JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF GRADUATE STUDIES

FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING
ENVIRONMENTAL ENGINEERING CHAIR

DEVELOPMENT OF SOLAR PHOTO-FENTON PROCESS FOR THE REMOVAL OF POLLUTANT FROM INSTITUTIONAL WASTEWATER: OPTIMIZATION THROUGH RESPONSE SURFACE METHODOLOGY.

BY: ANDUALEM ARKA AMMONA

A Thesis submitted to School of Graduate Studies, Jimma University, Jimma Institute of Technology, Faculty of Civil and Environmental Engineering in Partial Fulfillment of the Requirements for the Degree Master of Science in Environmental Engineering.

OCTOBER, 2021

JIMMA, ETHIOPIA

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Main-Advisor: Dr.Asaithambi Perumal (Assistant professor)

Co-Advisor: Mr.Seifu Kebede (MSc)

OCTOBER, 2021

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APPROVAL SHEET

As a thesis advisor, we hereby approved that we have read and evaluated this thesis Prepared, under our guidance, by Andualem Arka Ammona entitled Development of solar photo-Fenton (Fe^{2+}/H_2O_2) process for the removal of pollutant from institutional wastewater: optimization through response surface methodology. We recommend that it can be submitted as fulfilling thesis requirement.

Dr.Asaithambi Perumal ____________________ ______________

(MAIN ADVISOR) Signature Date

Mr.Seifu Kebede ____________________ ______________

(CO-ADVISOR) Signature Date

As a member of board examiner of MSc. thesis final defense examination, we certify that we have read, evaluate thesis prepared by Andualem Arka Ammona and examined the candidate. We recommend that, the thesis could be accepted as fulfilling the thesis requirements for the degree of masters of Science in Environmental Engineering.

____________________________ ______________ ______________

(External Examiner) Signature Date

____________________________ ______________ ______________

(Internal Examiner) Signature Date

____________________________ ______________ ______________

(Chair person) Signature Date

DECLARATION

I, Andualem Arka declare that, this proposal entitled “Development of solar photo-Fenton process for the removal of pollutant from institutional wastewater: Optimization through response surface methodology.” is my original work and has not been submitted as a requirement for the award of any degree in Jimma University or elsewhere.

Andualem Arka Ammona	___________	06/10/2021
(Researcher)	(Signature)	(Date)

As research Adviser, I hereby certify that I have read and evaluated this thesis paper prepared under my guidance, by Andualem Arka Ammona entitled “DEVELOPMENT OF SOLAR PHOTO-FENTON PROCESS FOR THE REMOVAL OF POLLUTANT FROM INSTITUTIONAL WASTEWATER: OPTIMIZATION THROUGH RESPONSE SURFACE METHODOLOGY.” and recommend and would be accepted as a fulfilling requirement for the Degree Master of Science in Environmental Engineering.

NAME	SIGNATURE	DATE
Dr.Asaithambi Perumal (Main Advisor)	_________	06/10/2021
Mr.Seifu Kebede (Co – Advisor)	_________	06/10/2021

ABSTRACT

Water is fundamental to survival on earth. It is one of the important needs in human life. Wastewater from public are often rich in color and containing of chemical which needs a proper treatment before it is realizing into the environment. To make sure environmental protection, it is important to find the best method to overcome this environmental problem. It follows experimental methods for the treatment of institutional waste water. The objective of this study was to investigate the performance of employing solar photo-Fenton to treat institutional wastewater from jimma institute of technology. The color and COD removal percentages were analyzed by using an UV/Vis spectrophotometer and closed reflux method respectively. The effect of operating parameters on solar photo-Fenton process such as reaction time, hydrogen peroxide, solar radiation, and ferric on color, COD and turbidity removal were analyzed. The process was experimented by determining dependent variable by using operating independent parameters. The operating parameters were optimized by response surface methodology (design of expert 11.1.2.0). The quadratic regression models with estimated coefficients were selected for the percentage removal of COD, color and turbidity. It was observed that the model predictions match with experimental values with an R^2 *for COD removal, color removal and turbidity removal. The CCD was selected in this study because of its efficiency with respect to number of runs required for fitting a second order response surface model. Finally the study has much significance in using cheap and locally available solar radiation for the institutional wastewater treatment in solar photo Fenton process. The evaluation of this process by a central composite design with response surface methodology was evaluated. The relationship among operating variables such as pH,* H_2O_2 *dosage,* Fe^{2+} *dosage, and reaction time to identify the optimum operating conditions were evaluated. Quadratic models proved to be significant with very low probabilities (<0.0001) for the following responses: chemical oxygen demand (COD), Color and Turbidity. The optimum conditions were* H_2O_2 *dosage (781 mg/L),* Fe^{+2} *dosage (63 mg/L), pH (3.62) and reaction time (118.49 min) in this method. The experimental results of the maximum COD, Color and Turbidity removal rates corresponded well with the predictions, which were 99.78%, 100% and 100 %, respectively. The current study revealed that the solar photo-Fenton process in an advanced oxidation process was well efficient in the institutional wastewater treatment, achieving a 99.78% COD removal at conditions; pH=3.62,* H_2O_2/Fe^{+2} *ratio =12.4. This method achieved well degradation efficiencies for COD, Color and Turbidity reduced the treatment time comparing with the previous study. It was also recommended that the development of solar photo Fenton process effectively works in tropical zone of the globe thus it is better to the implementation of the method in large scale to the treatment of wastewater.*

Key words:- *Wastewater; Solar photo-Fenton process; COD removal; Color removal; Turbidity removal; Central Composite Design; and Optimization.*

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ACRONYMS

ANOVA	Analyses of Variance
AP	Adequate Precision
AoPs	Advanced Oxidation Processes
BBD	Box Behnken Design
BOD	Biological Oxygen Demand
CCD	Central Composite Design
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DoE	Design of Expert
EB	Ethiopian Birr
EPA	Environmental Protection Authority
JIT	Jimma Institute of Technology
MCL	Maximum Contaminant Level
RSM	Response Surface Methodology
SDWA	Safe Drinking Water Act
SPF	Solar Photo Fenton
TDS	Total Dissolved Solids
TS	Total Solid
USEPA	United State Environmental Protection Agency

US	United States
WW	Wastewater
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background

Water is an important resource for life. Entire living organisms on earth need water for life. Today, the quality of water becomes a major problem that needs serious attention. Good quality water has become an expensive item, because many water sources has been polluted by waste coming from the various human activities. This leads to the declining quantity of water sources that could not meet the ever growing need.

Water is an essential natural resource for life. It is a primary need for health, and it should, therefore, be considered as one of the basic human rights. In today's societies, water has become a very precious commodity. Due to its scarcity, it is a necessity of life, and economic development is also dependent on the availability of water. The natural water cycle has a great capacity for purification. But, this ease of regeneration and its apparent abundance make the usual waste dump: pesticides, chemical waste, heavy metals, radioactive waste(Samet and Hmani, 2012).

Water is fundamental to survival on earth. It is one of the important needs in human life. About 75 % of the earth's surface is covered by water, but only a small fraction is really available for human consumption. Increasing water demand from the world population has become a major global concern(Machulek *et al.*, 2012). In recent decades, the scarcity of water resources has become more and more evident and led to reclaimed water use in a variety of applications (Laws *et al.*, 2011).Water is essential for the existence of life on the earth. It provides medium to all biochemical activities in the living organisms. It is used for residential, agricultural and industrial purposes. Due to improper treatment of wastewaters, contaminants are being added in natural water resources. Therefore, water pollution has become a major problem in the world. To meet the environmental standards and regulations, treatment of effluent is must before letting out to the environment.

The reuse of wastewater has become an absolute necessity. Demands to the cleaning industrial and domestic wastewater to avoid environmental pollution and especially contamination of pure water resources are becoming national and international issues. Innovative, cheap and effective methods of purifying and cleaning wastewater before discharging into any other water systems are needed(Faiqun *et al.*, 2007).

At the beginning of the 21st century, the world faces a water quality crisis resulting from continuous population growth, urbanization, land use change, industrialization, food production practices, increased living standards and poor water use practices and wastewater management strategies. Wastewater management has a direct impact on the biological diversity of aquatic ecosystems, disrupting the fundamental integrity of our life support systems, on which a wide range of sectors, from urban development to food production and industry, depend. It is essential that wastewater management be considered as part of an integrated, full life cycle, ecosystem-based management system that operates across all three dimensions of sustainable development (social, economic and environmental), geographical borders, and includes both freshwater and marine waters (Roy, Das and Bhattacharya, 2011). The World Water Forum meeting in March (2012) echoed the problems and the need to bring wastewater to the fore in world water politics and described the existing situation. In a scenario of water-scarcity, wastewater reuse appears to be one of the most attractive options to develop non-conventional water resources, agricultural irrigation being the most established application. Despite wastewater reuse being able to provide important economic benefits by reducing wastewater disposal and irrigation costs, some public health and environmental concerns must be addressed for safe and rational implementation of wastewater reuse in agricultural settings(Jeong and Adamowski, 2016). In recent years, Fenton reaction has been widely applied in the field of environmental remediation, especially for the decontamination of wastewaters containing chemically and biologically recalcitrant organic pollutants(Steter, Brillas and Sirés, 2017). The conventional homogeneous Fenton process used dissolved Fe^{2+} and H_2O_2 to generate hydroxyl radicals ($OH^{\cdot}$), which is the second strongest oxidant only weaker than fluorine. Various organic pollutants could be attacked non-selectively by $\cdot OH$ and decomposed to CO_2, H_2O and inorganic ions(White and Han, 2016)(Liu *et al.*, 2018). However, the major disadvantages that hinder the practical application of the traditional Fenton process include: (i) optimum conditions at strong acidic pH (2.8–3.5); (ii) high iron sludge yield in the final effluent; (iii) high demand for H_2O_2 (Lan *et al.*, 2015)(Brillas, Sire and Oturan, 2009).To overcome these drawbacks, heterogeneous photo-Fenton system has been developed as a promising alternative by virtue of widened application pH range, less iron leaching, and easy separation for cyclic utilization(Li *et al.*, 2016). Photo-Fenton process involves sunlight or an artificial light irradiation, which increases the rate of contaminants degradation by increasing the production of $^{\cdot}OH$ from H_2O_2 decomposition and synchronously accelerating the reduction of Fe^{III} to Fe^{II}. Moreover, the photolysis of H_2O_2 also plays an important role in the photo-Fenton process to break the O–O bond for the production of $OH^{\cdot}$ (Clarizia *et al.*, 2017)(Giannakis, 2019)**.**

