below, color removal process shows increasing efficiency with increasing pH until center point and further increasing results in lower removal efficiency since more hydroxyl radicals are generated at pH of 3.5. This is because color removal is most efficient at pH of 3.5 due to high generation of hydroxyl radicals and less generation of (H₃O₂)⁺ and Fe(OH)₃. Hence, the removal efficiency of color increases with pH value up to 3.5 and the effect of pH is not significantly effective beyond 3.5 because the removal efficiency of color by Fenton oxidation process is effective at pH of 3.5 due to high generation of hydroxyl radical and less generation of (H₃O₂)²⁺ and Fe (OH)₃. The probability value of 0.0184 indicates that the model with dose of pH is significant. Which means 1.84% of probability value could not explain color removal efficiency by quadratic model due error and 98.16% of the color removal efficiency can be explained by the pH effects.

Design-Expert® Software

Color removal eff in %

● Design Points

X1 = C: pH

Actual Factors

A: Dose of Fe^{2+} = 20.00

B: Dose of H_2O_2 = 100.00

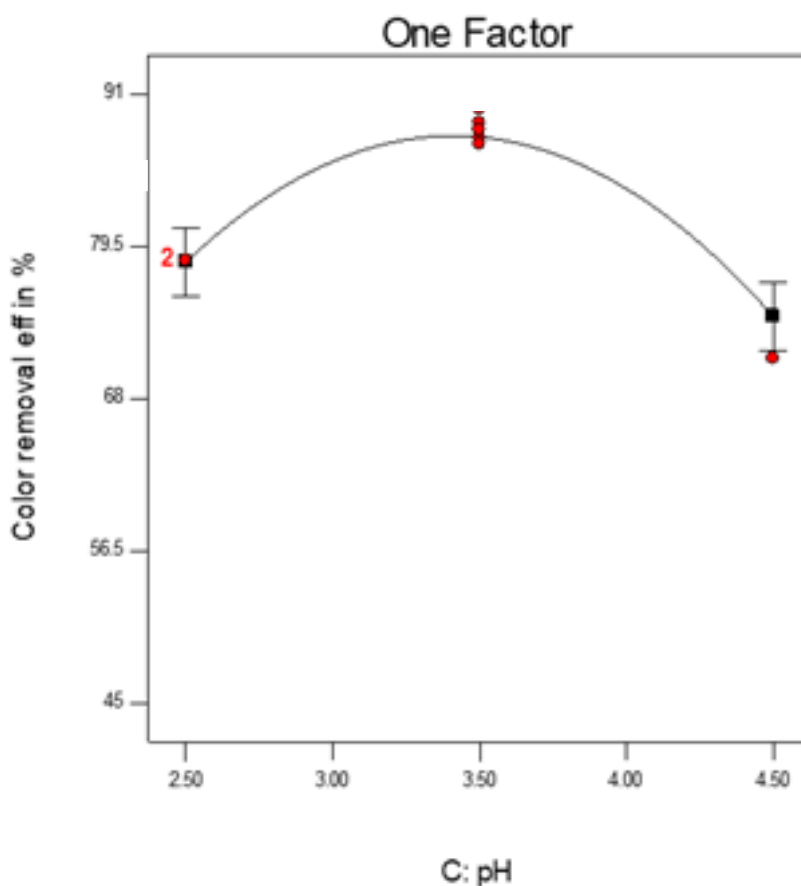


Figure 4.5 Effects of solution pH on color removal efficiency

4.2.3. Interaction Effects of Operating Variables on Color Removal Efficiency

Color removal efficiency can be affected by experimental variables owing to the nature of wastewaters can be treated with Fenton oxidation processes. In this study, after conducting experiments, were analyzed the interaction effect of operating parameters (pH, ferrous ion, and hydrogen per oxide) on color removal efficiency with three-dimensional response surfaces(Ahmadi *et al.*, 2018). Way of showing the interaction effects of this parameter on the color removal efficiency of reactive blue 19 dye is to understand the maximum and minimum removal efficiencies by 3D plots(Ahmadi *et al.*, 2018). The three-dimensional response surfaces effects were plotted in figures (4.6-4.8) as a function of the interactions of any two of the variables by holding the other value of the variable at the center point.

4.2.3.1. Ferrous ion catalyst and Hydrogen Peroxide Dosage

As shown in figure 4.6, the maximum and minimum color removal percentage values are obtained at 20 and 16 experimental runs respectively. Hence, maximum removal efficiency of color obtained is 90.8 % at a dose of 20mg/l of Fe^{2+} and 100 mg/l of H_2O_2 , and also its minimum removal efficiency value obtained is 45.5% at dosage of 25mg/l and 125 mg/l of Fe^{2+} and H_2O_2 respectively. Removal efficiency of color increases with increasing both the dose of catalyst and hydrogen peroxide up to its to center point and decrease when we go beyond center point. Because maximum hydroxyl radical generation is occurred at dose of 20mg/l for the Fe^{2+} and 100mg/l for H_2O_2 . As shown in table 4.5, the analysis of variance indicates that the two independent variables have significant interaction effect on the response ($p < 0.05$). The combined probability value of ferrous ion and hydrogen peroxide is 0.0001. Which means the interaction effect is 0.01% that could not explain color removal efficiency by quadratic model due to personal error and 99.99% of the response can be explained by the interaction effects.

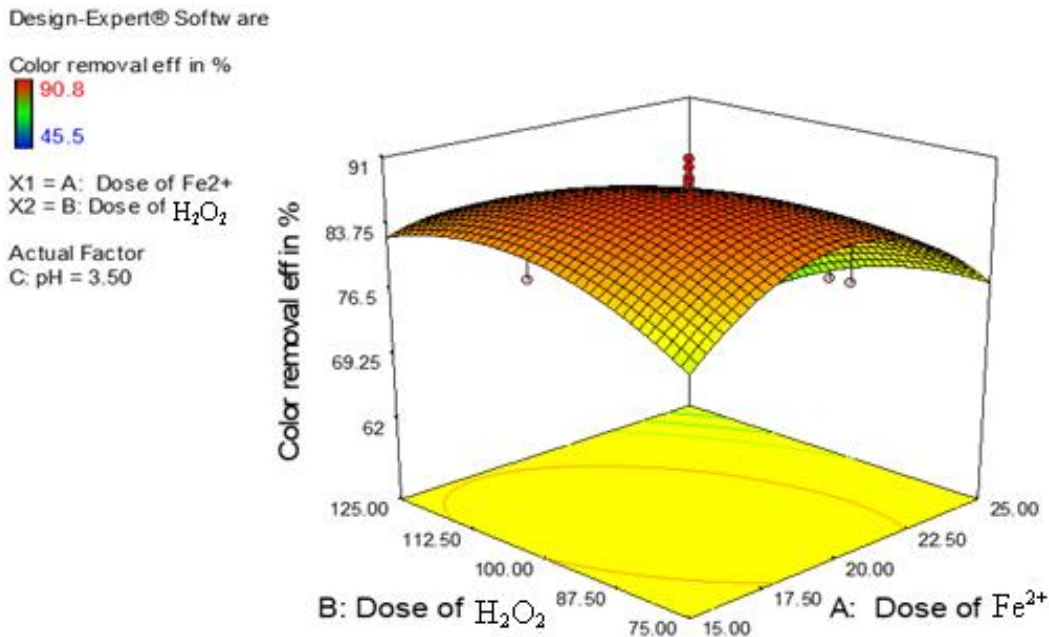


Figure 4.6 Interaction effects of Fe^{2+} and H_2O_2 dosage on color removal efficiency.

4.2.3.2. Catalyst Dosage and pH of Solution

According to the results obtained the doses of catalyst for the removal of color mostly depends on pH values of the solution. Figure 4.7 shows that the highest removal percentage of color is at the dose of 20mg/l of Fe^{2+} with pH of 3.5, and the lowest color removal percentage was obtained at 25mg/l of Fe^{2+} with pH value of 4.5. When the dosage of ferrous catalyst is raised, the removal efficiency of color also raised with pH value up to dosage of 20mg/l of Fe^{2+} but the further it rises the less color removal efficiency is obtained. The obtained results indicated that the removal efficiency of color is high at the center point and low at dosage of 15 and 25 mg/l with pH value of 2.5, 3.5 and 4.5. Because, if the pH value is 2.5, the removal efficiency is low due to generation of less oxonium ion (H_3O_2^+) or complex iron precipitates rather than more hydroxyl generation because the pH value is almost close to 2, since oxonium ion (H_3O_2^+) is generated below pH values of 2 in Fenton oxidation process and if pH value is 4.5 also removal efficiency is low due to generation of less iron oxide rather than generation of most hydroxyl radicals ($\text{FeOH})_3$ (Moghadam and Kohbanan, 2018). And also, the combined effects of catalyst and pH of solution on color removal is indicated by probability value. The probability value of catalyst and pH interaction is 0.024 which is below 0.05. This indicates that 2.4% of the color removal efficiency is not explained by the quadratic model.

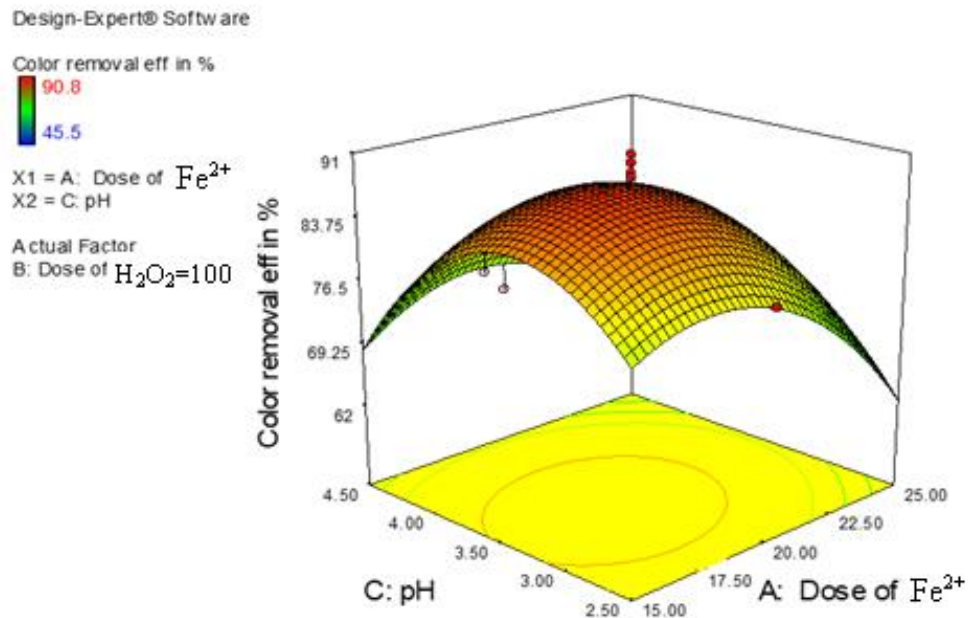


Figure 4.7 Interaction effects of pH and Fe^{2+} on color removal efficiency

4.2.3.3. Hydrogen Peroxide Doses and pH of solution

As shown in the figure 4.8, high color removal percentage was at the dosage of 100mg/l of hydrogen peroxide and the least removal efficiency is at the dose of 125mg/l of hydrogen peroxide. Therefore, the result of color removal efficiency decreases with decreasing dose of H_2O_2 and increases with increasing dosage of hydrogen peroxide owing to the generation of high hydroxyl radical to remove color with accompanied effects of pH values. Subsequently, oxidizing potential of hydrogen peroxide is high at center point, and below and above it oxidizing potential of hydrogen peroxide is low because of pH values, accordingly, its color removal percentage is low. Due to this reason the graph shows that the color removal percentage value is high with center point dose and minimum below and above this value. The interaction effects of H_2O_2 and pH on color removal efficiency is indicated by 0.0001 probability values which shows the significance of a model and hence 99.99% of the response was explained.