$$Fe^{II}+H_2O_2\rightarrow Fe^{III}+ {}^{\cdot}OH + OH^{-} \tag{1}$$

$$Fe^{III}+H_2O_2\rightarrow Fe^{II}+HO_2^{\cdot}+H^{+} \tag{2}$$

$$[Fe^{III}\,(OH)]^{2+}+h\nu\rightarrow Fe^{II}+ {}^{\cdot}OH \tag{3}$$

$$Fe^{III}+H_2O+h\nu\rightarrow Fe^{II}+{}^{\cdot}OH + H^{+} \tag{4}$$

$$Fe^{III}\,(RCO_2) +h\nu\rightarrow Fe^{II}+CO_2+ {}^{\cdot}R \tag{5}$$

$$H_2O_2+h\nu\rightarrow {}^{\cdot}OH \tag{6}$$

$${}^{\cdot}OH + \text{organic pollutants} \rightarrow CO_2+H_2O \tag{7}$$

$$O2+2H^{+}+2e^{-}\rightarrow H_2O_2 \tag{8}$$

As is well-known, it is generally considered that the continuous external supplement of H_2O_2 is indispensable to maintain the photo-Fenton reaction. In this regard, there still exist two problems needing to solve for tradition photo-Fenton. On the one hand, high demand of commercial H_2O_2 will increase the operating cost. On the other hand, H_2O_2 is a powerful oxidizer, which is quite corrosive and unstable, inducing inconvenient and hazardous for transport and storage. So, it is urgent to develop some effective approaches to overcome these drawbacks. On the bright side, some interesting results were discovered that H_2O_2 may be generated on certain special semiconductor materials in aqueous solution under light irradiation(Li *et al.*, 2016). Compared with traditional methods, the photo catalytic synthesis of H_2O_2 has advantages of non-pollution and low energy consumption. Undoubtedly, the discovery is of significance for the development of photo-Fenton process. It is assumed that the cost of H_2O_2 consumption will be saved, and its transportation and storage risk also will be avoided if a proper photo catalyst is developed as an efficient H_2O_2 supplier for a heterogeneous photo-Fenton system. The classic Fenton reaction efficiency was affected by the conversion rate from Fe^{3+} to Fe^{2+}. Recent methods have promoted the in situ circulation from Fe^{3+} to Fe^{2+}.A combination of hydrogen peroxide and UV radiation with Fe^{2+}or Fe^{3+} oxalate ion [photo-Fenton (PF) process] produces more $OH^{\cdot}$ Compared to the conventional Fenton method (Zepp, 1992). The hydroxy-Fe^{3+}complexes after Fenton reaction mainly exists in the form of $Fe(OH)^{2+}$ at pH 2.8–3.5. The photochemical regeneration of Fe^{2+} by photo-reduction of ferric Fe^{3+} occurs in the photo-Fenton reaction. The newly generated Fe^{2+} reacts with $H_2O_2$and generates $^{\cdot}OH$ and Fe^{3+} and the cycle continue:-

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\cdot} \tag{9}$$

Direct photolysis of H_2O_2 produces $OH^{\cdot}$ which can be used for the degradation of organic compounds, and in turn increases the rate of degradation of organic pollutants (Zuot, 1992).

$$H_2O_2 + h\nu \longrightarrow 2OH^{\cdot} \tag{10}$$

Conventional biological processes are usually the most cost effective alternatives for treating these effluents, but it is widely known that high concentrations of toxic or non-biodegradable compounds prevent mineralization(Trovo, 2005). Moreover, 12h are required to achieve chemical oxygen demand (COD) removal efficiencies higher than 90%(Ozbas *et al.*, 2006). Advanced oxidation processes (AOPs) are an efficient alternative that could be used to solve this problem. Among AOPs, the ferrioxalate-induced solar photo-Fenton process is a clean technology that is considered environmentally friendly and competitive at the industrial scale(Monteagudo *et al.*, 2012).

Response surface methodology is used to optimize the parameters chosen for the solar photo-Fenton process. It is a regression analysis used to predict the value of dependent variable based on the controlled values of independent variables. In RSM, the two most common designs extensively used are Box-Behnken Design (BBD) and Central Composite Design (CCD). The CCD was selected in this study because of its efficiency with respect to number of runs required for fitting a second order response surface model. In addition, CCD was ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points(Tak *et al.*, 2015) to provide high quality predictions over the entire design space in comparison with Box-Behnken Design(Tauber *et al.*, 2005).

The combined effect of experimental parameters using statistical analysis by CCD for the four chosen variables was studied. Design of Expert (DoE) version11.1.2.0 was used to optimize and study the effects of the selected operating variables on the treatment efficiency. Experimental data were fitted to a second-order polynomial equation and regression coefficients was been obtained.

Over the last years, the solar photo-Fenton process became one of the most interesting alternative processes for wastewater treatment given its simplicity and feasible application. Especially in sunny regions like Ethiopia (in tropical region), solar water detoxification will have advantages over lamp driven processes and electricity aided treatment technology, because a sufficient amount of solar energy is available with a high degree of foreseeability.

Institutional wastewater is a type of waste generated from household activities, which typically constitutes a combination of flows from the bathroom, kitchen, laundry, as well as the black water and water softeners. These wastes are sometimes defined as sanitary sewage with organic matter as the main component(Kumar *et al.*, 2020).

1.2 Statement of the problem

Wastewater from institution are often rich in color and containing of chemical which is needs a proper treatment before it is realizing into the environment. Under Environmental Regulation the parameter such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and also color effluent does not acceptable. To make sure environmental protection, it is important to find the best method to overcome this problem. That is why most economic, environmentally friendly, locally available and cost effective method of treatment technology was required. Contaminated water, both of the remaining results from human activities and natural issues in the institution bring discomfort to everyday people life. The daily life activity such as cleanings and washing activities contribute large of wastewater quantities. These activities always contribute a problem to the environment and the society. In fact of that, this study looked into the method of manage the institutional wastewater quality.

Nowadays Ethiopia has producing many of wastewater especially from the institutional sector, industrial sector, commercial sector and residential that mostly may affect the environmental life. In order to this problem there are some tertiary treatment methods that can use to reduce this problem such as sonication, electro coagulation, advanced electro coagulation, ozonation, membrane separation, cementation, nanofiltration and biodegradation process.

Large amount of water was used in the jimma institute of technology for different activity and, consequently, significant volume of institutional wastewater was generated. Among environmental problems, water-related ones are the most important to deal with because of the serious threats they represent for humankind. Consequently, solar photo-Fenton process has acquired a notice. Accordingly, the current study has considered the use of solar radiation as energy source in the process of solar photo-Fenton that reduces cost of chemical purchase for the wastewater treatment.

1.3 Objectives

1.3.1 General objective

The main objective of this study is to develop the solar photo Fenton process for the removal of pollutants from institutional wastewater.

1.3.2 Specific objectives

1. To investigate the treatment performance of solar photo Fenton process using four operating parameters.

2. To evaluate the performance of employing the solar photo Fenton process by a central composite design (CCD) with response surface methodology (RSM).

3. To evaluate the statistical relationships among operating variables and the responses removal efficiencies were selected as the responses for optimization.

4. To determine the optimum operational conditions of the solar photo Fenton method.

1.4 Research Questions

1 How the treatment performance of solar photo Fenton process using four operating parameters in removing pollutants from institutional wastewater was investigated?

2 How the performance of employing the solar photo Fenton process by a central composite design (CCD) with response surface methodology (RSM) to degradation of COD, Color, and Turbidity from the institutional wastewater was evaluated?

3 What were the statistical relationships among operating variables and the responses removal efficiencies were selected as the responses for optimization?

4 What was the optimum operational condition of the solar photo Fenton method determined?

1.5 Significance of the study

The major advantage of solar photo-Fenton process is that the Fenton reagents, Fe^{2+} and H_2O_2, are safe to handle and environmentally benign. Because the solar photo-Fenton process requires ferrous salt for the oxidation reaction to take place, the iron sludge formed after the degradation has to be reused or removed before discharging(Palaniandy *et al.*, 2016)

The major significance of the study is, it allows to the planners, decision makers and communities to understand the institutional wastewater treatment system efficiency. The impacts that face planning system are well management in proper treatment of institutional wastewater. Management support tools in achieving sustainable economic development as well as minimizing threats on public health and surrounding environment. This study may use as input for other researchers that will be done on the same area. The process involves artless equipment and is easy to work. It requires low investment, maintenance, energy, and treatment costs. The treated solution gives palatable, pleasant, clear, colorless and odorless water. Highly important in reducing cost of treatment because, it uses solar radiation as source of energy. The solar radiation offers an inexpensive and environmental friendly source of energy, and it will be particularly advantageous if it could be introduced to wastewater treatment processes. Solar radiation is cheaply available in our environment and easily available for everyone. So, it is significantly important in reducing cost of treatment and its availability locally. The hydroxyl radical generated at the time of solar photo-Fenton process facilitates the separation refractory pollutants from wastewater easily. Generally the significance of this study is the solar energy is locally available (cost effective) and environmentally friendly so it is sustainable for the development. Solar radiation I used was a replacement for commercial chemical salts for treating institutional wastewater.

1.6 Scope of the study

The scope of this study was to determine the effect of different parameters in removal efficiency of color, COD and turbidity. And also there was optimization through Response Surface Methodology (RSM). The main scope of this study was to add some value on using or applying the solar photo-Fenton process for the wastewater treatment technology. It was accomplished by locally available solar energy, hydrogen peroxide and ferrous salt. Their treatment potential was evaluated. The study was focused only on the development of technology in removing pollutants from institutional wastewater to avoid the adverse impacts of wastewater on the environment and public health in the Jimma institute of technology, Oromia regional state of Ethiopia. These studies were four parts: I) investigating treatment performance of solar photo-Fenton process using different operating parameters in removing pollutants from institutional wastewater, II) investigating the performance of employing the solar photo Fenton process by a central composite design (CCD) with response surface methodology (RSM) to degradation of COD, Color, and Turbidity from the institutional wastewater, III) evaluating the statistical relationships among operating variables (H_2O_2 dosage, Fe^{+2} dosages, pH and reaction time) and the responses, which COD, Color and Turbidity removal efficiencies were selected as the responses for optimization and IV) determining the optimum operational conditions of the solar photo Fenton method. It was laboratory parts for the preparation of reagents to experiment and also outside the laboratory for the solar radiation. After the experiment done the collected data were used for optimization process. Optimization through RSM was done by using Design of Experiment (DoE) version 11.1.2.0 application.

1.7 Organizations of the study

The thesis of the document was organized from five chapters. Chapter one has focused on introduction, statements of the problems, general and specific objectives, and research questions, significance of the study and the scope of the study. Chapter two focused on literature review related with the study. Chapter three was focused on methods and materials used which includes area of the study, data collection and data processing. Chapter four was about results and discussions and chapter five focused on the conclusions and recommendation.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

The organic WW requires to be managed in a sustainable way to avoid depletion of natural resources, minimize risk to human health, reduce environmental burdens and maintain an overall balance in the ecosystem(Sanz-Bobi *et al.*, 2012).Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharge by domestic residences, commercial properties, industries, institutions or agriculture and can encompass a wide range of potential contaminant and concentration. In the most common usage, it refers to the institutional wastewater that contains a broad spectrum of contaminant resulting from the mixing of wastewater from different usage. Wastewater is characterized in terms of its physical, chemical and biological composition. The main physical properties including color, odor, total solids (TS) and temperature. The biological properties including Carbohydrates, Fats, Oil, Grease, Proteins, and Surfactants and the chemical properties including pH, Chlorides, nitrogen, Phosphorus, Sulfur Gases - Hydrogen sulfide, Methane, Oxygen. Generally waste water is synonymously with sewage. Even though; sewage is a more general term that refers to any polluted water including; wastewater which may contain organic and inorganic substance. In other words, waste water can be describe as using the water with dissolved or suspended solid, discharge from homes, commercial establishment, farms and industries.

Wastewater is simply that part of the water supply to the community or to the industry which has been used for different purposes and has been mixed with solids either suspended or dissolved. Wastewater is 99.9% water and 0.1% solids. The main task in treating the wastewater is simply to remove most or all of this 0.1% of solids. Institutional wastewater is a type of waste generated from household activities, which typically constitutes a combination of flows from the bathroom, kitchen, laundry, as well as the black water and water softeners. These wastes are sometimes defined as sanitary sewage with organic matter as the main component(Kumar *et al.*, 2020). Institutional wastewater contains pollutants and exceed the level of contaminants beyond standards(Kumar, Othman and Mohd-asharuddin, 2020). In recent times, institutional waste water has become a matter of concern because of its potential hazardous effect. A satisfactory level of study to minimize this problem is yet to be reached because of various limitations. Many institutes discard their waste water directly to the surroundings as they do not have proper sewage treatment system(Roy, 2016) and See figure 2.1.

Figure 2.1 Institutional wastewater in jimma institute of technology

2.2 Characteristics of Wastewater

2.2.1 Physical characteristics of wastewater

The important physical characteristic of wastewater is its total solid content, which is composed of floating matter, settliábale matter, colloidal matter, and matter in solution. Other important physical characteristics include odor, temperature, color, turbidity, Odor, pH, Conductivity of wastewater.

2.2.1.1 pH

The pH value of wastewater indicates the negative log of hydrogen ion concentration present in wastewater. The pH= - log H^+. It is, thus, an indicator of the alkalinity of WW. If the pH value is less than 7, the WW is acidic, and if the pH value is greater than 7, the WW is alkaline. The determination of pH value of WW is important, because of the fact that efficiency of certain treatment methods depends upon the availability of a suitable pH value. The pH value can be measured quickly and automatically with the help of pH meter, which measure the electrical potential exerted by the hydrogen ions, and thus indicating their concentration. The hydrogen-ion concentration is an important quality parameter of wastewater. The concentration range suitable for the existence of most biological life is quit narrow and critical. Wastewater with an adverse concentration is not altered before discharge; the wastewater effluent may alter the concentration in the natural water.

2.2.1.2 Total Solids

The total solids content of a wastewater is meaning as all the matter that grains as residue up on evaporation, at 103°C to 10°C matter that has a significant vapor pressure at this temperature is lost during evaporation it is not define as a solid.

Total solids, or residue upon evaporation can be further classified as non-filterable (suspended) or filterable by passing a known volume of liquid through a filter. The dissolved solid consist of both organic and inorganic molecule and irons that are present in true solution in water. The colloidal fraction cannot be removed by settling. The suspended solid are found in considerable quantity in many industrial wastewater. They are screened and settled out at the treatment plant. Solids are removed by settling and separated from wash water are called sludge, which may then be pumped to filter for extraction of additional water. Thus, Total solids are nothing but summation of total dissolved solids and total suspended solids(Engineering *et al.*, 2019)

2.2.1.3 Turbidity

Turbidity is the measure of relative clarity of a liquid. It is the amount of cloudiness in the water(Sheet, no date). It is also an optical characteristic of water and is a measurement of the amount of light that is scattered by material in the water when a light is shined through the water sample. The higher the intensity of scattered light: the higher the turbidity. Excessive turbidity, or cloudiness, in drinking water is aesthetically unappealing, and may also represent a health concern. Turbidity can provide food and shelter for pathogens. The importance of this test is to remove the turbidity of water. It's a measure of the light-transmitting properties of water. WW is normally turbid, resembling dirty dish H2O or WW from baths having other floating matter like faecal matter, pieces of paper, cigarette- ends, match sticks, greases, vegetable debris, and fruit skins, soaps etc. the degree of turbidity can be measured and tested by turbidity rods or by turbid meter. Drinking water should have a turbidity of 5 NTU/JTU or less. Turbidity of more than 5 NTU/JTU would be noticed by users and may cause rejection of the supply. Where water is chlorinated, turbidity should be less than 5 NTU/JTU and preferably less than 1 NTU/JTU for chlorination to be effective(Sheet, 2018).

2.2.1.4 Temperature

Temperature of wastewater is commonly higher than that of water supply. Depending on the geographic location the mean annual temperature varies in the range of 10 to 21^{o}C with an average of 16^{o}C. It affects chemical reactions during the wastewater treatment process. It also affects aquatic life (Like, Fish). Oxygen solubility is less in worm water than cold water. Optimum temperature for bacterial activity is in the range of 25°C to 35. Aerobic digestion and nitrification stop when the temperature rises to 50^{o}C. When the temperature drops to about 15°c, methane producing bacteria become inactive, essential to all environmental studies. Also Controls many ecological processes including chemical reactions. Temperature of surface water varies from space and time. The temperature of ground waters various not only space and time but also with reference to depth. It is measured using thermometer. The temperature of surface water influenced is by atmospheric conditions.

2.2.1.5 Color

Color in water means that the water will absorb light energy in the visual spectral range, i.e. from 400 to 700 nm. Color is the perception registered as radiation of various wavelengths strikes the retina of the eye. Materials decayed from vegetation and inorganic matters create this perception and impart color to water. This color may be objectionable not for health reason but for aesthetics. Natural colors give a yellow-brownish appearance to water, hence, the natural tendency to associate this color with urine. A major provision of the Safe Drinking Water Act (SDWA) is the promulgation of regulations. This promulgation requires the establishment of primary regulations which address the protection of public health and the establishment of secondary regulations which address aesthetic consideration such as taste, appearance, and color. To fulfill these requirements, the U.S. Environmental Protection Agency (USEPA) establishes maximum contaminant levels (MCL). The secondary MCL for color is 15 color units(Engineering *et al.*, 2019).

2.2.1.6 Odor

Odor is produced by gas production due to the decomposition of organic matter or by substances added to the wastewater. Detection of odor: Odor is measured by special instruments such as the Portable H_2S meter which is used for measuring the concentration of hydrogen sulfide.

2.2.2 Chemical Characteristics of wastewater

The chemical characteristics of wastewater are: COD, Hardness, Fluoride, Oil, Grease, Alkalinity, Acidity, Chloride, Iron, Manganese, Sulphate, Sulphide, Dissolved Oxygen, Ammonia Nitrogen, Nitrate Nitrogen, Nitrite Nitrogen and Kjeldahl Nitrogen.

Chemical of wastewater are typically classified as organic and inorganic. Organic constitutes in wastewater can be classified as aggrega and individual. Meanwhile, inorganic constituents in water can be. Divided into individual elements such as Zinc (Zn), iron (Fe), chloride (Cl), and a wide variety of compound, for example, nitrate (NO_3) and sulfate (SO_4). The inorganic and organic compound in the wastewater will be discussed in details in the following discussion.

Points of concern regarding the chemical characteristics of wastewater are:

- Organic matter
- Measurements of organic matter
- Inorganic matter
- Gases

Many parameters have been used to measure the concentration of organic matter in wastewater. The following are the most common used methods:

2.2.2.1 Organic Compounds

Normally, organic compounds are composed of carbon, hydrogen, and oxygen, together with nitrogen in the same cases. Other important elements, such as sulfur phosphorus, and iron, may also be present. Not only the industrial wastewater may contain small quantities of a large number of different synthetic organic molecules ranging from simple to extremely complex in structure. For example include surfactants, organic priority pollutant, volatile organic compounds and agricultural pesticides. The presence of these substances has complicated industrial wastewater treatment because many of them either cannot be or are very slowly decomposed biologically.

2.2.2.2 Chemical Oxygen Demand (COD)

It is the oxygen equivalent of organic matter. It is determined by measuring the dissolved oxygen used during the chemical oxidation of organic matter in 3 hours.

Chemical oxygen demand (COD) is termed as the amount of a specific oxidizing agent that reacts with sample under controlled conditions and it is expressed as oxygen equivalence. This parameter indicates the extent of organic matter contamination of water and is always higher than the biochemical oxygen demand (BOD). It is used to indicate organic matter contamination and it helps in knowing overall organic load to the receiving body.

The COD test is used to measure the organic matter in industrial wastewater that contains compounds that are toxic to biological life. The COD of wastewater is in generally higher than that of BOD_5 because more compounds can be chemically oxidized then can he biologically oxidized. For many types of wastewater, it is possible to correlate COD with BOD_5. This can be very useful because COD can be determined in 3 hours, compare with 5 days for the BOD_5. Once the revelation has been established, COD measurement can be used to good advantage for treatment-plant control and operations.

2.2.2.3 Inorganic Chemicals

Several inorganic components of wastewater are important in establishing and controlling wastewater quality. Industrial wastewater has to be treated for removal of the inorganic constituents that are added in the life cycle. Concentrations of inorganic constituents also are increased by the natural process, which removes some of surface water and leaves the inorganic substance in wastewater.

2.2.3 Biological characteristics of wastewater

The main microorganisms of concern in wastewater treatment are Bacteria, Fungi, Algae, Protozoa, Viruses, and pathogenic microorganisms groups. Mainly characterized by B.O.D. of Wastewater and Coli forms in Wastewater

2.2.3.1 Biological Oxygen Demand (BOD)

BOD5 is the oxygen equivalent of organic matter. It is determined by measuring the dissolved oxygen used by microorganisms during the biochemical oxidation of organic matter in 5 days at 20^{o}C.

The Biochemical Oxygen Demand (B.O.D.) of sewage or of polluted water is the amount of oxygen required for the biological decomposition of dissolved organic matter to occur under aerobic condition and at the standardized time and temperature. Usually, the time is taken as 5 days and the temperature 20°C as per the global standard.

The BOD test is used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test measure the oxygen utilized during a specified incubation period for the biochemical degradation of organic material. It is also used to determine treatment plant efficiency. These parameters are chemical procedure for determining how fast biological organism uses up oxygen in body of water. It is used in water quality management assessment, ecology and environmental science. BOD is not an accurate quantitative test although it could be considered as an inclination of the quality of a water sources.

2.3 Effect of Wastewater on Public Health and Environment

Wastewater contains pathogenic microorganisms lead to dangerous diseases to humans and animals. Hazardous matter such as heavy metals that are toxic Produces, odorous gases and bad smell. Raw Wastewater leads to septic conditions in the environment and consequently leads to the deterioration of surface and groundwater quality and pollutes the soil. Raw wastewater is rich with nitrogen and phosphorus (N, P) and leads to the phenomena of EUTROPHICATION. EUTROPHICATION is the growth of huge amounts of algae and other aquatic plants leading to the deterioration of the water quality. Raw wastewater is rich with organic matter which consumes oxygen in aquatic environment. Raw wastewater may contain toxic gases and volatile organic matter.

Nowadays, it is normally involves determination of dissolved organic and inorganic material are well as suspended solid present in the wastewater. Lack of facilities and miss handling of waste water is polluting the environment and human health. Toxic metal compound have to be identified and quantitatively measured if present even in trace levels.

2.4 Wastewater Treatment

Wastewater treatment or Sewage treatment is the process of removing contaminants from wastewater and household sewage, both runoff (effluents) and domestic. It includes physical, chemical, and biological processes to remove physical, chemical and biological contaminants. Its objective is to produce a waste stream (or treated effluent) and a solid waste or sludge suitable for discharge or reuse back into the environment. There are different processes of wastewater treatment including electrochemical, photo assisted electrochemical, photo catalysis, Fenton, sonication, ozone-assisted electrochemical, Electrocoagulation, UV-ozone process, sono-assisted electrochemical methods, Fenton and radiolytic methods. Hybrid treatment methods such as photo-Fenton, electro-Fenton, and sono-Fenton are not economically viable techniques to degrade large volumes of effluent disposed of by the industries and institutions. Most experimental studies have been conducted at the laboratory scale; thus, a more detailed investigation is required for the Fenton process to be considered feasible for industrial treatment plants. Further research on the advancement of the Fenton process is needed to demonstrate the economic and commercial feasibility of this process(Patients *et al.*, 2012)

2.5 Advanced oxidation process

Advanced oxidation processes (AOPs), in which the hydroxyl radical ($^{\cdot}OH$), being a strong oxidant, is produced, have applications in water and wastewater treatment. At the present time, a variety of technologies are available to produce the $^{\cdot}OH$ radical in the aqueous phase.(Taylor, Sekine, *et al.*, 2012). AOPs have demonstrated to be innovative suitable technologies to reduce organic load or toxicity and enhance biotreatability of landfill leachate, because they are able to oxidize refractory organic compounds into harmless substances and even lead to mineralization end-products such as carbon dioxide and water(Sun *et al.*, 2009). The advanced oxidation processes (AOP) are environmentally friendly technologies and have shown the capability of mineralizing organic pollutants(Álvarez-gallegos *et al.*, 2017). The high efficiency of AOPs is associated with the generation of highly reactive $HO^{\cdot}$ radicals, which can oxidize many organic compounds. Eventually, complete mineralization to CO2, water, and mineral compounds can be obtained(Guzman *et al.*, 2017).