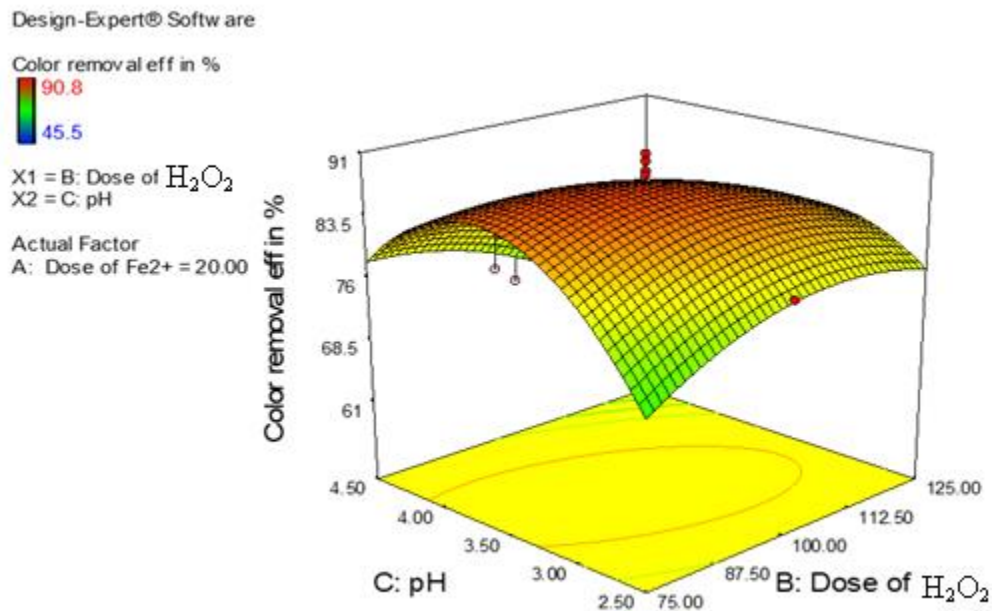


Figure 4.8 Interaction effects of pH and dose of H_2O_2 on color removal efficiency

4.2.4. Optimization of Operating Variables for Color removal Efficiency

Optimization of the removal efficiency can be understood as finding the values for those controllable independent variables that give good values of the response. In this study numerical optimization was done by considering each value of the efficiency and the aim is to maximize the removal of color in a given range of the process variables. Optimization with design expert software specifically numerical optimization gives different alternative solution in order to optimize the removal efficiency. Design expert software also has an important application in the design, development, and formulation of new products, as well as improvement of existing product designs. The optimization conditions of constraints for color removal efficiency of textile wastewater were summarized in figure 4.9.

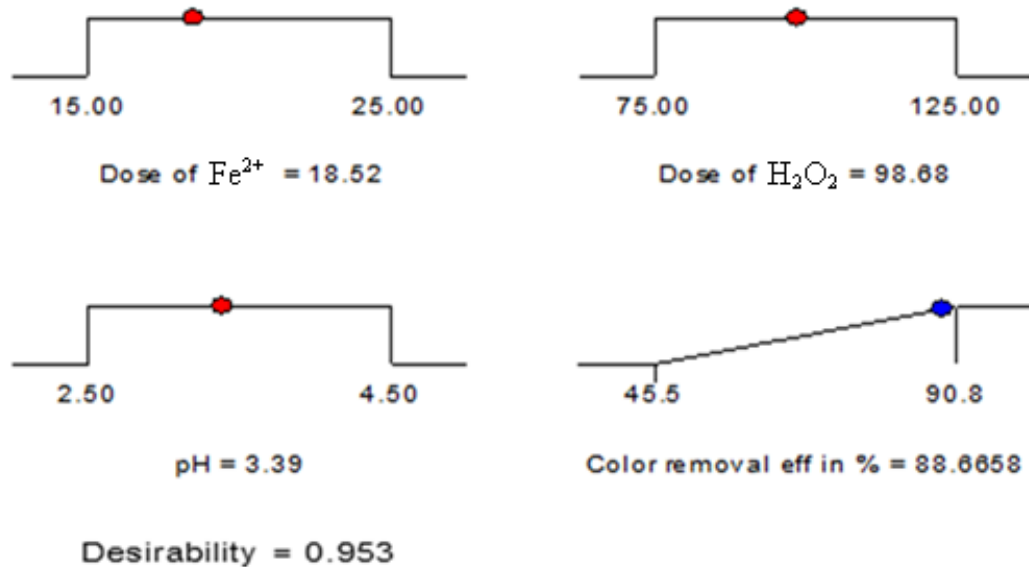


Figure 4.9 Optimization constraints and its color removal efficiency

4.3. Analysis of Variance (ANOVA) for COD Removal Efficiency

Analysis of variance using a central composite design with three factors (dose of catalyst, pH, and dose of hydrogen per oxide) was used to determine COD removal efficiency and investigate its model statistical analysis (Mahtab, Islam, and Farooqi, 2020). The sequential model sum of squares for COD removal efficiency was concise in (table 4.8)

Table 4.8 The model summary statistics

| Source | Std Dev | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
|------------------|-------------|---------------|--------------------|---------------------|---------------|------------------|
| Linear | 13.43 | 0.1566 | -0.0015 | -0.6553 | 5665.50 | |
| 2FI | 12.26 | 0.4294 | 0.1660 | -3.1972 | 14365.32 | |
| <u>Quadratic</u> | <u>2.81</u> | <u>0.9770</u> | <u>0.9562</u> | <u>0.7904</u> | <u>717.29</u> | <u>Suggested</u> |
| Cubic | 1.78 | 0.9944 | 0.9824 | -1.1495 | 7356.84 | Aliased |

The quadratic model is suggested from the other models as shown in above table. This is due to the highest value of the "Adjusted R-Squared" and the "Predicted R-Squared" and also the model is not aliased in cubic due to negative Predicted R-Squared values as seen in table 4.8.

4.3.1. Response Surface Quadratic Model

ANOVA used to analyze the COD removal efficiency by quadratic model with the effects of parameters listed as a factor (pH, Fe²⁺ and H₂O₂). Probability values in statistics indicates that the consequence of each coefficient, which also shown the interaction effects of each parameter on COD removals. If the p-values are less, higher the significance of the corresponding coefficient (M.Sah, A.Kumar *et al.*, 2010). Analysis of variance results from CCD software is shown in table 4.9.

Table 4.9 Analysis of variance from quadratic model for COD removal efficiency

| ANOVA for Response Surface Quadratic Mode | | | | | | |
|---|----------------|----|-------------|---------|------------------|-------------|
| Source | Sum of Squares | Df | Mean Square | F Value | P-value Prob > F | Remark |
| Model | 3343.77 | 9 | 371.53 | 47.12 | <0.0001 | significant |
| A-Dose of Fe ²⁺ | 313.60 | 1 | 313.60 | 39.77 | < 0.0001 | |
| B-Dose of H ₂ O ₂ | 183.18 | 1 | 183.18 | 23.23 | 0.0007 | |
| C-PH | 39.20 | 1 | 39.20 | 4.97 | 0.0499 | |
| AB | 432.18 | 1 | 432.18 | 54.81 | < 0.0001 | |

| | | | | | | |
|----------------|---------|----|--------|-------|----------|-----------------|
| AC | 92.48 | 1 | 92.48 | 11.73 | 0.0065 | |
| BC | 408.98 | 1 | 408.98 | 51.87 | < 0.0001 | |
| A ² | 148.75 | 1 | 148.75 | 18.87 | 0.0015 | |
| B ² | 107.58 | 1 | 107.58 | 13.64 | 0.0042 | |
| C ² | 220.51 | 1 | 220.51 | 27.97 | 0.0004 | |
| Residual | 78.85 | 10 | 7.88 | | | |
| Lack of Fit | 65.81 | 5 | 13.16 | 5.05 | 0.0501 | not significant |
| Pure Error | 13.04 | 5 | 2.61 | | | |
| Cor Total | 3422.61 | 19 | | | | |

The F-value of 47.12 indicates the model is substantial. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of probability less than 0.05 indicates model terms are significant. In this occasion, A, B, C, AB, AC, BC, A², B², C² are noteworthy model terms. Hence, all model terms are less probability values which indicates all model terms explained the response with less chance of variances in COD removal efficiency. Values greater than 0.1 indicates the model terms are not momentous. If there are many irrelevant model terms, model reduction may improve the model, and also model significant indicates by lack of fit values. Since, lack of fit indicates missing data in quadratic model during analysis, so non significant lack of fit value as shown in above table indicates no missing data during the analysis and it indicates the model is good. Table 4.10 shows model accuracy measured value.

Table 4.10 Model adequacy measure

| List | Value | List | Value |
|-----------|--------|----------------|--------|
| Std. Dev. | 2.81 | R-Squared | 0.9770 |
| Mean | 80.78 | Adj R-Squared | 0.9562 |
| C.V. % | 3.48 | Pred R-Squared | 0.7904 |
| PRESS | 717.29 | Adeq Precision | 26.353 |

4.3.2. Development of Regression Model Equation

The model equation was expressed in a single equation that helps to optimize the response. The model equation that correlates the response (COD removal efficiency) to the process

variables in terms of actual values after excluding the in significant terms was given below. The estimated coefficients value for coded factor equation is written in table 4.11. The predicted model equation in terms of the coded factors is given in (equation 4.3).

Table 4.11 Estimated coefficient values for coded factor equation

| Coefficient Factor | Standard Estimate | df | Error | 95% CI | | VIF |
|---|----------------------|----|-------|--------|-------------|------|
| | | | | Low | High | |
| Intercept | 92.06 | 1 | 0.97 | 89.91 | 94.21 | |
| A-Dose of Fe ²⁺ | -5.60 | 1 | 0.89 | -7.58 | -3.62 | 1.00 |
| B-Dose of H ₂ O ₂ | -4.28 | 1 | 0.89 | -6.26 | -2.30 | 1.00 |
| C-PH | -1.98 | 1 | 0.89 | -3.96 | -1.520E-003 | 1.00 |
| AB | -7.35 | 1 | 0.99 | -9.56 | -5.14 | 1.00 |
| AC | -3.40 | 1 | 0.99 | -5.61 | -1.19 | 1.00 |
| BC | -7.15 | 1 | 0.99 | -9.36 | -4.94 | 1.00 |
| A ² | -7.35 | 1 | 1.69 | -11.13 | -3.58 | 1.82 |
| B ² | -6.25 | 1 | 1.69 | -10.03 | -2.48 | 1.82 |
| C ² | -8.95 | 1 | 1.69 | -12.73 | -5.18 | 1.82 |

Estimated coefficients are coefficients that estimates of the unknown parameters and describes the relationship between a predictor variable and the responses. The values of estimated coefficients for coded factor equation are describes by confidence intervals. A positive coefficient indicates that as the value of the independent variable increases, the mean of the dependent variable also tends to increase. The negative coefficient suggests that as the independent variable increases, the dependent variable tends to decrease.

Final Equation in terms of Coded Factor for COD Removal Efficiency

$$\text{COD removal eff (\%)} = 92.06 - 5.60 * A - 4.28 * B - 1.98 * C - 7.35 * A * B - 3.40 * A * C - 7.15 * B * C - 7.35 * A^2 - 6.25 * B^2 - 8.95 * C^2 \dots \dots (4.3)$$

Where,

- A, dose of Fe²⁺
- B, dose of H₂O₂
- C, pH of the solution

The above equation indicates that the COD removal efficiency of coded factors. Removal efficiency of COD was affected by operating variables such as dose of Fe^{2+} (A), dose of H_2O_2 (B) and solution pH (C), and pure quadratic terms (A^2 , B^2 , and C^2) and interaction quadratic factors (AB, AC, and BC). Based on the coefficients in (equation 4.3) the dose of factors that affect the percentage of COD removal positively and negatively. However, in this analysis all factors have negative linear, quadratic and interaction effects on COD removal efficiency. Thus, linear terms (A, B and C), interaction of doses of Fe^{2+} and pH (AC), interaction of doses of Fe^{2+} and dose of H_2O_2 (AB), and doses of H_2O_2 and pH (BC), and also all quadratic terms (A^2 , B^2 and C^2) have a negative effect on COD removal efficiency.

Final Equation in terms of Actual factors for COD Removal Efficiency

$$\begin{aligned}
 \text{COD removal eff (\%)} = & -454.23 + 18.91 * \text{dose of } Fe^{2+} + 4.01 * \\
 & \text{dose of } H_2O_2 + 102.90 * \text{pH} - 0.06 * \text{dose of } Fe^{2+} * \\
 & \text{dose of } H_2O_2 - 0.68 * \text{dose of } Fe^{2+} * \text{pH} - 0.29 * \\
 & \text{dose of } H_2O_2 * \text{pH} - 0.29 * \text{dose of } Fe^{2+2} - 0.01 * \\
 & \text{dose of } H_2O_2^2 - 8.95 * pH^2 \dots \dots \dots (4.4)
 \end{aligned}$$

- Where, A, dose of Fe^{2+}
- B, dose of H_2O_2
- C, pH of the solution

The equation established from the regression model represents the percentage of COD removal efficiency. The efficiency was affected by linear terms such as doses of Fe^{2+} , dose of H_2O_2 and solution pH, and pure quadratic terms (doses of Fe^{2+2} , doses of $H_2O_2^2$, and pH^2) and interaction quadratic terms (doses of $Fe^{2+} * doses of H_2O_2$, doses of $Fe^{2+} * pH$, and doses of $H_2O_2 * pH$). Based on the coefficients in (equation 4.4), it indicates dose of factors affect the percentage of COD removal positively and negatively. Consequently, all factors have a positive linear effect on COD removal efficiency in actual factor equation. All interaction and quadratic terms have a negative effect on COD removal efficiency in actual factor equation.