The advanced oxidation processes (AOPs) could be promising towards the degradation of persistent contaminants which are not removed during a biological process. The high efficiency of AOPs is associated with the generation of highly reactive $HO^{\cdot}$ radicals, which can oxidize many organic compounds. Eventually, complete mineralization to CO_2, water, and mineral compounds can be obtained. The most extensively studied AOPs are solar photo-Fenton process (SPF), photo catalysis, UV/H_2O_2, and others(Belén *et al.*, 2021).

2.5.1 Electrochemical treatment method

The electrochemical oxidation is one of the advanced oxidation processes, potentially a powerful method of pollution control, offering high removal efficiencies in compact reactors with simple equipments for control and operation. These processes generally operate at a low temperature and usually prefer adding electrolyte solutes to increase the conductivity of wastewater. In recent years, there has been a growing interest in the treatment of industrial effluents by electrochemical methods(Asaithambi and Matheswaran, 2016).

The electrochemical oxidation is one of the advanced oxidation processes, offering high removal efficiencies in compact reactors with treatment of effluent. Many researchers have investigated the electrochemical oxidation method for the treatment of various types of wastewater containing phenol, pentachlorophenol, tannery, olive mill, coffee curing, textile wastewater, resin, pharmaceutical industrial effluent, deproteinated whey wastewater, distillery spent wash, dairy manure, and organic pollutants. Few investigators have studied the treatment of institutional effluent.

2.5.2 Electrocoagulation

Electrocoagulation is an electrolytic process consisting in the dissolution of sacrificial anodes made out of iron or aluminum upon application of a current between two electrodes for treatment of liquid wastewater containing inorganic or organic matter. As a matter of fact, Al^{3+}or Fe^{2+}/Fe^{3+} ions generated by the dissolution form neutral hydroxide complexes which act as coagulating agents for the suspended pollutants. With an iron anode, $Fe(OH)_n$ with n= 2 or 3 is formed. Two mechanisms have been suggested for this production.(Taylor and Asaithambi, 2015).

Electrocoagulation (EC) is one of the important technologies that combine the advantages of conventional coagulation, flotation, and adsorption in water and wastewater treatment. Process depends on dissolution of the anode electrode. Oxidation reactions take place on anode while reduction reactions occur on cathode(Dizge *et al.*, 2018)

2.5.3 UV-ozone process

Ozone is a strong oxidants having the potential of 2.08 V, reacts with organic directly or indirectly. Previous research has proved that ozone alone degrades the pollutant less effectively. Hence, ozone combined with AOPs degrades the pollutant effectively and efficiently. AOP using ozone and ultraviolet radiation begins with the photolysis of the ozone, which produces the formation of hydroxyl radical as shown in the following reaction(Asaithambi, Saravanathamizhan and Matheswaran, 2014)

$$O_3+H_2O+hv \longrightarrow H_2O_2+O_2 \qquad (11)$$

$$H_2O_2+hv \longrightarrow 2^{\cdot}OH \qquad (12)$$

$$H_2O_2+OH^- \longrightarrow HO_2 + H_2O \qquad (13)$$

The only disadvantage of ozonation process for water treatment is the high energy cost required for its generation.

2.5.4 Sono-Fenton process

The combined treatment using ultrasound with Fenton reagent is known as sono-Fenton, which provides a synergistic effect on organic degradation. Ultrasound can enhance the Fenton's oxidation rate due to the generation of more $^{\cdot}OH$ caused by the cavitation within ultrasonic irradiation. The physical effect of cavitation is the generation of intense convection in the medium through the phenomena of micro turbulence and shock waves, whereas the chemical effect of cavitation is the generation of radical species, such as oxygen ($^{\cdot}O$), hydroperoxyl ($^{\cdot}OOH$), and $^{\cdot}OH$ through the dissociation of solvent vapor during transient collapse of cavitation bubbles. On the other hand, Fe^{3+} continuously reacts with H_2O_2, according to equation (22) below. A part of Fe^{3+} after a Fenton reaction exists in the form of $Fe\text{-}OOH^2$. $Fe\text{-}OOH^2$ can be quickly decomposed into Fe^{2+} and $^{\cdot}OOH$; thereby, the phenomenon promotes the Fe^{3+}/Fe^{2+} redox cycle. In addition, ultrasound provides stirring and mass transfer effects to promote the diffusion of reactants in solution and improve the efficiency of Fenton reaction. However, sono-Fenton has some disadvantages, such as high cost and energy intensive, so it is limited in practical application(Patients *et al.*, 2012).

2.5.5 Fenton process of wastewater treatment

Fenton's reagent, firstly discovered by Fenton in the 1890s (Fenton, 1894), is an aqueous mixture of $Fe^{2+}$and H_2O_2 that produces $^{\cdot}OH$. Hydroxyl radicals can effectively oxidize refractory organic pollutants in wastewater and even completely mineralized them into CO_2, water, and inorganic salts. Due to its high oxidation power, Fenton oxidation process stands out among the most promising AOPs for the treatment of refractory organic pollutants wastewater. In the last few decades, using Fenton oxidation process for the treatment of institutional wastewater has been widely reported. However, Fenton reaction has some limitations in the practical application, such as the requirement for large quantity of chemical reagents, large production of ferric hydroxide sludge, and very slow catalysis of the ferrous ions generation.(Sun *et al.*, 2009). Fenton is considered to be one of the most effective advanced treatment processes in the removal of many hazardous organic pollutants from refractory/toxic wastewater. It has many advantages, but drawbacks are significant such as, the cost of reagents consumption, and the large production of ferric sludge, which limits Fenton's further application(Xu, Wu and Zhou, 2019). The Fenton process has three major steps(Palaniandy *et al.*, 2016).

a) Production of hydroxyl radicals ($^{\cdot}OH$)

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + {}^{\cdot}OH \quad (14)$$

b) Reproduction of Fe^{+2} ions by energy

$$[Fe(OH)]^{+2} + hv \longrightarrow Fe^{+2} + {}^{\cdot}OH \quad (15)$$

$$[Fe(COOCR)]^{+2} \xrightarrow{hv} Fe^{+2} + CO_2 + R \quad (16)$$

c) Degradation of the organic compounds by hydroxyl radicals ($^{\cdot}OH$)

$$^{\cdot}OH + RH \longrightarrow \text{Oxidation products} \quad (17)$$

$$^{\cdot}OH + RH \longrightarrow CO_2 + H_2O \quad (18)$$

2.5.6 Solar photo-Fenton process

The physical, chemical, and biological technologies have been widely used to treat wastewater. However, most of the real wastewater contains many organic pollutants with high toxicity and low biodegradability(Patients *et al.*, 2012). Organic pollutants are very difficult to break down biologically and cannot be treated individually by biological, chemical, and physical methods alone. So that biological technologies are not enough. Moreover, the physical and chemical techniques are often effective for color, macromolecular organics, and suspended matter removal. In order to improve the wastewater quality, advanced treatment needs the removal of refractory organics from the wastewater. To overcome these difficulties, in recent years there has been increasing attention towards advanced oxidation process (AOP) like solar photo Fenton process. Solar photo Fenton has been used to treat refractory wastewater by combining Fenton process with the aid of solar radiation in wastewater treatment technologies.

The Fenton reaction efficiency was affected by the conversion rate from Fe^{3+} to Fe^{2+}. Recent methods have promoted the in situ circulation from Fe^{3+} to Fe^{2+}. A combination of hydrogen peroxide and solar radiation with Fe^{2+} or Fe^{3+} oxalate ion[solar photo-Fenton (SPF) process] produces more OH compared to the Fenton method. The hydroxy-Fe^{3+} complexes after Fenton reaction mainly exists in the form of $Fe(OH)^{2+}$ at pH 2.8–3.5. The solar photo regeneration of Fe^{2+} by photo-reduction (Eq. (19)) of ferric Fe^{3+} occurs in the solar photo-Fenton reaction. The newly generated Fe^{2+} reacts with H_2O_2 and generates $^{\cdot}OH$ and Fe^{3+}, and the cycle continues.

$$Fe(OH)^{2+} + hv \longrightarrow Fe^{2+} + {}^{\cdot}OH \qquad (19)$$

Direct solar photolysis of H_2O_2(Eq. (20)) produces $^{\cdot}OH$, which can be used for the degradation of organic compounds, and in turn increases the rate of degradation of organic pollutants.

$$H_2O_2 + hv \longrightarrow 2{}^{\cdot}OH \qquad (20)$$

Compared with the Fenton process, solar photo-Fenton has many advantages. A solar photo-induced Fe^{3+}/Fe^{2+} redox cycle could decrease the dosage of catalyst in Fenton process, which effectively reduce the formation of iron sludge(Xu, Wu and Zhou, 2019). Meanwhile, solar light can increase the utilization of H_2O_2, and possess solar photolysis on several small molecule organics.

Solar photo-Fenton process is a clean technology that is considered environmentally friendly and competitive at any wastewater treatment(Monteagudo *et al.*, 2012). Over the last years, the solar photo-Fenton process became one of the most interesting alternative process for wastewater treatment, given its simplicity and feasible application(Cruz *et al.*, 2013). Besides the enhancement of the photo-Fenton process for wastewater treatment using natural products and solar radiation, another important factor worthy of consideration is the iron source. Up to date, different iron materials have been tested as precursors of the photo-Fenton process, including natural iron oxide(Mechakra *et al.*, 2016), residue-based iron(Dias *et al.*, 2016) , zero valent metallic iron(Devi, Srinivas and Arunakumari, 2016), magnetic composites(Chai *et al.*, 2016), or modified clays and carbon-based materials(Almazán-sánchez *et al.*, 2015) to promote organic pollutant degradation. However, among the iron species, a special attention is associated to the ferric ion, given that in natural conditions, Fe^{2+} is oxidize to Fe^{3+} by oxygen or H_2O_2, increasing the investigative interest for ferric sources.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-} \qquad (21)$$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+$ (22)

$[Fe^{3+} (OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\cdot}OH$ (23)

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^{\cdot}OH + H^+$ (24)

$Fe^{3+} (RCO_2) + h\nu \rightarrow Fe^{2+} + CO_2 + {}^{\cdot}R$ (25)

$H_2O_2 + h\nu \rightarrow {}^{\cdot}OH$ (26)

$OH^{\cdot}$ + organic pollutants $\rightarrow CO_2 + H_2O$ (27)

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (28)

The major drawbacks of Fenton process were iron complexation by carboxylic intermediates. But these complexes could be photo-activated by solar photo-Fenton process and additional hydrogen peroxide ($HO^{\cdot}$) generation. Therefore, solar photo-Fenton experiments were applied to treat institutional wastewater.

The solar photo-Fenton process was conducted in two ways. One is inside the laboratory to determine results using different parameters. The second one is which conducted in the aid of solar radiation. The experiment uses ferrous salt, hydrogen peroxide and solar light in the different reaction time.

Since solar energy is a widely accessible energy source its application in processes beyond the generation of current or process heat will give a benefit in sustainability to a wide range of industrial techniques. The detoxification of waste water by different solar photo catalytic systems is an extensive worked on research field(Eduardo *et al.*, 2004).

Solar photo-Fenton is based on using solar radiation to increase production of hydroxyl radicals (${}^{\cdot}OH$) and photoactive complexes through the Fenton process. Using solar energy in AOPs could reduce processing costs and make it more affordable for commercial use(Palaniandy *et al.*, 2016).

Table 2.1 Overview of work done in the area of solar photo-Fenton application in recent years

№	The process	Wastewater type	Removed material	Max. removal Efficiency (%)	References
1	UV/H_2O_2/Fe^{2+}	Textile wastewater	Color	91.92 %	(Lima Santos Klienchen Dalari *et al.*, 2020)
2	UV/H_2O_2/Fe^{2+}	Winery wastewater	COD Color	70±3.3% 75±2.2%	(Ioannou and Fatta-Kassinos, 2013)
3	UV/H_2O_2/Fe^{2+}	Citrus wastewater	COD Color	77% 53%	(Pe and Zú, 2018)
4	Fe^{2+}/H_2O_2	Colored wastewaters	Color	95%	(Lon and Koprivanac, 2007)
5	UV/H_2O_2/Fe^{2+}	Municipal wastewater	COD	50%	(Guzman *et al.*, 2017)
6	UV/H_2O_2/Fe^{2+}	Textile industrial wastewater	COD	83%	(Gilpavas,Dobrosz-gómez and Gómez-garcía, 2018)
7	UV/Fe^{2+}/H_2O_2	Industrial wastewater	COD Color	84.40% 96.50%	(Asaithambi *et al.*, 2017)
8	UV/Fe^{2+}/H_2O_2	Wastewater	COD	90%	(Vijay, Peralta-herna and Pacheco-a, 2018)

9	$UV/Fe^{2+}/H_2O_2$	Colored soft drink wastewater	COD	99.3%	(Rizzo *et al.*, 2019)
10	$UV/Fe^{2+}/H_2O_2$	Petroleum wastewater	COD	74.7 %	(Palaniandy *et al.*, 2016)

2.6 Response Surface Methodology

The optimization study is also required to explain the interactions between independent factors and their role in removing contaminants from wastewater. In this matter, response surface methodology (RSM) is among the best methods that can be used to achieve high efficiency with a minimum number of experiments. The effects of two or more variables are determined by factorial design.

In order to optimize the experimental conditions, by solar photo-Fenton process was performed using response surface methodology (RSM) was used. Response Surface Methodology: - RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions(Grätzel and Han, 2015). Response surface methodology (RSM), a multivariate technique which mathematically fits the requirement of the experimental design, is proposed to solve these problems. Its application makes it possible to evaluate the impacts of potential influencing factors on treatment efficiency and figure out their interactions with a limited number of experiments(Grätzel and Han, 2015). The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications. The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs(Ravikumar *et al.*, 2006).

2.7 Research Gap

Solar photo-Fenton process is one of the advanced oxidation processes most investigated for wastewater treatment due to its ability to generate a high amount of hydroxyl radicals by a reaction between iron and the oxidant H_2O_2 which is decomposed into H_2O and O_2 and therefore without generating chemical residues. In the presence of solar radiation as direct energy source, the rate of hydroxyl radicals production increases, the solar photo-Fenton process taking place where the ferric ions (Fe^{3+}) produced during solar photo-Fenton reactions are photo-catalytically converted to ferrous ions (Fe^{2+}), generating additional hydroxyl radicals. The research gap here is that direct usage of solar radiation makes it cost effective because of reduction of cost invested in even purchase of solar panel for energy storage. The solar photo-Fenton process involves the direct photolysis of H_2O_2 by direct radiation that remained from catalysis by ferrous salt. The solar radiation can also be employed to enhance the pollutant decomposition by producing highly reactive $HO^\bullet$ radicals by direct photolysis. Using this process much better COD, color and turbidity reduction efficiency was investigated. Solar Photo-Fenton treatment involves the catalytic breakdown of H_2O_2 in reaction with ferrous iron in an acidic medium (optimum pH = 3.619) to form active transitory species such as $HO^\bullet$, in the presence of natural sunlight. In addition, operating the Fenton process with solar radiation has resulted in added advantages to this type of photochemical advanced oxidation process, as the process is simple and more efficient than solely chemical advanced oxidation processes. Direct photolysis of H_2O_2 produces $OH^\cdot$ which can be used for the degradation of organic compounds, and in turn increases the rate of degradation of organic pollutants.

Therefore the main goal of this study was to develop solar photo-Fenton for pollution reduction of institutional wastewater with low cost (cost effective) and environmentally friendly manner.

CHAPTER 3

MATERIALS AND METHODS

3.1 Sampling location

Jimma town is situated in the southwestern part of Oromia Regional State at latitude of 7^0 40` N and longitude $36^0$ 50` E at a distance of 352 km from Addis Ababa. The town lies on gentle slope with an elevation varying from 1700 meter above sea level to 2020 meter above sea level and it is characterized by temperate humid climatic zone. The existing intake of treatment plant is an impounding weir constructed across Gilgel Gibe River located at X, Y coordinates 265415, 846258m and at an average elevation of 1708 meter above sea level. It is approximately 900 m from Boye treatment Plant Site (Jimma town water supply expansion project, 2018). Jimma Institute of Technology is one of the eminent educational institutions in Ethiopia. This institute has a good number of laboratories in various departments, residential units, students' cafeteria, academic blocks and a number of dormitories for its students.

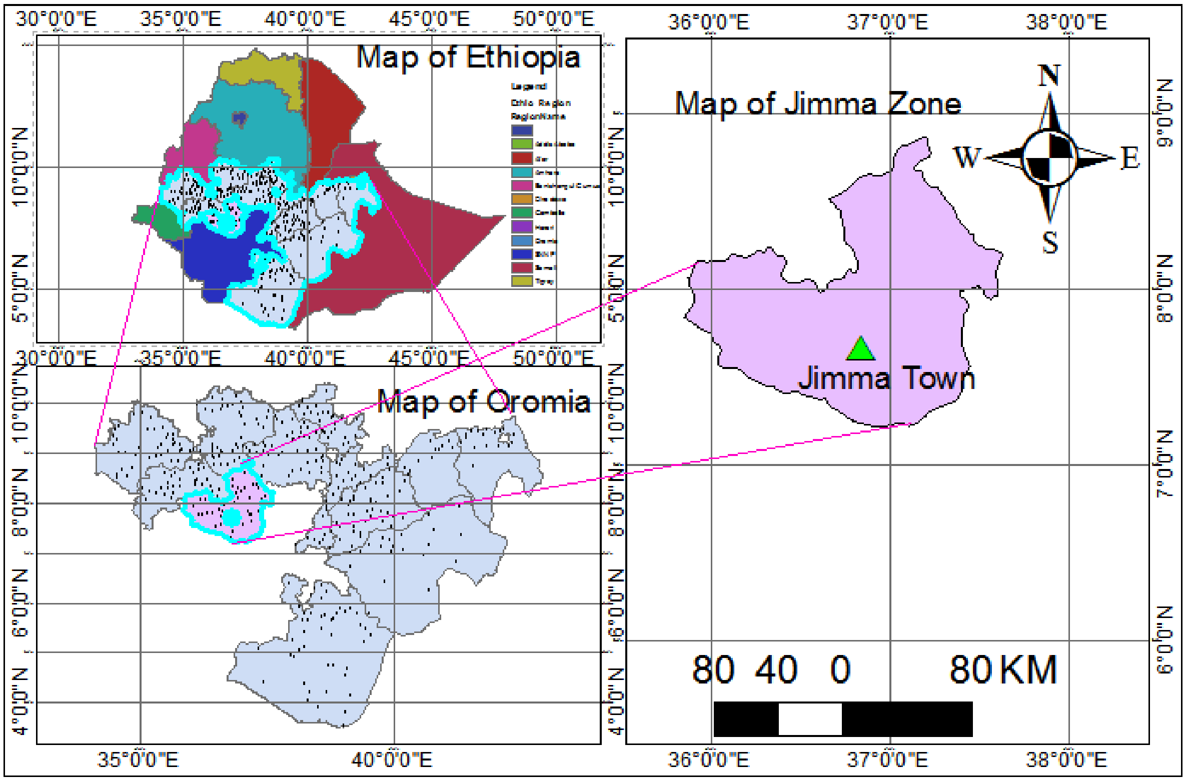


Figure 3.1 Map of study area (Jimma town)

3.2 Materials

Samples of the institutional wastewater were collected from jimma institute of technology (JIT), jimma, Oromia, Ethiopia. Hydrogen peroxide (30%), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) (which was used as source of Fe^{+2} in the solar photo-Fenton treatment) and exposed to direct solar irradiation by sun light. They were used for the solar photo-Fenton process to degradation of COD, color and turbidity. Sulfuric acid (30 %) and sodium hydroxide were used to adjust the pH to the desired values. All the experiments were conducted at room temperature. The weight of substances was measured by the digital weighing balance model. The pH and temperature of the solutions were measured with a professional field proven pH/mV-meter with backlit graphic display. The COD concentration was tested by closed reflux method using different materials such as: COD vial, COD digester, Desiccator, Pipette, Wash bottle, Burette stand, Burette, Conical flask, Dropper, beaker, Color vial, Spoon, Gloves, Tissue paper and funnel. The color absorbance was measured with UV/Vis Spectrophotometer 6700 (Bibby scientific Ltd). COD was estimated before and after treatment. Before each analysis, samples were filtered by glass microfibre filters (circles 55mm diameter, cat no 1827 055).

3.3 Methods

3.3.1 Analytical methods

The COD concentration in wastewater sample was measured by closed reflux method. The color absorbance in wastewater was measured with UV/Vis Spectrophotometer 6700 (Bibby scientific Ltd). The turbidity of wastewater sample and treated water was measured by microprocessor turbidity meter (HI 93703). Dissolved oxygen was measured dissolved oxygen meter (9500 DO_2 meter). The pH was measured by pH meter (pH 3310). Oakton waterproof portable meter kit also measured pH, ORP, ION, Conductivity, TDS, Salinity, Resistivity, Dissolved Oxygen and Temperature. Chemicals used in this study were Potassium dichromate, concentrated sulfuric acid, ferrous ammonium sulphate (FAS), Mercuric sulphate, Silver sulphate, Ferron indicator, Organic free distilled water, Sodium hydroxide, Diluted sulfuric acid, ferrous iron, and hydrogen peroxide.

3.4 Data Source

The data for the study were collected from both primary and secondary data sources.

3.4.1 Primary data

The primary data were collected by using different methods like direct taking of the sample from the source and direct observation of the study area for further clarification. And by direct observing methods which meant that it was the condition of getting good and reliable information by directly looking or observing the institutional waste sample. And also direct measuring of wastewater in laboratory for characterization of different wastewater parameters. The primary data were COD, color, turbidity, DO, TDS, and pH of the sample water.

3.4.2 Secondary data

From various published and unpublished sources, Books, journals and research reports. Secondary data were collected from different written documents in the library.