4.3.3. Normal Probability Plot

Figure 4.10 as shown below is the normal probability plot that indicates the residuals succeeding by the normal probability distribution, and in this experimental result analysis the points as show in the figure are follows stright line, Hence, it displays in a good fit to the model and this presents the quadratic polynomial models satisfy the analysis of the expectations of variance (ANOVA). Since, the error distribution is approximately normal.

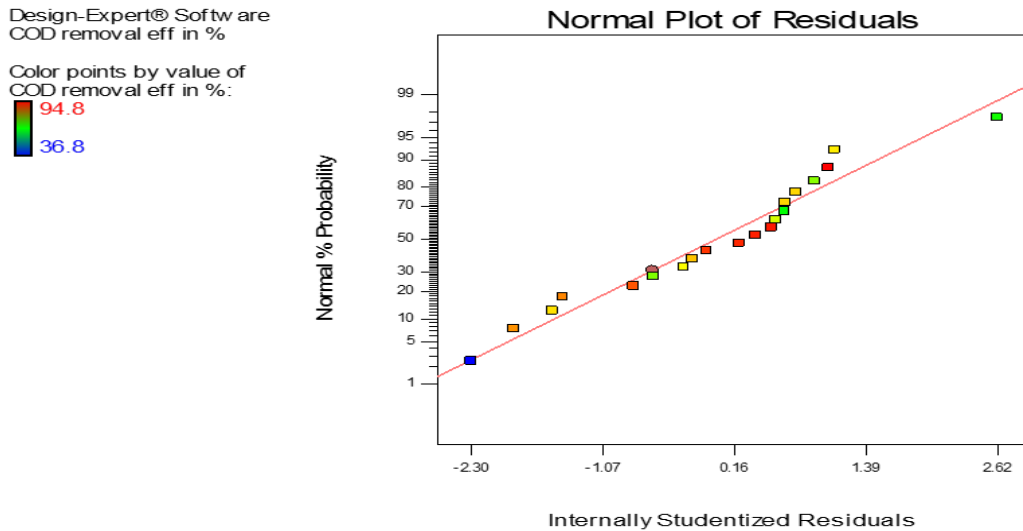


Figure 4.10 Normal probability plots of COD removal efficiency

4.3.4. Residual versus Predicted Plot

A simple check is to plot the residuals versus the fitted (predicted) values as shown in figure 4.11. A plot of the residuals versus the predicted response value tests the expectations of variance. The plot shows random scatter which shows no need of modifying to minimize personal error.

Design-Expert® Software
COD removal in %

Color points by value of
COD removal in %:

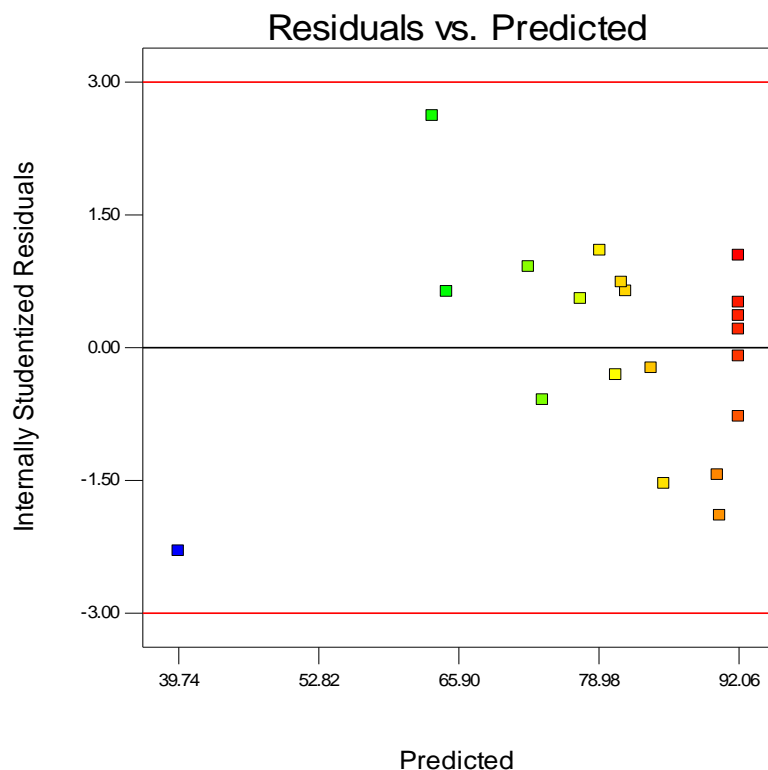


Figure 4.11 Residuals versus predicted plot of COD removal efficiency

4.3.5. Individual Effects of Experimental Variables on COD Removal Efficiency

4.3.5.1. Ferrous ion Doses on COD Removal Efficiency

It can be seen from table 4.2 that the removal efficiency of COD increased with increasing the dosage of catalyst. The maximum catalyst dose on COD removal is 20 mg/l. However, the excessive ferrous ion reacted with hydrogen peroxide which was subsequently associated with the reduced oxidation of organic compounds and removal efficiency of COD. Consequently, it is very important to control ferrous ion doses in the Fenton reaction. The efficiency of Fenton oxidation process was decreased by exceeding this dose in solution beyond 20mg/l. The effect of iron catalyst on COD removal efficiency can be shown in figure 4.12. The analysis of variance with probability value of 0.0001 indicates that the model with dose of catalyst is significant. Which means 0.01% probability value could not explain COD removal efficiency by quadratic model due to personal error and 99.99% of the COD removal efficiency can be explained by the catalyst effects.

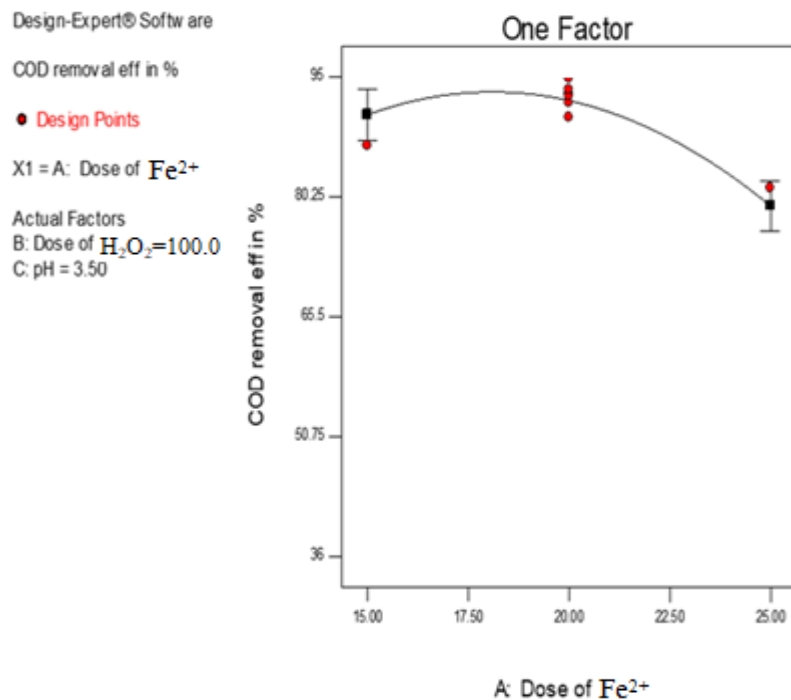


Figure 4.12 Effects of iron catalyst dose on COD removal efficiency

4.3.5.2. Hydrogen per oxide Dose on COD Removal Efficiency

Influence of hydrogen peroxides dosage on COD removal efficiency performs somewhat similar to ferrous catalyst dosages. High H_2O_2 dosages leads to the scavenging of hydroxyl radicals (Mahtab, Islam, and Farooqi, 2020). COD removal efficiency increased with the increasing doses of hydrogen peroxide until its middle point value while both pH and catalyst values are 3.5 and 20mg/l respectively. This is because further increase in dose of hydrogen per oxide results in decomposes of H_2O_2 in to water and oxygen (Moghadam and Kohbanan, 2018). In this study, COD removal efficiency increase to 100mg /l of hydrogen per oxide dose, and decrease beside of this value. In this study, the removal efficiency was low at low dose of oxidant and increase as the doses increases, because as the dose of H_2O_2 up to 100mg/l and $\cdot\text{OH}$ formed increase, the removal efficiency of COD increases. The effects of hydrogen peroxide doses on COD removal efficiency are shown in figure 4.13 below. The analysis of variance with probability value of 0.0007 indicates that the model with dose of H_2O_2 is significant. Which means 0.07% probability value could not explain COD removal efficiency by quadratic model due error and 99.93% of the COD removal efficiency can be explained by the H_2O_2 effects.

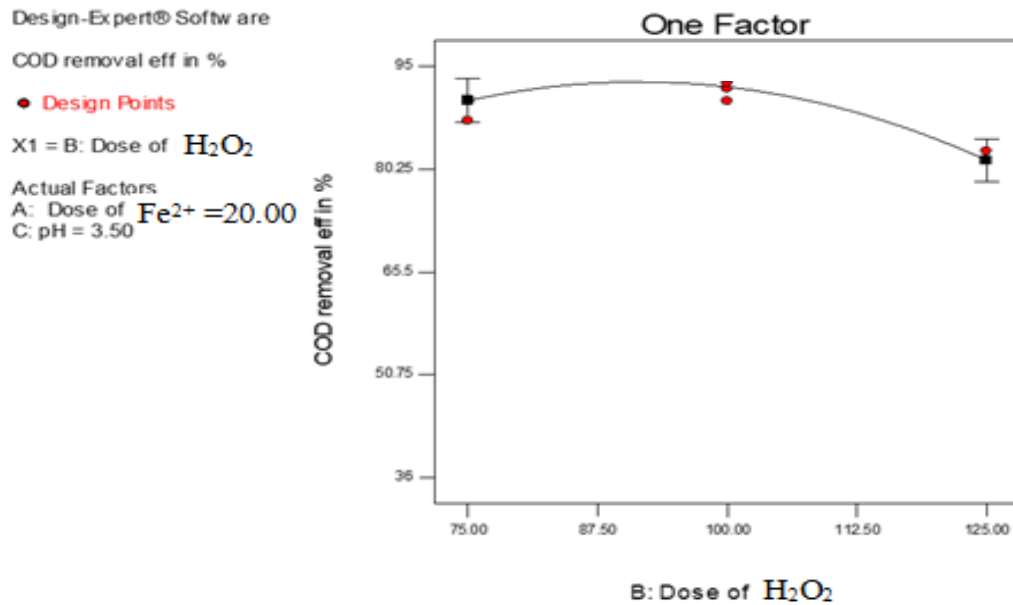


Figure 4.13 Effects of H_2O_2 dose on COD removal efficiency

4.3.5.3. pH Values on COD Removal Efficiency

COD removal efficiency by Fenton reaction is greatly influenced by pH, as shown in figure 4.14, since pH regulates the formation of $\cdot OH$ radicals and hence affects the oxidation efficiency (Wali, 2015). The COD removal efficiency of Fenton oxidation process is mostly affected by pH values in strong acidic media. The removal efficiency of COD with Fenton reagent increases with pH value up to a critical limit and the effect of pH is not significantly effective beyond that limit because the removal efficiency of COD by Fenton oxidation process is effective at pH of 3.5 due to high generation of hydroxyl radical and less generation of $(H_3O_2)^{2+}$ and $Fe(OH)_3$. The probability value of 0.04499 indicates that the model with dose of pH is significant. Which means 4.499% of probability value could not explain COD removal efficiency by quadratic model due error and 95.501% of the COD removal efficiency can be explained by the pH effects.

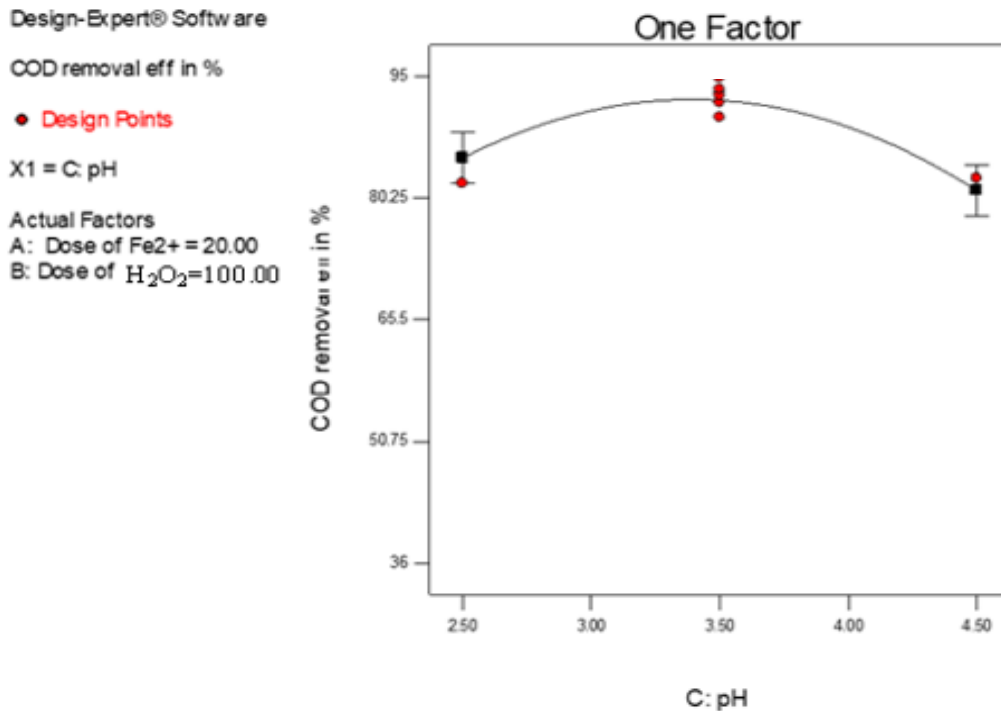


Figure 4.14 Effects of pH on COD removal efficiency

4.3.6. Interaction Effects of Operating Variables on COD Removal Efficiency

COD removal efficiency can be affected by experimental variables depending on the nature of wastewater that can be removed with Fenton oxidation processes. In this study, after conducting experiments, the interaction effects of working variables (pH, ferrous catalyst, and hydrogen per oxide) on COD removal efficiency were analyzed using CCD software. The interaction effects of parameters on COD removal efficiency are plotted in 3D graphs to understand the maximum and minimum removal efficiencies. Figures (4.15-4.17) indicates the three-dimensional response surfaces influence as a function of the interactions of any two variables by keeping the other variables value at the center point.

4.3.6.1. Ferrous ion and Hydrogen peroxide Dosages

The maximum removal efficiency of COD is 94.8% at the dosage of 20 mg/l of Fe²⁺, 100 mg/l of hydrogen per oxide and also its minimum removal efficiency of COD in this experimental work obtained is 36.8% at the dosage of 25mg/l and 125 mg/l of Fe²⁺ and H₂O₂ respectively. These results are closely related with findings of Patil and Raut (2014)

which are 89% and 42.5% of maximum, and minimum removal efficiency of COD respectively. The combined effects of both ferrous ion and H_2O_2 dosages on COD removal efficiency shows negative effect on coded factor (equation 4.3) and actual factor (equation 4.4). The probability value indicates that 0.01% of COD removal efficiency is not explained due to error and 99.99 % of COD removal efficiency is explained. Figure 4.15 shows interaction effects of catalyst and hydrogen per oxides.

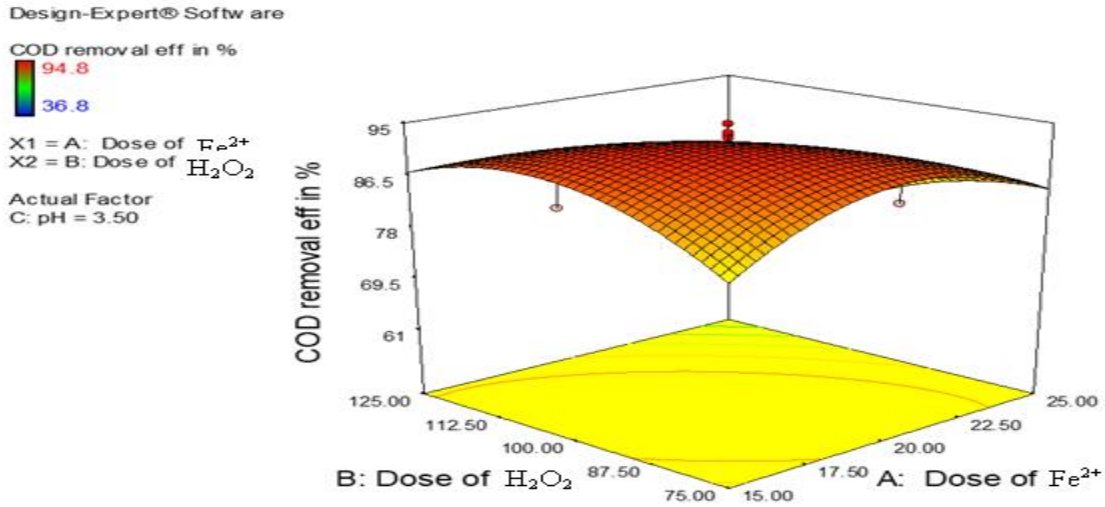


Figure 4.15 Interaction effects of Fe^{2+} and H_2O_2 dose on COD removal efficiency

4.3.6.2. Catalyst Doses and pH values of the Solution

As show in the figure 4.16, the maximum removal efficiency of COD is at pH of 3.5 with dose 20 mg/l of Fe^{2+} , and also the minimum removal efficiency of COD lies at pH of 4.5 with dosage of 25 mg/l of Fe^{2+} . These results indicated that greatest result is obtained at center point doses and also smallest values of COD removal result is obtained outside of center points. COD removal increase with an increase in pH value up to its optimum dose. However, if pH values further increases the removal efficiency of COD decrease. This is because the generation of high hydroxyl radical is obtained at optimum values of both catalyst and pH. The interaction effects of catalyst and pH explains 99.35% of COD removal efficiency and 0.65% is not explained due to personal error.

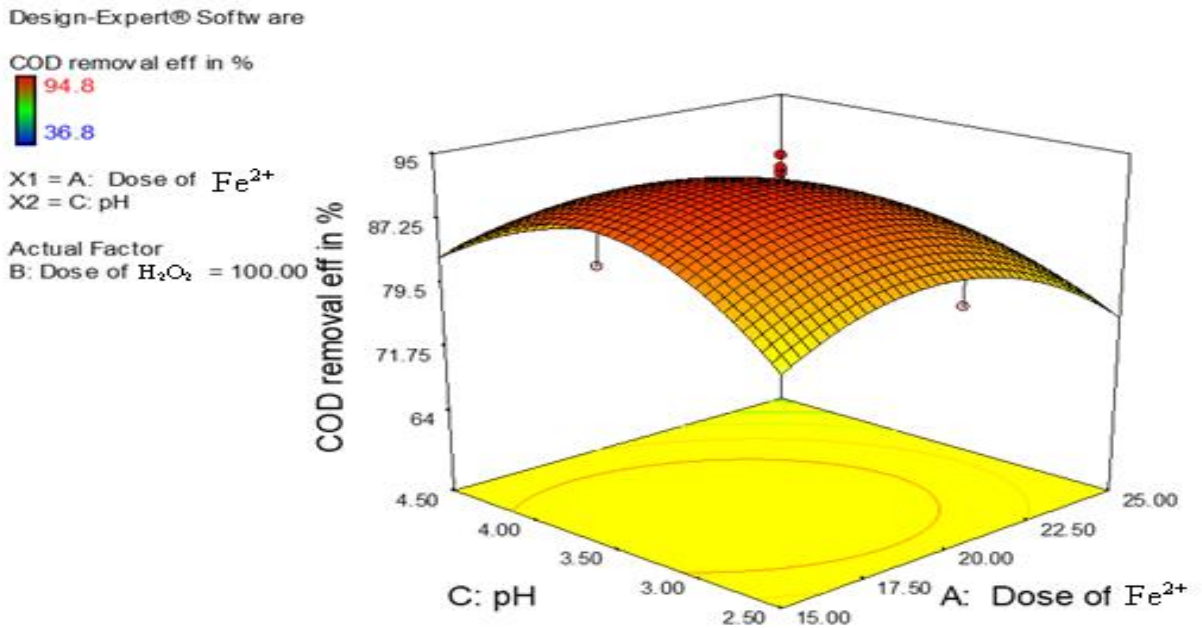


Figure 4.16 Interaction effects of Fe^{2+} doses and pH on COD removal efficiency

4.3.6.3. H_2O_2 doses and pH values of Solution on COD Removal Processes

COD removal efficiency of reactive blue 19 dye was enhanced by increasing the dose of hydrogen peroxide and pH value of the solution up to its finest values. The combined effects of high pH and H_2O_2 on COD removal leads to decomposition of H_2O_2 into H_2O and O_2 (Moghadam and Kohbanan, 2018). Figure 4.17 shows that the highest removal percentage of COD was found at the dose of 100mg/l of H_2O_2 with pH value of 3.5. The effects of H_2O_2 and pH of the solution on COD removal shows that 99.99% of COD removal was explained and have negative interaction effects on COD removal efficiency in both coded factor (equation 4.3) and actual factor equations (4.4).

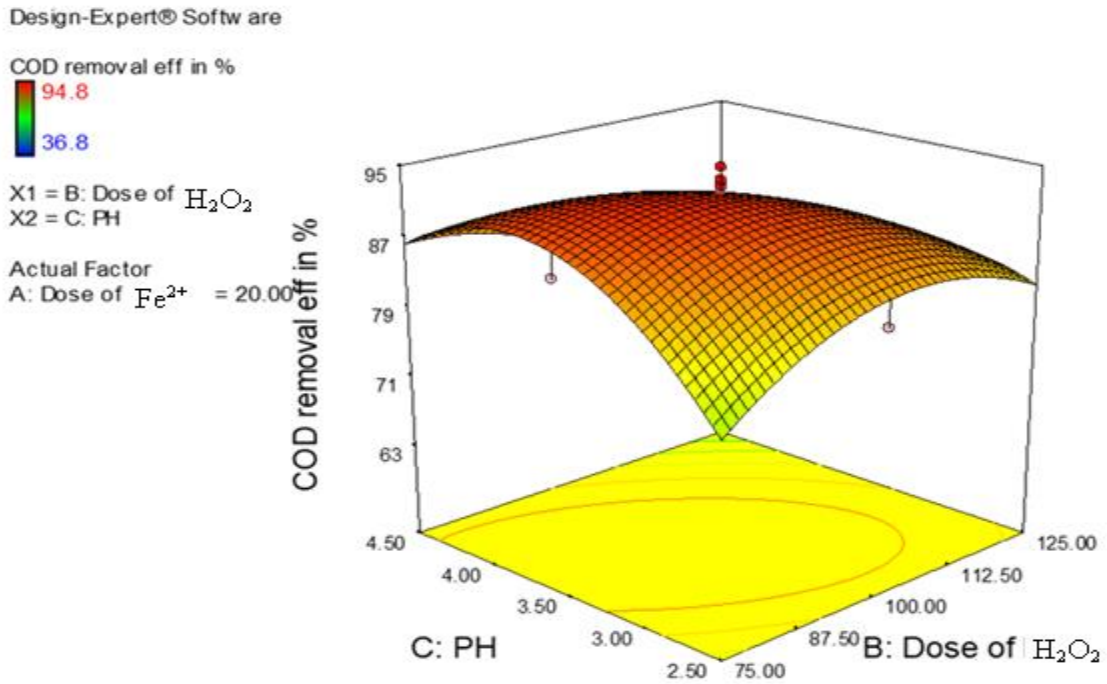


Figure 4.17 Interaction effects of H_2O_2 and pH on COD removal efficiency

4.3.7. Optimization Conditions

The optimization process for maximizing the COD removals was carried out by keeping process variables or factors within the range. Design-expert software takes the following inputs for optimizations such as target, minimize, maximize, and within the range of constraints to resolve the final solution. Optimized conditions for COD removal efficiency from textile wastewater were summarized in figure 4.18.