3.5 Data Collection Procedure

Primary data which was taken from source was with the aid of glove. Data which was obtained by observation was written down in the paper. Secondary data from different books, journals, research reports had been also written down in the note book. Data from laboratory was recorded in the computer and note book for further discussion.

3.5.1 Sampling technique

Sample of the study was taken from of jimma institute of technology. The sampling method had been random sampling technique. Samples were collected by plastic bottles having 20 liter volume. The water sample was taken by inserting the plastic bottle to half meter depth of the wastewater at the different positions. Then the sample collected was merged together to form composite sample. The experimental tests of sample were conducted in jimma university jimma institute of technology environmental engineering laboratory to analyze its characteristics. Then experimental sample were conducted inside the laboratory and outside the laboratory in aid of solar radiation.

3.5.2 Data Quality Assurance

The quality of the data was assured through replication of analysis of the samples in operating procedures for quality purpose and software's (excel software, RSM software) were used for data analysis and report. Wastewater taken from source in plastic bottle having volume of twenty liters was caped there and taken to laboratory to put it in the room temperature to preserve its characteristics. The sample wastewater put in the refrigerator at room temperature in the laboratory before analysis. The control of data for the purpose of quality assurance were handled properly starting from source to end of the experimentation.

3.6 Wastewater characteristics

The physiochemical characteristics of the institutional wastewater from jimma institute of technology (JIT) were summarized in Table 3.1. Samples of the institutional waste water were collected on different days. Samples were transferred to the laboratory and stored under refrigeration until use. Samples were characterized before the experiments to obtain their chemical and physical properties. The institutional wastewater characterization was determined by the quantification of chemical oxygen demand (COD), pH, conductivity, total dissolved solids (TDS), dissolved oxygen (DO), turbidity, odor, temperature and color according to the standard methods for the examination of waste water methodology.

Table 3.1 Characteristics of the institutional wastewater from jimma institute of technology

№	Parameters	Range of concentrations in institutional wastewater
1	COD	1296 mg/L
2	pH	6.54
3	Conductivity	2.508 Micro S/cm
4	TDS	1358 mg/L
5	DO	46 mg/L
6	Turbidity	89.65 NTU
7	Temperature	20.9 ^{o}C

8	Odor	Objectionable
9	Color	Dark brown

3.7 Experimental Setup

The solar Photo degradation of experiments were carried out in a 500 mL beaker (Figure 3.2 below) under natural solar irradiation, outside the Laboratory of Environmental Engineering, jimma institute of technology, jimma university by mixture of hydrogen peroxide, ferrous salt and adjusting to different pH with 500 ml sample. The experiment repeated for thirty runs. The working volume of beaker was 500 ml. The Fe concentration used in all SPF experiments was 0.01, 0.045, and 0.08 g/L. The H_2O_2 concentration used in all SPF experiment was 0.5, 0.75, and 1 g/L. The reaction time interval used in all SPF experiment was 60, 120, and180 min. The pH was adjusted at the beginning of each run to the range from 2 to 6. All pH adjustments were done with analytical grade sodium hydroxide (NaOH) and sulpheric acid (H_2SO_4). The pH range used in all experiment was 2, 4, and 6. During the solar photo-Fenton treatment, the wastewater was exposed to solar light for different duration of time.

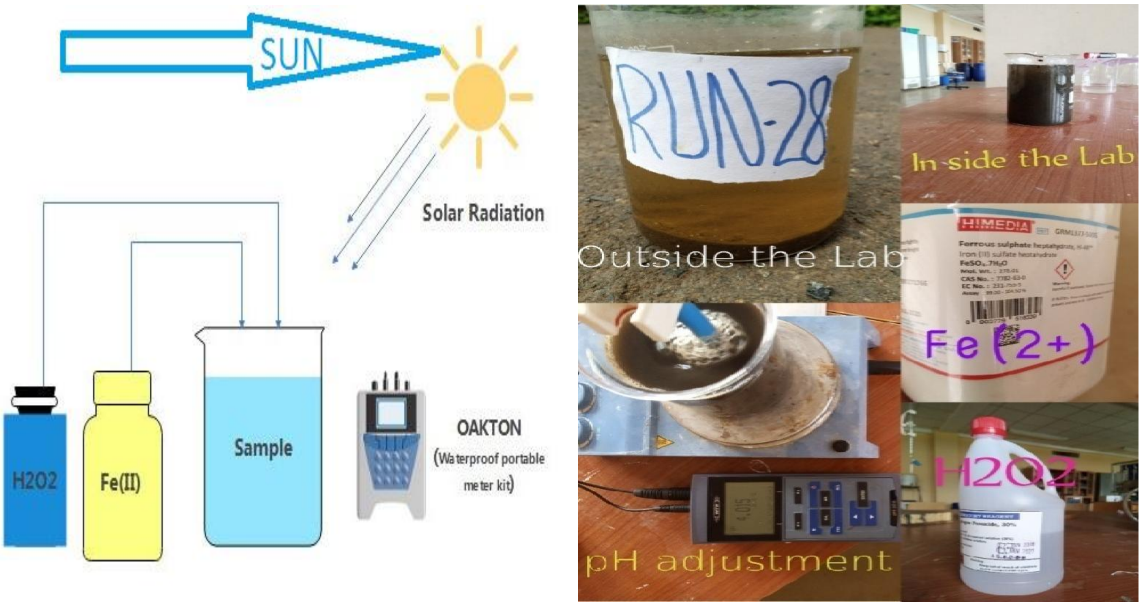


Figure 3.2 Experimental setup of solar photo Fenton process

3.8 Analysis and interpretations

The collected data were analyzed by using descriptive Statistical analysis and the output was expressed by using tables and graphs. The data also were analyzed at 95% confidence interval. The results of turbidity, color and COD removal were analyzed by a multi-factorial analysis of variance (ANOVA) using the program design expert version 11.1.2.0. Analyses of variance (ANOVA) performed to determine which of the factors evaluated or which combination of factors have a significant effect on turbidity, color and COD removal. And also charts were used for comparison of operating parameters.

3.8.1 The Percentage COD Removal

Chemical Oxygen Demand (COD) of wastewater is a measurement of the amount of oxygen required to oxidize (decrease) the organic matter content of a sample that is susceptible to oxidation by strong oxidant (such as potassium dichromate). Most organic compound will oxidize under the influence of oxidizing agents in acid conditions-oxidation of most organic compounds is 95-100% of the theoretical value. BOD values are often lower than COD values as some materials (such as cellulose) will react with the dichromate present in COD tests, but not the oxygen present under biological conditions(Vijay, Peralta-herna and Pacheco-a, 2018).

$$\% \, COD \, removal = \frac{\text{CODi} - \text{CODt}}{\text{CODi}} * 100 \qquad (29)$$

Where: COD_i is initial Chemical Oxygen Demand (mg/L) and,

COD_t is the Chemical Oxygen Demand at time t (mg/L).

I) Determination of COD

Procedure

1 Wash 25 mL of COD vials.

2 In COD vials put 0.05 g of $HgSO_4$ + 2.5 mL sample + 1.5mL $K_2Cr_2O_7$ + 3.5 mL concentrated H_2SO_4.

3 Add small amount of silver sulphate.

4 Shake well and reflux for 2 hr.

5 Cool and add little amount of distilled water to the flask through the condenser.

6 Titrate the solution in the flask against FAS using Ferron indicator

7 End point green color to reddish brown

Figure 3.3 COD measuring processes at the laboratory

3.8.2 The Percentage Color Removal

In water and wastewater treatment, we make a distinction between true color and apparent color. True color is the result of dissolved organic minerals or chemicals in water. When testing the color of a water sample the goal is to measure the true color of the water. However, suspended materials in the water (turbidity) can change the apparent color of the water (the color of the water before treatment). Two types of procedures can be used to measure the color in water the visual method or the instrumental method(Palaniandy *et al.*, 2016). The visual method is the simplest since it consists of a water sample being compared to a series of colored slides or tubes. This method can be used in most cases, but it is not appropriate for use on water which has been contaminated by institutional wastes(Steter, Brillas and Sirés, 2017). Various instrumental methods can be used to create a more accurate portrayal of the water's color if the color cannot be matched using the visual method. In this study color was measured at the wavelength corresponding to maximum absorbance λ max (450 nm) using UV/Vis spectrophotometer.

$$\%\ Colorremoval = \frac{\mathrm{Absi}-\mathrm{Abst}}{\mathrm{Absi}} * 100 \qquad (30)$$

Where: Abs_i is the initial maximum absorbance to corresponding wavelength λ max and,

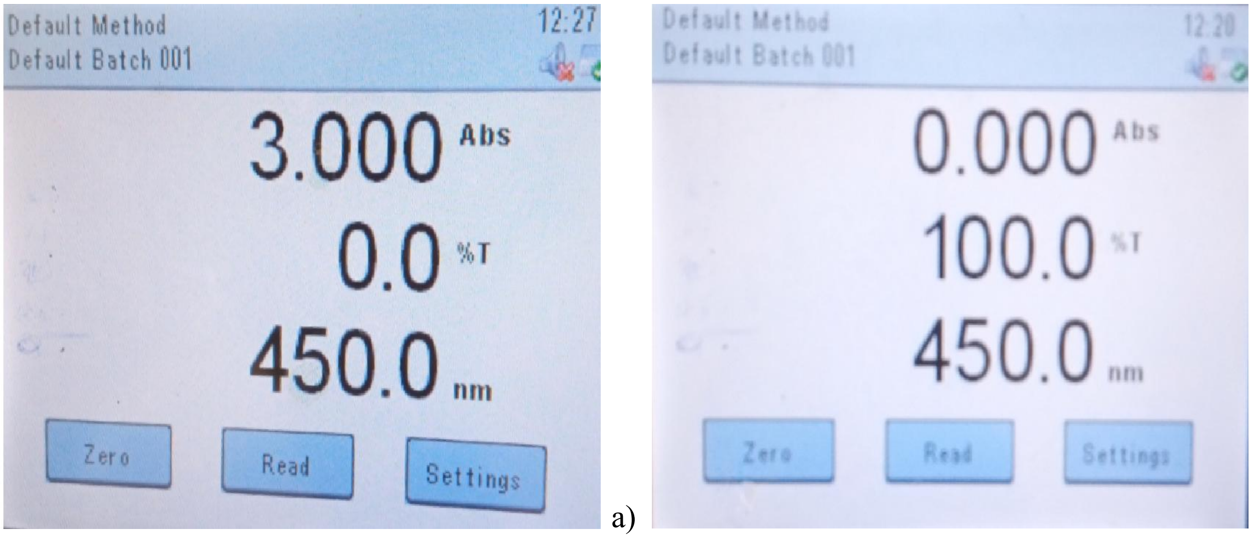
Abs_t is the maximum absorbance after t time to corresponding wavelength λ max.