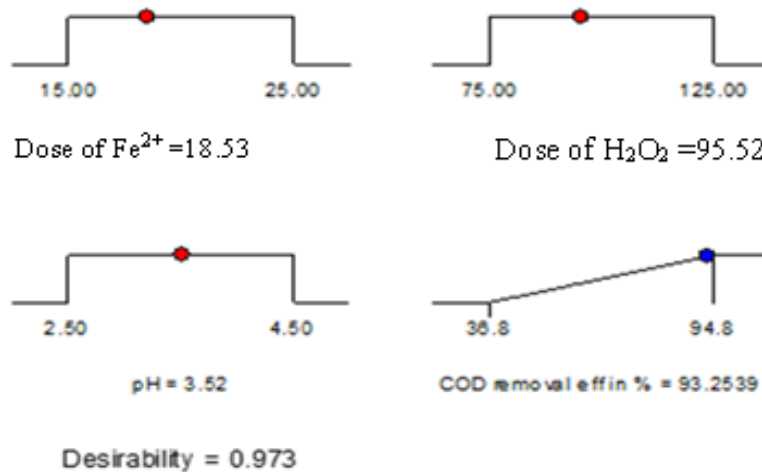


Figure 4.18 Optimization condition of COD from design expert software

4.4. Model Validation Analysis

Through using optimized conditions obtained from the central composite design software experiments were conducted to check validity of the model. These optimized values are 18.52 mg/l of Fe^{2+} , 98.68 mg/l of H_2O_2 and pH of 3.39 for color, and 18.53mg/l of Fe^{2+} , 95.52mg/l of H_2O_2 and 3.52 of pH values for COD removals efficiency. The removal efficiency results of both color and COD from sample wastewater obtained are 87.4 and 91.6% respectively. Close results are observed in the experiments with the design expert software for both color and COD. Since these related results show that the selected model for removal of reactive blue 19 dye is good and hence it indicates the validity of the model. Therefore, the model is considered to be accurate and reliable for predicting removal efficiency of RB19 dye from textile wastewater.

4.5. Textile Wastewater Experimental Results

Effluents from Bahir Dar textile factory contains high concentrations of organic and inorganic chemicals which are characterized by high Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solids (TDS), pH, Total Suspended Solids (TSS) and colors (Mehari, Gebremedhin, and Ayele, 2015). The experiments were done at optimized conditions of CCD software values to determine removal efficiency of textile wastewater. These optimized values are 18.52 mg/l of Fe^{2+} , 98.68 mg/l of H_2O_2 and pH of 3.39 for color removal efficiency, and 18.53mg/l of Fe^{2+} , 95.52mg/l of H_2O_2 and pH value of 3.52 for COD removal efficiency. The removal efficiency results were obtained from actual wastewater of Bahir Dar textile share company with the optimized values of Fenton reagents and pH of the solution were 86.5% and 88.3% for color and COD removal respectively. Removal efficiency values of both color and COD from real textile wastewater is lower compared to synthetic wastewater results because of the presence of the effect of other organic pollutants in real textile wastewater. Hence, the scavenging effects of different organic pollutants indicates reduction of removal efficiency performance of Fenton oxidation process.

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

In this study, experiments were carried out to determine color and COD removal efficiency of wastewater by Fenton removal process. Effects of the process variables and interaction among each other on removal efficiency were studied with the help of design expert software. A model statistic reveals that a significance of model with F-value of 63.10 for color removal and COD removal of 47.12 with probability of 0.0001 for both color and COD removal efficiencies. A good fit of both color and COD removal efficiency were obtained a model with R-square value of 0.9827 and 0.9671 value of adjusted R-square for color removal efficiency and 0.977 value of R-squared and 0.9562 value of adjusted R-squared for COD removal efficiency.

The percentages maximum removal efficiency of reactive blue 19 dye in this experimental works were 90.8% for color and 94.8% for COD with pH of 3.5, 20 and 100 mg/l of Fe^{2+} and H_2O_2 respectively. This revealed that Fenton oxidation process was able to remove reactive blue 19 dye from textile wastewater with center point doses of Fenton reagents in acidic media. In Fenton oxidation process both color and COD removal efficiency is higher than that of conventional textile wastewater treatment methods because organic pollutants could not be removed effectively by conventional methods due to complex structures. Hence, according to Assefa and Sahu, (2016), Mahmoudabadi, Talebi, and Jalili, (2019) and Nawaz and Ahsan, (2014), the COD removal efficiency is in a arrange of 30-60 %, 46% and 58% respectively.

It is observed from these results that the removal efficiency of both color and CODs from textile wastewaters by Fenton oxidation processes increase up to its center point doses and decrease beyond center point for the parameters such as Fe^{2+} , H_2O_2 and pH. This is because high hydroxyl radical is generated at center points doses and less generation of $(\text{H}_3\text{O}_2)^+$ and $\text{Fe}(\text{OH})_3$ that is at high pH Fe^{2+} changed to $\text{Fe}(\text{OH})_3$ and at low pH Fe^{2+} catalyze the process to $(\text{H}_3\text{O}_2)^+$ and reduce the effectiveness of Fenton oxidation process due to less generation of hydroxyl radicals.

Generally, the optimum removal efficiency of both color and COD by Fenton oxidation process lies at optimum conditions. Hence, the parameters values are Fe^{2+} with dose of (18.52mg/l), H_2O_2 with dose of (98.68mg/l) and pH of 3.39 for color, and also dose of Fe^{2+} (18.53mg/l), H_2O_2 dose (95.52mg/l) and pH of 3.52 for COD.

5.2.RECOMMENDATION

Fenton processes is a process that is used for the treatment of textile wastewaters to remove colors and COD. Availability of chemicals, not requiring expensive instruments, and laboratory equipment, simplicity of the process is the advantageous of this method for future work. And also, we suggest this application for next works in different areas of colored wastewater discharge treatments for preventing environmental pollutions. The present study was done at constant operating time condition, but further research works will be considering the operating time and its removal effects. The researchers will be focused on this area for treatment of wastewater in future on iron-free catalytic systems using various other metal ions (Zn, Mn, Ti, Cr, Cu, Co, Ni, Cd, and Pb) for the activation of H_2O_2 to remove organic pollutants and to compare removal efficiency of color and COD with iron catalyst.

In this study, an investigation of color and COD removal efficiency of Fenton oxidation process with the interaction effects of ferrous ions, hydrogen peroxide and pH of solutions is carried out with the ratio of 5:1. However, for future study changing the ratio of Fenton oxidation reagents to 5:2 and 10:1 to compare color and COD removal efficiency in pH interval of 2-5.

REFERENCE

- Ahmadi, Shahin, Leili Mohammadi, Chinenye Adaobi, Igwegbe Somayeh, Rahdar Artur, and Marek Banach. 2018. "Application of Response Surface Methodology in the Degradation of Reactive Blue 19 Using - H₂O₂ / MgO Nanoparticles Advanced Oxidation Process." *International Journal of Industrial Chemistry* 9 (3): 241–53. <https://doi.org/10.1007/s40090-018-0153-4>.
- Ahmadi, Shahin, Leili Mohammadi, Chinenye Adaobi Igwegbe, Somayeh Rahdar, and Artur Marek Banach. 2018. "Application of Response Surface Methodology in the Degradation of Reactive Blue 19 Using H₂O₂/MgO Nanoparticles Advanced Oxidation Process." *International Journal of Industrial Chemistry* 9 (3): 241–53. <https://doi.org/10.1007/s40090-018-0153-4>.
- Ajmal, Anila, Imran Majeed, and Naseem Malik. 2014. "RSC Advances Principles and Mechanisms of Photocatalytic Dye Degradation on TiO₂ Based Photocatalysts : A," no. 2005: 37003–26. <https://doi.org/10.1039/c4ra06658h>.
- Akyol, Kemal. 2020. "Decolorization of the Reactive Blue 19 from Aqueous Solutions with the Fenton Oxidation Process and Modeling with Deep Neural Networks."
- Assefa, Tadele, and Omprakash Sahu. 2016a. "Performance Analysis of Textile Industry Wastewater Treatment Plant with Physicochemical Characterizations" 4 (1): 22–30.
- . 2016b. "Performance Analysis of Textile Industry Wastewater Treatment Plant with Physicochemical Characterizations." *Journal of Environmental Treatment Techniques* 4 (1): 22–30.
- Bakar, Norshila Abu, N Othman, Z M Yunus, Zawawi Daud, and Nur Salsabila. 2020. "Physico-Chemical Water Quality Parameters Analysis on Textile Physico-Chemical Water Quality Parameters Analysis On." <https://doi.org/10.1088/1755-1315/498/1/012077>.
- Barbusiński, K. 2005. "The Modified Fenton Process for Decolorization of Dye Wastewater" 14 (3): 281–85.

- Barbusinski, Krzysztof. 2016. "Fenton Reaction - Controversy Concerning the Chemistry," no. January 2009.
- Barrera-salgado, Karen E, Gabriela Ramírez-robledo, Alberto Álvarez-gallegos, Carlos A Pineda-arellano, Fernando Z Sierra-espinosa, J Alfredo Hernández-pérez, and Susana Silva-martínez. 2016. "Fenton Process Coupled to Ultrasound and UV Light Irradiation for the Oxidation of a Model Pollutant" 2016: 16–18.
- Bhatia, Deepika, Neeta Raj, Sharma Ramesh, and Kanwar Joginder. 2018. "Physicochemical Assessment of Industrial Textile Effluents of Punjab (India)." *Applied Water Science* 8 (3): 1–12. <https://doi.org/10.1007/s13201-018-0728-4>.
- Bhatt, Drashti K, and Upendra D Patel. 2021. "Journal of Physics and Chemistry of Solids Photocatalytic Degradation of Reactive Black 5 Using Ag 3 PO 4 under Visible Light." *Journal of Physics and Chemistry of Solids* 149 (April 2020): 109768. <https://doi.org/10.1016/j.jpics.2020.109768>.
- Bich, Thi, Viet Nguyen, Ngan Nguyen-bich, Ngoc Duy Vu, Hien Ho Phuong, and Hanh Nguyen Thi. 2021. "Degradation of Reactive Blue 19 (RB19) by a Green Process Based on Peroxymonocarbonate Oxidation System" 2021.
- Bidu, J M, M J Rwiza, and K N Njau. 2021. "Uncorrected Proof Uncorrected Proof," 1–14. <https://doi.org/10.2166/wst.2021.133>.
- Buthiyappan, Archina, Abdul Raman, Abdul Aziz, Wan Mohd, and Ashri Wan. 2015. "Recent Advances and Prospects of Catalytic Advanced Oxidation Process in Treating Textile Effluents." <https://doi.org/10.1515/revce-2015-0034>.
- Chen, Yan-jhang, Tang-yu Fan, Li-pang Wang, Ta-wui Cheng, Shiao-shing Chen, Min-hao Yuan, and Shikun Cheng. 2020. "Application of Fenton Method for the Removal of Organic Matter in Sewage Sludge at Room Temperature." *Sustainable Water Resources Management* 2 (01518): 1–10.
- D. Patil, Amruta, and Prof. Dr. P. D Raut. 2014. "Treatment of Textile Wastewater by Fenton's Process as a Advanced Oxidation Process." *IOSR Journal of Environmental Science, Toxicology and Food Technology* 8 (10): 29–32. <https://doi.org/10.9790/2402->

081032932.

- Değermenci, Nejdnet, and Kemal Akyol. 2020. “Decolorization of the Reactive Blue 19 from Aqueous Solutions with the Fenton Oxidation Process and Modeling with Deep Neural Networks.” *Water, Air, and Soil Pollution* 231(2).
<https://doi.org/10.1007/s11270-020-4402-8>.
- Domingues, Eva, João Gomes, Margarida J. Quina, Rosa M. Quinta-Ferreira, and Rui C. Martins. 2018. “Detoxification of Olive Mill Wastewaters by Fenton’s Process.” *Catalysts* 8 (12). <https://doi.org/10.3390/catal8120662>.
- Dutta, Suvanka, Ananya Ghosh, Sankar Chandra Moi, and Rajnarayan Saha. 2015. “Application of Response Surface Methodology for Optimization of Reactive Azo Dye Degradation Process by Fenton’s Oxidation” 6(11).
<https://doi.org/10.7763/IJESD.2015.V6.705>.
- Elkhattabi, El Hassan, Mohamed Lakraimi, Mohamed Badreddine, Ahmed Legrouri, Omar Cherkaoui, and Moha Berraho. 2013. “Removal of Remazol Blue 19 from Wastewater by Zinc–Aluminium–Chloride-Layered Double Hydroxides.” *Applied Water Science* 3 (2): 431–38. <https://doi.org/10.1007/s13201-013-0092-3>.
- Engineeringin, Environmental. 2020. “Removal of Reactive Red Dyes from Textile Wastewater by Biosorption Using Banana and Orange Peels.”
- Garrido-cardenas, Jos Antonio, and Ana Agüera. 2020. “Wastewater Treatment by Advanced Oxidation Process and Their Worldwide Research Trends.”
- GD, Kumaravel, and Saranya R. 2018. “Influence of H₂O₂ Activation with Doped Catalyst for Treating Recalcitrant Textile Dyes.” *Journal of Thermodynamics & Catalysis* 09 (01): 1–5. <https://doi.org/10.4172/2157-7544.1000197>.
- Ghaly, A E, R Ananthashankar, M Alhattab, and V V Ramakrishnan. 2017. “Chemical Engineering & Process Technology Production , Characterization and Treatment of Textile Effluents :A Critical Review,” no. January 2014. <https://doi.org/10.4172/2157-7048.1000182>.
- Gore, Mohan M, Virendra Kumar, Dipak V Pinjari, Prakash V Chavan, and Aniruddha B