I) Determination of color

Procedure

1. Prepare sample holder
2. Add sample to sample holder
3. Calibrate UV/Vis spectrophotometer
4. Fix the values to acceptable range
5. Put the sample to the UV/Vis spectrophotometer
6. Run the operation
7. Take the reading

Figure 3.4 UV/Vis spectrophotometer for color measurement


Default Method
Default Batch 001
12:27
3.000 Abs
0.0 %T
450.0 nm

Default Method
Default Batch 001
12:20
0.000 Abs
100.0 %T
450.0 nm

a)

b)

Figure 3.5 a) Absorbance before treatment and b) Absorbance after treatment

3.8.3 The Percentage Turbidity Removal

Turbidity is the amount of cloudiness in the water. It is very important to measure the turbidity of institutional wastewater, as these supplies often undergo some type of water treatment which can be affected by turbidity. For example, during the rainy season when mud and silt are washed into rivers and streams, high turbidity can quickly block filters and stop them from working effectively. High turbidity will also fill tanks and pipes with mud and silt, and can damage valves and taps. Turbidity can be measured using either an electronic turbidity meter or a turbidity tube. Both methods have advantages and disadvantages, as shown below. Turbidity is usually measured in nephelometric turbidity units (NTU) or Jackson turbidity units (JTLJ), depending on the method used for measurement. The two units are roughly equal. Drinking water should have a turbidity of 5 NTU/JTU or less(Sheet, 2019).

$$\% \text{ Turbidity removal} = ((\text{Turbidity}_{\text{initial}} - \text{Turbidity}_{\text{final}}) / \text{Turbidity}_{\text{initial}}) * 100$$

I) Determination of Turbidity

Procedure:

1. Switch on the turbidity meter.

2. Prepare 400 NTU solution.

3. Calibrate the turbidity meter to 400 NTU using the standard solution by adjust the calibration knob.

4. Calibrate the turbidity meter to 0 NTU using the distilled water by adjust the calibration knob.

5. Read the turbidity meter by inserting the sample.

a) b)

Figure 3.6 Turbidity measurement of the sample a) before treatment and b) after treatment

3.9 Study Period and Design

The study was conducted from February 2021 to August 2021. Three major activities were carried out throughout the study period. The first activity was taking wastewater sample from of jimma institute of technology. Next activity was characterization of the raw wastewater sample which was finding of the pollution concentration and the results were recorded. The characterization activity was included color, chemical oxygen demand (COD), turbidity, conductivity, total dissolved solid (TDS), dissolved oxygen (DO), temperature, odor and pH. The final task was treatment of the institutional wastewater sample by using solar photo Fenton process.

3.9.1 Study design

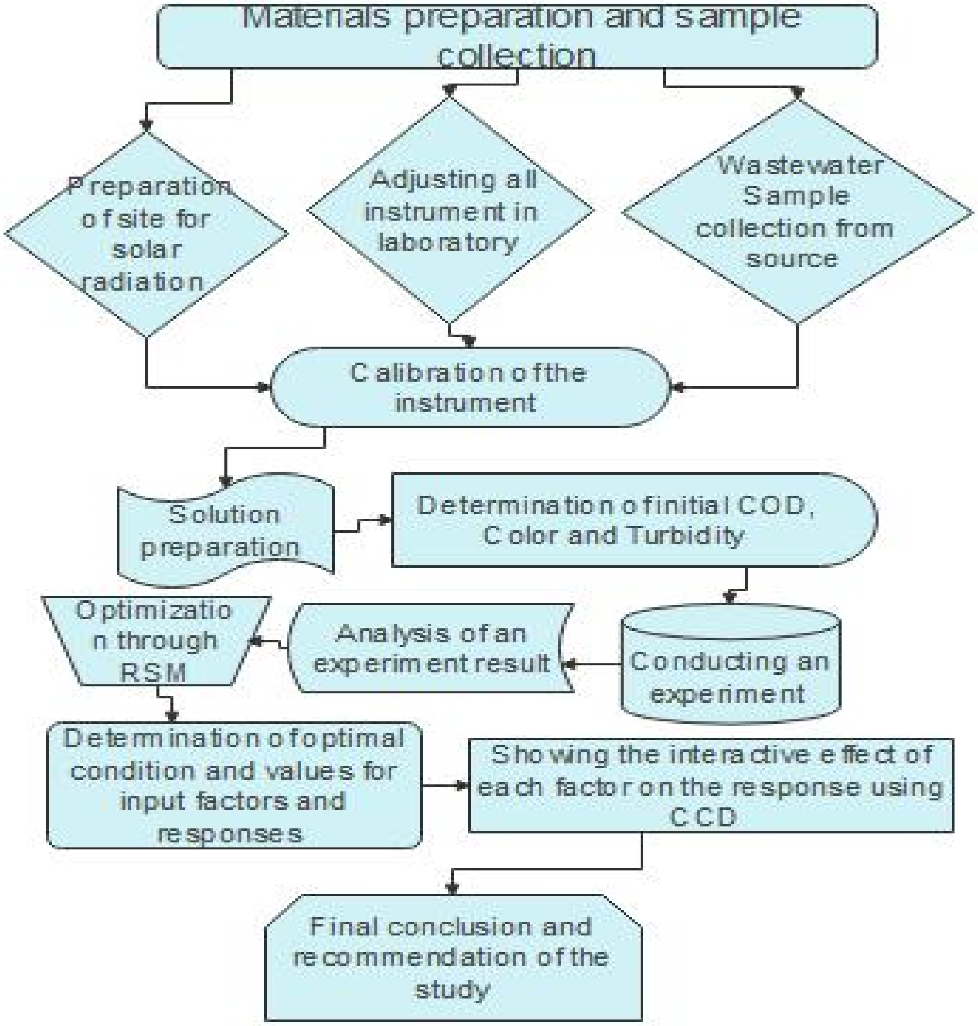


Figure 3.7 Flow chart of study design

3.10 Study Variables

The main study variables are dependent and independent variables.

3.10.1 Dependent variables

- Chemical oxygen demand(COD)
- Color
- Turbidity

3.10.2 Independent variables

- Initial Hydrogen peroxide concentration(H_2O_2)
- Reaction time(contact time)
- Initial iron concentration(Fe^{2+})
- Initial effluent pH

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 EXPERIMENTAL DESIGN AND THE ANALYSIS OF VARIANCE (ANOVA)

Central composite design and response surface methodology were employed in the statistical design of the experiments, data analysis, explaining the optimal conditions of the independent variables and assessment of the relationships among four significant independent variables, which were pH,H_2O_2 dosage, Fe^{+2} dosage, and reaction time as shown in Table 4.1.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO + HO^{\cdot} \quad (31)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(OH)^{+2} + HO^{\cdot} \quad (32)$$

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + HO^{\cdot} \quad (33)$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + HO^{\cdot} + H^{+} \quad (34)$$

The $HO^{\bullet}$ formed in these above reactions react with organic species (RH) present in the system, promoting their oxidation, as indicated in the equation 35.

$$HO^{\cdot} + RH \longrightarrow H_2O + R^{\cdot} \quad (35)$$

The regeneration of Fe^{2+} by photo-reduction of Fe^{3+}, supports the solar photo-Fenton process. The complex Fe $(OH)^{2+}$ is fundamental for the required reaction, because large amount ($^{\cdot}OH$) hydroxyl radicals are available during its solar photo-reduction. However, a pH around 2.8 is the optimal for Fenton-like reactions. Under this condition, both Fe^{3+} and Fe $(OH)^{2+}$ have approximately the same concentration which is fundamental for an efficient degradation process. At lower pH, $Fe(OH)^{2+}$ concentration decreases, and at higher pH Fe^{3+} hydroxide precipitates(Machado *et al.*, 2004). The solar photo-Fenton reaction possesses a better efficiency at acidic conditions of pH=3.619.

The adequacy of the proposed model for degradation of COD, Color and Turbidity of the Institutional wastewaters by solar photo Fenton process was evaluated at optimum conditions. Each independent variable was varied over three levels according to face centered CCD as -1, 0, and +1 respectively at the determined ranges based on a set of preliminary experiments. The total number of experiments conducted for the four factors according to Equation 36.

№ of Experiments=2^k+2k+6 (36)

Where, k was the number of factors.

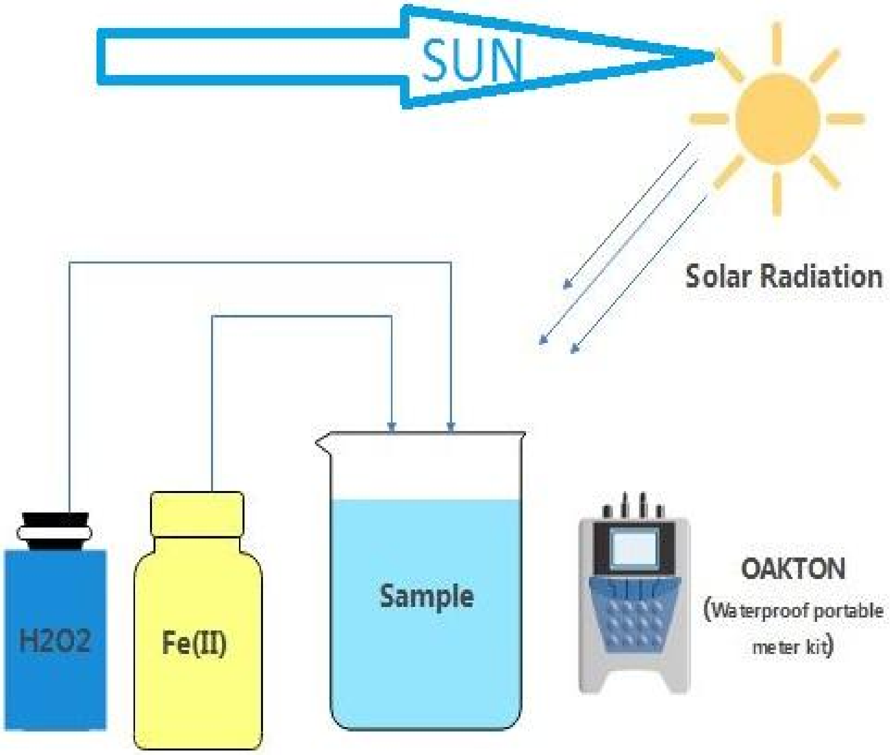


Figure 4.1 A sketch of the solar photo-Fenton process

Table 4.1 Central composite design (CCD) independent variables

The factors	Level of value		
	-1	0	+1
pH	2	4	6
H_2O_2(g/L)	0.5	0.75	1
Fe^{+2}(g/L)	0.01	0.045	0.08
Reaction time(min)	60	120	180

The design consisted of 2^k factorial points augmented by 2k axial points and six replications for a center point. In this work, the total number of experiments conducted for the four factors were 30 with 16 factorial points, eight axial points and six replications to assess the pure error and got a good estimate. The COD, Color and Turbidity removal were the dependent variables (responses) during this process. Performance was evaluated by analyzing the COD, Color and Turbidity removal efficiencies as shown in Table 4.2.The behavior of the system was explained through an empirical second-order polynomial model, as shown in Equation 37:(Calfee and Piontkowski, 2016)

$$Y = b_o + \sum_{j=1}^{n} b_j x_j + \sum_{j=1}^{n} b_{jj} x_j^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} b_{ij} x_i x_j + e_i \qquad (37)$$

Where, Y was the response, X_i and X_j were the variables, b was the regression coefficient, n was the number of factors studied and optimize in the experiment, e_i was the random error.