- Pandit. 2014. "Ultrasonics Sonochemistry Degradation of Reactive Orange 4 Dye Using Hydrodynamic Cavitation Based Hybrid Techniques." *Ultrasonics - Sonochemistry* 21 (3): 1075–82. <https://doi.org/10.1016/j.ultsonch.2013.11.015>.
- Günes, Elçin, Deniz Izlen Çifçi, Ali Riza Dinçer, and Yalçın Günes. 2021. "Removal of COD, Aromaticity and Color of a Pretreated Chemical Producing Industrial Wastewater: A Comparison between Adsorption, Ozonation, and Advanced Oxidation Processes." *Turkish Journal of Chemistry* 45 (3): 551–65. <https://doi.org/10.3906/kim-2010-48>.
- Haque, Asma, Shumaila Kiran, Sofia Nosheen, Gulnaz Afzal, Tahsin Gulzar, Salman Ahmad, Shaifq Ur-Rehman, and Muhammad Hassan Tariq. 2020. "Degradation of Reactive Blue 19 Dye Using Copper Nanoparticles Synthesized from Labeo Rohita Fish Scales: A Greener Approach." *Polish Journal of Environmental Studies* 29 (1): 609–16. <https://doi.org/10.15244/pjoes/104663>.
- Javaid, Rahat. 2019. "Catalytic Oxidation Process for the Degradation of Synthetic Dyes : An Overview," 1–27.
- Jia, Lijuan, Zhemin Shen, Weimin Guo, Yanan Zhang, Huichen Zhu, Wenchao Ji, and Maohong Fan. 2014. "Journal of the Taiwan Institute of Chemical Engineers QSAR Models for Oxidative Degradation of Organic Pollutants in the Fenton Process." *Journal of the Taiwan Institute of Chemical Engineers*. <https://doi.org/10.1016/j.jtice.2014.09.014>.
- Kalantary, Roshanak Rezaei, Ali Esrafil, and Mitra Gholami. 2013. "ENVIRONMENTAL HEALTH Evaluation of Fenton Oxidation Process Coupled with Biological Treatment for the Removal of Reactive Black 5 from Aqueous Solution," no. May 2014. <https://doi.org/10.1186/2052-336X-11-13>.
- Kehinde, Fagbenro Luwakemi, and Hamidi Abdul Aziz. 2014. "Textile Waste Water and the Advanced Oxidative Treatment Process , an Overview" 3 (8): 10–12. <https://doi.org/10.15680/IJRSET.2014.0308034>.
- Kothai, A, C Sathishkumar, R Muthupriya, K Siva, and R Dharchana. 2020. "Materials

- Today : Proceedings Experimental Investigation of Textile Dyeing Wastewater Treatment Using Aluminium in Electro Coagulation Process and Fenton ' s Reagent in Advanced Oxidation Process.” *Materials Today: Proceedings*, no. xxxx. <https://doi.org/10.1016/j.matpr.2020.07.094>.
- Lavanya, C. 2014. “Review Article Degradation of Toxic Dyes : A Review” 3 (6): 189–99.
- Lellis, Bruno, Cíntia Zani Fávaro-Polonio, João Alencar Pamphile, and Julio Cesar Polonio. 2019. “Effects of Textile Dyes on Health and the Environment and Bioremediation Potential of Living Organisms.” *Biotechnology Research and Innovation* 3 (2): 275–90. <https://doi.org/10.1016/j.biori.2019.09.001>.
- Mahmoudabadi, Tahereh Zarei, Parvaneh Talebi, and Mahrokh Jalili. 2019. “Removing Disperse Red 60 and Reactive Blue 19 Dyes Removal by Using Alcea Rosea Root Mucilage as a Natural Coagulant.” *AMB Express*. <https://doi.org/10.1186/s13568-019-0839-9>.
- Mahtab, Mohd Salim, Dar Tafazul Islam, and Izharul Haq Farooqi. 2020. “Engineering Science and Technology , an International Journal Optimization of the Process Variables for Landfill Leachate Treatment Using Fenton Based Advanced Oxidation Technique.” *Engineering Science and Technology, an International Journal*, no. xxxx. <https://doi.org/10.1016/j.jestch.2020.08.013>.
- Matavos-aramyan, Sina, and Mohsen Moussavi. 2017. “Advances in Fenton and Fenton Based Oxidation Processes for Industrial Effluent Contaminants Control-A Review” 2 (4). <https://doi.org/10.19080/IJESNR.2017.02.555594>.
- Meerbergen, Ken. n.d. “DECOLORIZATION OF TEXTILE WASTEWATER , WITH AN EMPHASIS ON MICROBIAL TREATMENT PROCESSES,” no. March 2018.
- Mehari, Abrehet Kahsay, Shewit Gebremedhin, and Belayneh Ayele. 2015. “Effects of Bahir Dar Textile Factory Effluents on the Water Quality of the Head Waters of Blue Nile River , Ethiopia” 2015.
- Meride, Yirdaw, and Bamlaku Ayenew. 2016. “Drinking Water Quality Assessment and

- Its Effects on Residents Health in Wondo Genet Campus, Ethiopia.” *Environmental Systems Research* 5 (1): 1–7. <https://doi.org/10.1186/s40068-016-0053-6>.
- Moghadam, Fahimeh, and Najmeh Nori Kohbanan. 2018. “Removal of Reactive Blue 19 Dye Using Fenton From Aqueous Solution” *5*(1):50–55. <https://doi.org/10.15171/ajehe.2018.07>.
- Moghadam, Fahimeh, and Najmeh Nori Kohbanan. 2018. “Removal of Reactive Blue 19 Dye Using Fenton From Aqueous Solution.” *Avicenna Journal of Environmental Health Engineering* 5 (1): 50–55. <https://doi.org/10.15171/ajehe.2018.07>.
- Mokhbi, Yasmina, Mourad Korichi, and Zineb Akchiche. 2019. “Combined Photocatalytic and Fenton Oxidation for Oily Wastewater Treatment.” *Applied Water Science* 9 (2): 1–9. <https://doi.org/10.1007/s13201-019-0916-x>.
- Mostafa, M Rafiqul Islam M G. 2020. “Characterization of Textile Dyeing Effluent and Its Treatment Using Polyaluminum Chloride.” *Applied Water Science* 10 (5): 1–10. <https://doi.org/10.1007/s13201-020-01204-4>.
- Najdanović, Slobodan M., Milica M. Petrović, Miloš M. Kostić, Jelena Z. Mitrović, Danijela V. Bojić, Milan D. Antonijević, and Aleksandar Lj Bojić. 2020. “Electrochemical Synthesis and Characterization of Basic Bismuth Nitrate [Bi₆O₅(OH)₃](NO₃)₅·2H₂O: A Potential Highly Efficient Sorbent for Textile Reactive Dye Removal.” *Research on Chemical Intermediates* 46 (1): 661–80. <https://doi.org/10.1007/s11164-019-03983-1>.
- Nakhate, Pranav H, Keyur K Moradiya, Hrushikesh G Patil, Kumudini V Marathe, and Ganapati D Yadav. 2019. “Case Study on Sustainability of Textile Wastewater Treatment Plant Based on Lifecycle Assessment Approach.” *Journal of Cleaner Production*, 118929. <https://doi.org/10.1016/j.jclepro.2019.118929>.
- Nawaz, Muhammad Saqib, and Muhammad Ahsan. 2014. “Comparison of Physico-Chemical , Advanced Oxidation and Biological Techniques for the Textile Wastewater Treatment.” *Alexandria Engineering Journal* 53 (3): 717–22. <https://doi.org/10.1016/j.aej.2014.06.007>.

- Network, Neural. n.d. "Prediction and Optimization of the Fenton Process for the Treatment of Landfill Leachate Using an Artificial Neural Network." <https://doi.org/10.3390/w10050595>.
- Nidheesh, P, Minghua Zhou, Mehmet A Oturan, P Nidheesh, Minghua Zhou, and Mehmet A Oturan. 2018. "An Overview on the Removal of Synthetic Dyes from Water by Electrochemical Advanced Oxidation Processes . To Cite This Version : HAL Id : Hal-01721053."
- Oturan, Mehmet A, Ignasi Sirés, Nihal Oturan, Stéphanie Pérocheau, and Jean-luc Laborde. 2008. "Sono-electro-Fenton Process : A Novel Hybrid Technique for the Destruction of Organic Pollutants in Water." *Journal of Electroanalytical Chemistry* 624 (1–2): 329–32. <https://doi.org/10.1016/j.jelechem.2008.08.005>.
- Patil, Amruta D, and Prof P D Raut. 2014a. "Treatment of Textile Wastewater by Fenton ' s Process as a Advanced Oxidation Process" 8 (10): 29–32.
- . 2014b. "Treatment of Textile Wastewater by Fenton ' s Process as a Advanced Oxidation Treatment of Textile Wastewater by Fenton ' s Process as a Advanced Oxidation Process," no. November. <https://doi.org/10.9790/2402-081032932>.
- . 2014c. "Treatment of Textile Wastewater by Fenton ' s Process as a Advanced Oxidation Treatment of Textile Wastewater by Fenton ' s Process as a Advanced Oxidation Process," no. October. <https://doi.org/10.9790/2402-081032932>.
- Perkowski, Jan, and Lech Kos. 2002. "Treatment of Textile Dyeing Wastewater by Hydrogen Peroxide and Ferrous Ions," no. September: 2–5.
- Profile, S E E. 2018. "Removal Of Remazol Brilliant Blue from Aqueous Solution by Iraqi Porcelanite Removal Of Remazol Brilliant Blue from Aqueous Solution by Iraqi Porcelanite Rocks," no. March.
- Qi, Chengdu, Xitao Liu, Jun Ma, Chunye Lin, Xiaowan Li, and Huijuan Zhang. 2016. "Chemosphere Activation of Peroxymonosulfate by Base : Implications for the Degradation of Organic Pollutants." *Chemosphere* 151:280–88. <https://doi.org/10.1016/j.chemosphere.2016.02.089>.

- Rabbi, M Ahasanur, Jewel Hossen, Mirja Sarwar, Pijush Kanti Roy, Sharmin Binte Shaheed, and M Mehedi Hasan. 2018. "Investigation of Waste Water Quality Parameters Discharged from Textile Manufacturing Industries of Bangladesh" 13 (2).
- Racyte, Justina, and Mindaugas Rimeika. 2015. "UV / H₂O₂ - Advanced Oxidation Processes Possibilities for Textile Reactive Dyes Decolorization ENVIRONMENTAL," no. January 2008.
- Review, Applications A. 2014. "Advanced Oxidation Processes in Water / Wastewater Treatment : In Water / Wastewater Treatment : Principles and Applications . A Review," no. December. <https://doi.org/10.1080/10643389.2013.829765>.
- Sadri Moghaddam, S., M. R. Alavi Moghaddam, and M. Arami. 2010. "Coagulation/Flocculation Process for Dye Removal Using Sludge from Water Treatment Plant: Optimization through Response Surface Methodology." *Journal of Hazardous Materials* 175(1–3):651–57. <https://doi.org/10.1016/j.jhazmat.2009.10.058>.
- Sah, Mahesh Kumar, Arvind Kumar, and Pramanik K. 2010. "The Extraction of Fibroin Protein From Bombyx Mori Silk Cocoon: Optimization of Process Parameters." *International Journal of Bioinformatics Research* 2(2):33–41. <https://doi.org/10.9735/0975-3087.2.2.33-41>.
- Scholz, D A Yaseen M. 2019. *Textile Dye Wastewater Characteristics and Constituents of Synthetic Effluents : A Critical Review. International Journal of Environmental Science and Technology*. Vol.16. Springer Berlin Heidelberg. <https://doi.org/10.1007/s13762-018-2130-z>.
- Sci, J Environ, Natural Resources, A Munnaf, M S Islam, T R Tusher, M H Kabir, and M A H Molla. 2014. "Investigation of Water Quality Parameters Discharged from Textile Dyeing Industries" 7 (1): 257–63.
- Senthilkumar, M, and M Muthukumar. 2007. "Studies on the Possibility of Recycling Reactive Dye Bath Effluent after Decolouration Using Ozone" 72. <https://doi.org/10.1016/j.dyepig.2005.08.019>.

- Serrano-martínez, Ana, María Teresa Mercader-ros, Isabel Martínez-alcalá, Carmen Lucas-abellán, José Antonio, and Vicente M Gómez-lópez. 2020. "Journal of Water Process Engineering Degradation and Toxicity Evaluation of Azo Dye Direct Red 83 : 1 by an Advanced Oxidation Process Driven by Pulsed Light." *Journal of Water Process Engineering* 37(February):101530. <https://doi.org/10.1016/j.jwpe.2020.101530>.
- Shiying, Yang, Wang Ping, Yang Xin, W E I Guang, Zhang Wenyi, and Shan Liang. 2009. "A Novel Advanced Oxidation Process to Degrade Organic Pollutants in Wastewater : Microwave-Activated Persulfate Oxidation." *Journal of Environmental Sciences* 21 (9): 1175–80. [https://doi.org/10.1016/S1001-0742\(08\)62399-2](https://doi.org/10.1016/S1001-0742(08)62399-2).
- Siddique, Maria, Robina Farooq, and Gareth J. Price. 2014. "Synergistic Effects of Combining Ultrasound with the Fenton Process in the Degradation of Reactive Blue 19." *Ultrasonics Sonochemistry* 21(3):1206–12. <https://doi.org/10.1016/j.ultsonch.2013.12.016>.
- Silva, Laís G M, Francisca C Moreira, Maria Alice, P Cechinel, Luciana P Mazur, A Ulson, De Souza, et al. 2020. "Integration of Fenton ' s Reaction Based Processes and Cation Exchange Processes in Textile Wastewater Treatment as a Strategy for Water Reuse" 272 (December 2019). <https://doi.org/10.1016/j.jenvman.2020.111082>.
- Tavangar, Tohid, Mohammad Karimi, Mashallah Rezakazemi, Karkala Raghava Reddy, and Tejrjaj M Aminabhavi. 2019. "Textile Waste , Dyes / Inorganic Salts Separation of Cerium Oxide-Loaded Loose a Department Department of Textile Engineering , Amirkabir University of Technology (Tehran Polytechnic), d School." *Chemical Engineering Journal*, 123787. <https://doi.org/10.1016/j.cej.2019.123787>.
- Taylor, Publisher, Jian Long Wang, and L E J I N Xu. 2011. "Critical Reviews in Environmental Science and Technology Advanced Oxidation Processes for Wastewater Treatment : Formation of Hydroxyl Radical and Application Advanced Oxidation Processes for Wastewater Treatment : Formation of Hydroxyl Radical," no. August 2012: 37–41. <https://doi.org/10.1080/10643389.2010.507698>.
- Tesfahun, Agumassie. 2019. "Water Quality Problems , Related Challenges and Their

- Impact on Ethiopian Fishery” 13 (February): 66–73.
<https://doi.org/10.5897/AJEST2018.2606>.
- Ullah, Inam, Abdur Raziq, Fazli Akbar, Muhammad Saqib, Abdur Rahim, and Abdul Niaz. 2019. “KINETIC AND THERMODYNAMIC STUDY OF OXIDATIVE DEGRADATION OF” 33 (2): 243–54.
- Using, Wastewaters, and Fenton S Oxidation. 2015. “TREATMENT OF ORGANIC POLLUTANTS FROM PULP MILL,” no. March.
- Wali, Farouk K M. 2015. “Of Waste Resources Color Removal and COD Reduction of Dyeing Bath Wastewater by Fenton Reaction” 5 (1): 1–6. <https://doi.org/10.4172/2252-5211.1000171>.
- Wang, Jingang, Yunleiyu Guo, Peiquan Guo, Jiemei Yu, Weilin Guo, and Xikui Wang. 2014. “Degradation of Reactive Brilliant Red K-2BP in Water Using a Combination of Swirling Jet-Induced Cavitation and Fenton Process.” *SEPARATION AND PURIFICATION TECHNOLOGY* 130:1–6.
<https://doi.org/10.1016/j.seppur.2014.04.020>.
- Wara, Iddo, Wale Local, and Oromia Region. 2014. “Assessment of Physicochemical and Major Chemical Parameters of Spring” 7522 (June): 103–12.
- Yaseen, D A, and M Scholz. 2018. *Textile Dye Wastewater Characteristics and Constituents of Synthetic Effluents: A Critical Review. International Journal of Environmental Science and Technology*. Springer Berlin Heidelberg.
<https://doi.org/10.1007/s13762-018-2130-z>.
- Yazdanbakhsh, Ahmad Reza, Amir Sheikh Mohammadi, Abdol Azim Alinejad, Ghasem Hassani, Seyed Mohsen Mohseni, Mahdieh Sardar, and Vali Sarsangi. 2009. “Reduction of Non-Betalactam Antibiotics COD by Combined Coagulation and Advanced Oxidation Processes,” 2121–31.
<https://doi.org/10.2175/106143016X14733681695447>.
- Yi, Shixiong, Gang Sun, and Fangyin Dai. 2017. “Efficient Separation and Reuse of CI Reactive Blue 19 from Dyeing Effluent by Solvent Extraction.” *Fibers and Polymers*

18 (9): 1718–23. <https://doi.org/10.1007/s12221-017-1144-3>.

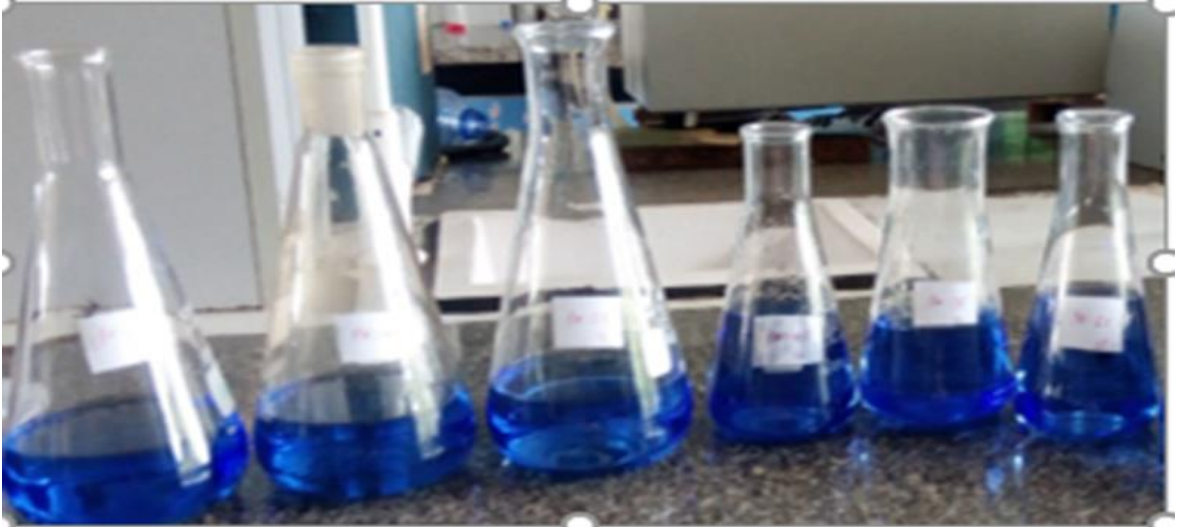
Yonar, Taner. 2014. “Decolorisation of Textile Dyeing Effluents Using Advanced Oxidation Processes,” no. October 2011. <https://doi.org/10.5772/18908>.

Zineb, Yahia. 2018. “REMOVAL OF CHEMICAL OXYGEN DEMAND FROM TANNERY WASTEWATER BY FENTON ’ S REAGENT,” no. April.

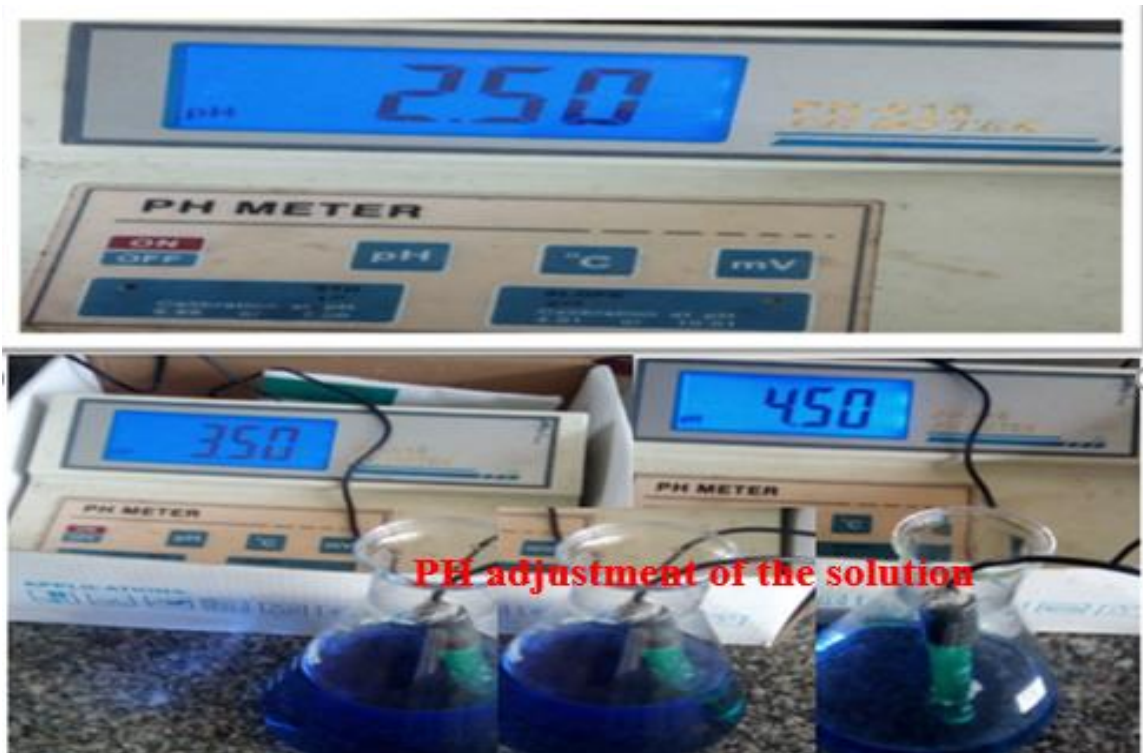
Zou, Rusen, Irimi Angelidaki, Biao Jin, and Yifeng Zhang. 2020. “Feasibility and Applicability of the Scaling-up of Bio-Electro-Fenton System for Textile Wastewater Treatment.” *Environment International* 134 (November 2019): 105352. <https://doi.org/10.1016/j.envint.2019.105352>.

APPENDIXES

Appendix A: Experimental works and treatment process images



1. Distilled water + RB19 dye solution



2. PH adjustment of the solution

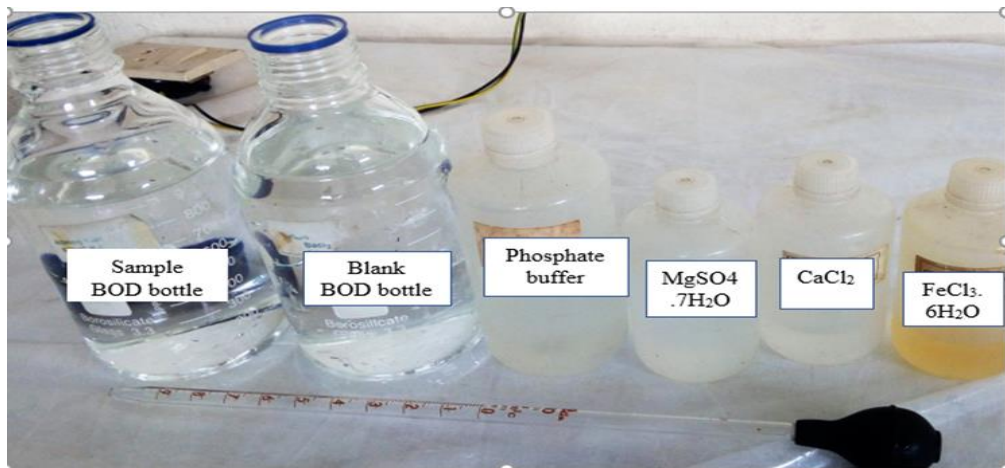


3. Mixing and filtration process

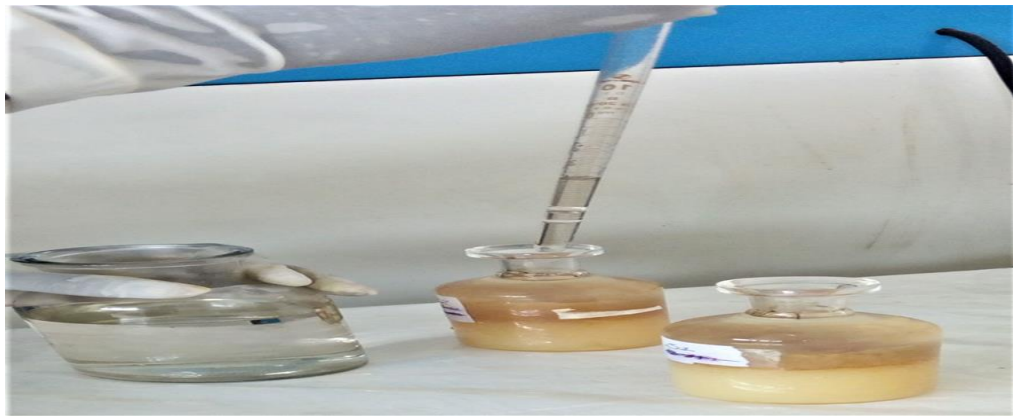


4. Treated wastewater sample after treatment

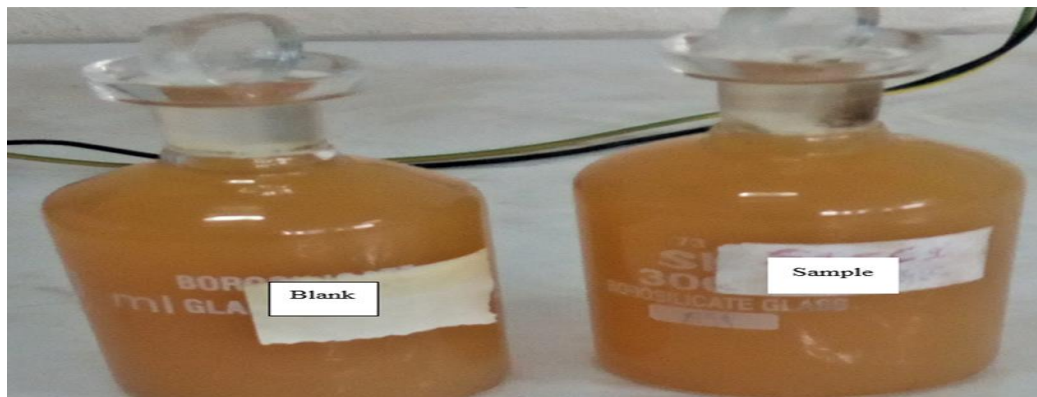
Appendix B: BOD determination steps



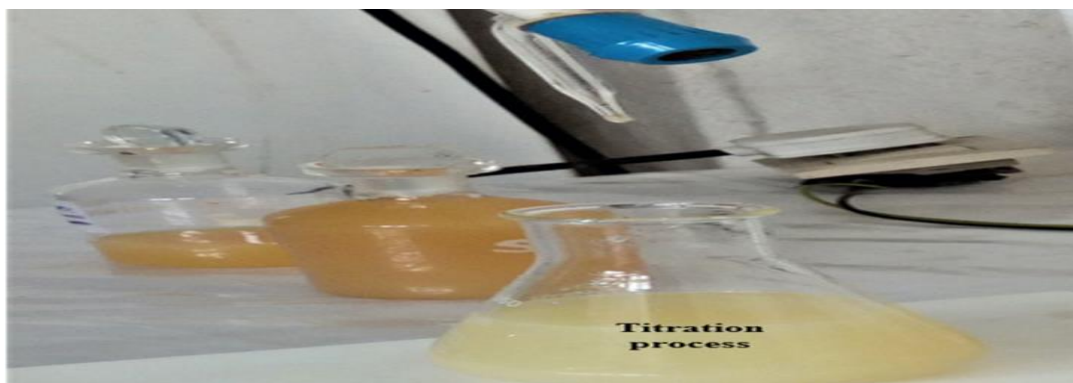
1. Addition of BOD reagents in sample and blank solution



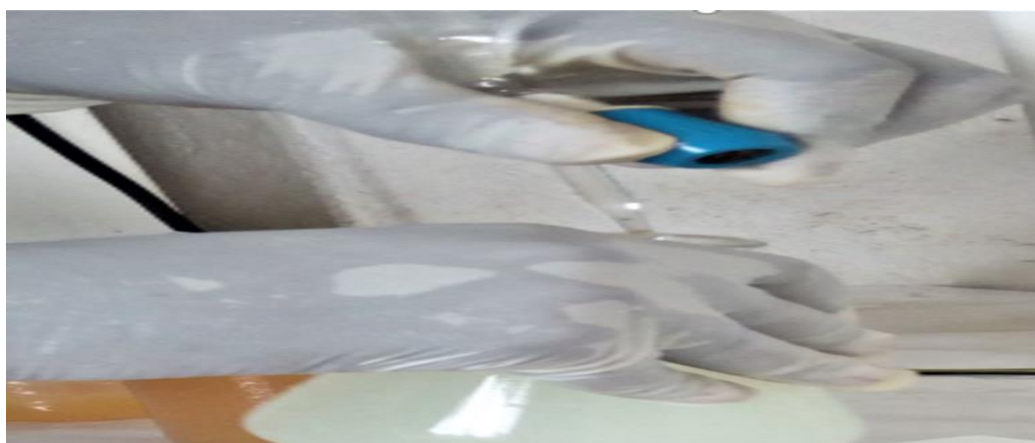
2. Addition of sulphuric acid droplets for dissociation of the solution



3. Blank and samples solution for BOD titration after addition of sulphuric acid



4. Titration process of BOD sample



5. Ending point of BOD titration processes

Appendix C: Design summary of color and COD removal efficiency

| Design summary of design expert software | |
|--|-------------------|
| Study type | Response surface |
| Initial design | Central composite |
| Design model | Quadratic |
| Run | 20 |
| Block | No block |

Appendix D: Constraints for optimization of color and COD removal efficiency

| Name | Goal | Lower limit | Upper limit |
|---------------------------------------|----------|-------------|-------------|
| Dose of Fe ²⁺ | in range | 15 | 25 |
| Dose of H ₂ O ₂ | in range | 75 | 125 |
| pH value | in range | 2.5 | 4.5 |
| Color | Maximize | 45.5 | 90.8 |
| COD | Maximize | 36.8 | 94.8 |

Appendix E: Optimized conditions and solutions of color and COD removal efficiency

| Response | Dose of Fe ²⁺ (mg/l) | Dose of H ₂ O ₂ (mg/l) | PH value | Removal efficiency(%) | Desirability |
|-------------------|---------------------------------|--|----------|-----------------------|--------------|
| Color removal eff | 18.52 | 98.68 | 3.39 | 88.6658 | 0.953 |
| COD removal eff | 18.53 | 95.52 | 3.52 | 93.2539 | 0.973 |

Appendix F: Absorbances value and removal efficiency calculations of color

| No of runs | Dose of Fe ²⁺ (mg/li) | Dose of H ₂ O ₂ (mg/li) | pH value | Initial absorbance before treatment (Abso) | Absorbance (AB1) | Absorbance (AB2) | Average absorbance (Abs) = $\frac{AB1 + AB2}{2}$ | Removal efficiency of color (η) = $\left(\frac{Abso - Abs}{Abso}\right) * 100$ |
|------------|----------------------------------|---|----------|--|------------------|------------------|--|--|
| 1 | 25.00 | 100.00 | 3.50 | 0.559 | 0.150 | 0.148 | 0.149 | 73.3 |
| 2 | 20.00 | 100.00 | 3.50 | 0.559 | 0.071 | 0.067 | 0.069 | 87.7 |
| 3 | 25.00 | 75.00 | 2.50 | 0.559 | 0.220 | 0.219 | 0.220 | 60.6 |
| 4 | 20.00 | 100.00 | 3.50 | 0.559 | 0.064 | 0.062 | 0.63 | 88.8 |
| 5 | 20.00 | 100.00 | 2.50 | 0.559 | 0.121 | 0.121 | 0.121 | 78.4 |
| 6 | 15.00 | 125.00 | 4.50 | 0.559 | 0.219 | 0.217 | 0.218 | 61 |
| 7 | 25.00 | 125.00 | 2.50 | 0.559 | 0.248 | 0.247 | 0.248 | 55.7 |
| 8 | 15.00 | 75.00 | 2.50 | 0.559 | 0.196 | 0.194 | 0.195 | 65.1 |
| 9 | 20.00 | 100.00 | 3.50 | 0.559 | 0.073 | 0.069 | 0.071 | 87.2 |
| 10 | 15.00 | 75.00 | 4.50 | 0.559 | 0.172 | 0.171 | 0.172 | 69.3 |

| | | | | | | | | |
|----|-------|--------|------|-------|-------|-------|-------|------|
| 11 | 20.00 | 100.00 | 3.50 | 0.559 | 0.068 | 0.062 | 0.065 | 88.3 |
| 12 | 15.00 | 125.00 | 2.50 | 0.559 | 0.108 | 0.107 | 0.108 | 80.6 |
| 13 | 20.00 | 125.00 | 3.50 | 0.559 | 0.102 | 0.102 | 0.102 | 81.8 |
| 14 | 15.00 | 100.00 | 3.50 | 0.559 | 0.099 | 0.098 | 0.099 | 82.2 |
| 15 | 20.00 | 75.00 | 3.50 | 0.559 | 0.101 | 0.101 | 0.101 | 81.9 |
| 16 | 25.00 | 125.00 | 4.50 | 0.559 | 0.306 | 0.304 | 0.305 | 45.5 |
| 17 | 25.00 | 75.00 | 4.50 | 0.559 | 0.152 | 0.150 | 0.151 | 72.9 |
| 18 | 20.00 | 100.00 | 3.50 | 0.559 | 0.066 | 0.058 | 0.062 | 89.9 |
| 19 | 20.00 | 100.00 | 4.50 | 0.559 | 0.166 | 0.158 | 0.162 | 71 |
| 20 | 20.00 | 100.00 | 3.50 | 0.559 | 0.052 | 0.050 | 0.051 | 90.8 |

Appendix G: COD removal efficiency calculations

| No of runs | Dose of Fe ²⁺ (mg/li) | Dose of H ₂ O ₂ (mg/li) | PH Value | Initial concentration (C _o) in mg/l Or initial COD | Final concentration(C) in mg/l | | | Removal efficiency of COD (η) $= \left(\frac{C_o - C}{C_o} \right) * 100$ |
|------------|----------------------------------|---|----------|---|--------------------------------|------------------|------------------|---|
| | | | | | Final COD | Volum e of blank | Volume of sample | |
| 1 | 25.00 | 100.00 | 3.50 | 1600 | 299.2 | 29.3 | 27.43 | 81.3 |
| 2 | 20.00 | 100.00 | 3.50 | 1600 | 118.4 | 21.5 | 20.76 | 92.6 |
| 3 | 25.00 | 75.00 | 2.50 | 1600 | 432 | 39.7 | 37 | 73 |
| 4 | 20.00 | 100.00 | 3.50 | 1600 | 131.2 | 25 | 24.18 | 91.8 |
| 5 | 20.00 | 100.00 | 2.50 | 1600 | 288 | 15.9 | 14.1 | 82 |
| 6 | 15.00 | 125.00 | 4.50 | 1600 | 422.4 | 28.6 | 25.96 | 73.6 |
| 7 | 25.00 | 125.00 | 2.50 | 1600 | 550.4 | 31.44 | 28 | 65.6 |
| 8 | 15.00 | 75.00 | 2.50 | 1600 | 531.2 | 32 | 28.7 | 66.8 |
| 9 | 20.00 | 100.00 | 3.50 | 1600 | 160 | 27 | 26 | 90 |
| 10 | 15.00 | 75.00 | 4.50 | 1600 | 316.8 | 16.5 | 14.52 | 80.2 |
| 11 | 20.00 | 100.00 | 3.50 | 1600 | 105.6 | 23.4 | 22.74 | 93.4 |
| 12 | 15.00 | 125.00 | 2.50 | 1600 | 262.4 | 37.3 | 35.66 | 83.6 |
| 13 | 20.00 | 125.00 | 3.50 | 1600 | 275.2 | 29.8 | 28.1 | 82.8 |
| 14 | 15.00 | 100.00 | 3.50 | 1600 | 216 | 19.4 | 18.05 | 86.5 |
| 15 | 20.00 | 75.00 | 3.50 | 1600 | 204.8 | 17.9 | 16.65 | 87.2 |
| 16 | 25.00 | 125.00 | 4.50 | 1600 | 1011.2 | 41.2 | 34.9 | 36.8 |
| 17 | 25.00 | 75.00 | 4.50 | 1600 | 352 | 18.5 | 16.3 | 78 |
| 18 | 20.00 | 100.00 | 3.50 | 1600 | 83.2 | 28.7 | 28.18 | 94.8 |
| 19 | 20.00 | 100.00 | 4.50 | 1600 | 278.4 | 40 | 38.26 | 82.6 |
| 20 | 20.00 | 100.00 | 3.50 | 1600 | 112 | 23.2 | 22.5 | 93 |