Table 4.2 Measured results for each Run

Run	H_2O_2(g/L)	Fe^{2+}(g/L)	pH	RT(min)	COD removal (%)		Color removal (%)		Turbidity removal (%)	
					Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.75	0.045	4	120	95	91.47	99.4	95.87	99.7	96.16
2	1	0.01	2	180	79	72.44	83.4	76.84	83.7	77.09
3	1	0.08	6	180	58.2	57.6	62.6	62	62.9	62.3
4	0.5	0.08	6	180	40.3	39.47	44.7	43.87	45	44.1
5	0.75	0.045	4	120	87	91.47	91.4	95.87	91.7	96.16
6	0.75	0.045	4	120	94	91.47	98.4	95.87	98.7	96.16
7	1	0.045	4	120	89	90.14	93.4	94.54	93.7	94.88
8	0.5	0.045	4	120	77	72.74	81.4	77.14	81.7	77.44
9	0.75	0.045	6	120	69	68.7	73.4	73.1	73.7	73.4

10	1	0.08	2	60	65	65.01	69.4	69.41	69.7	69.71
11	0.5	0.08	6	60	36.7	41.52	41.1	45.92	41.1	46
12	0.5	0.01	6	180	35.9	34.15	40.3	38.55	40.6	38.89
13	0.75	0.045	4	180	86	85.13	90.4	89.53	90.7	89.87
14	0.75	0.045	4	120	89.5	91.47	93.9	95.87	94.2	96.16
15	0.5	0.01	2	60	38.1	36.97	42.5	41.37	42.8	41.7
16	0.75	0.045	2	120	85	82.19	89.4	86.59	89.7	86.92
17	1	0.01	6	180	45.4	48.38	49.8	52.78	50.1	53.11
18	0.5	0.01	6	60	31	30.25	35.4	34.65	35.7	34.91
19	1	0.08	6	60	53.8	52.5	58.2	56.9	58.5	57.13
20	0.75	0.01	4	120	79.5	81.82	83.9	86.22	84.2	86.42
21	0.75	0.045	4	60	79	76.75	83.4	81.15	83.7	81.45
22	1	0.01	2	60	50.3	53.64	54.7	58.04	55	58.37
23	0.75	0.045	4	120	89	91.47	93.4	95.87	93.7	96.16
24	0.5	0.01	2	180	44.8	48.62	49.2	53.02	49.5	53.35
25	1	0.01	6	60	39.6	37.33	44	41.73	44.3	42.06
26	0.5	0.08	2	60	44.9	44.44	49.3	48.84	49.6	49.06
27	0.5	0.08	2	180	49.6	50.14	54	54.54	54.3	54.84
28	0.75	0.045	4	120	85	91.47	89.4	95.87	89.7	96.16
29	0.75	0.08	4	120	95.6	90.16	100	94.56	100	94.7
30	1	0.08	2	180	74.6	77.86	79	82.26	79.3	82.56

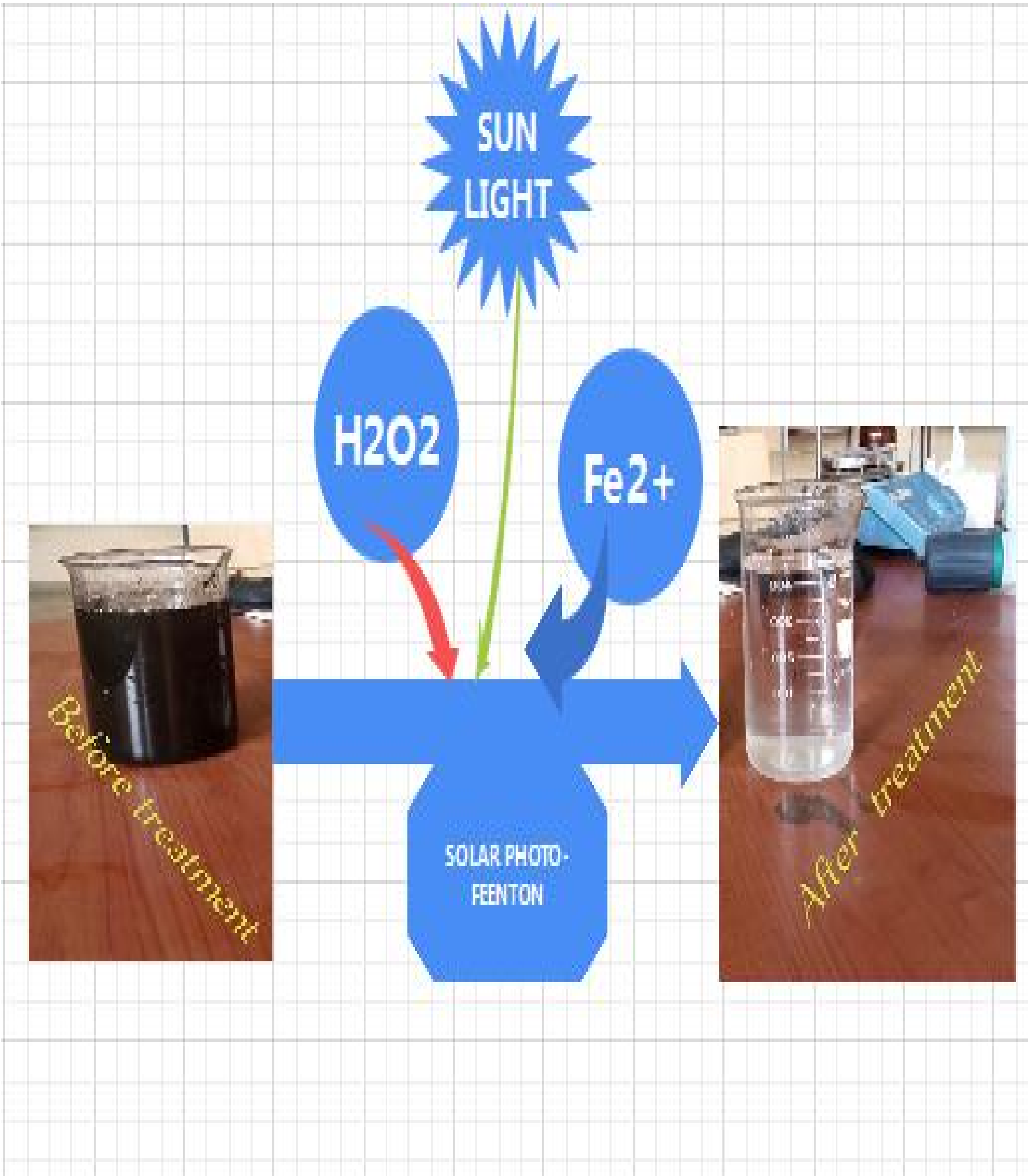


Figure 4.2 Solar photo-Fenton process depicts of wastewater treatment

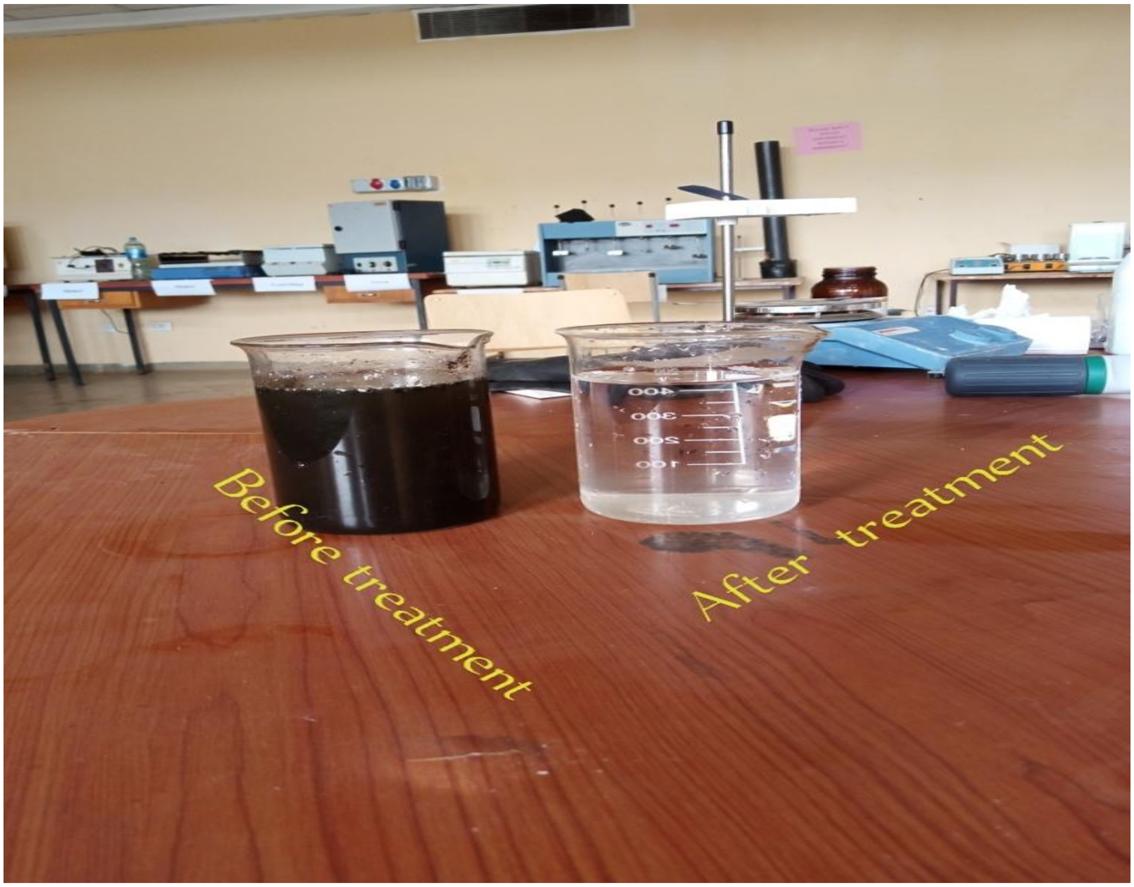


Figure 4.3 Wastewater before treatment and after treatment

4.2 Analysis of variance

The most important factors that affect the solar photo-Fenton (SPF) process are hydrogen peroxide, ferrous iron, initial effluent pH and reaction time in the reaction. In order to study the combined effect of these factors the experiments were conducted at different combinations of operating parameters. The encoded values and the corresponding percentage of COD removal, color removal and turbidity removal along with predicated values are given in Table 4.2.

The analysis of variance (ANOVA) was used for graphical analysis of data to obtain the interaction between the process variables and the responses. The quality of the fit polynomial model was expressed by coefficient of determination (R^2). Model terms were evaluated by the P value (probability) with 95 % confidence level. The analysis of variance (ANOVA) for COD, color and turbidity removal was represented in Table 4.3, 4.5, and 4.7. All the response surface quadratic models for parameters in this table were significant at the 5 % confidence level since the P values were less than 0.05. The correlation coefficients (R^2) for the COD, Color and Turbidity removal rates were 0.9791, 0.9795 and 0.9797 respectively, which were greater than 0.80, the cut-off for a model with good fit. A high coefficient (R^2) value ensured a satisfactory adjustment of the quadratic model to the experimental data and illustrated good agreement between the calculated and observed results and showed that a desirable and reasonable agreement with the adjusted R^2(Taylor *et al.*, 2016).

If the model terms had the P value (probability) more than 0.05, they were considered limited influence. So, they had to be excluded from the study to improve the models. The model of COD, Color and turbidity removal were considered significant using the F test at 5 % significant level ($P<0.05$). The ‘‘adequate precision’’ (AP) ratio values higher than four were desirable and confirm that the predicted models could be used to navigate the space defined by the central composite design (CCD)(Noordin *et al.*, 2004). The ‘‘adequate precision’’ (AP) ratio of the models in this study was adequate, which varied between 19.907, 20.056 and 20.064.

The regression method was used to fit the second order polynomial to the experimental data and to identify the relevant model term. The final equations obtained in terms of coded factors for percentage COD removal, color removal and turbidity removal are given by the Equation (38), (39), and (40) respectively.

$$\text{COD removal (\%)} =+91.47+8.70\,A+4.17\,B-6.74\,C+4.19\,D+0.9750\,AB-2.40\,AC+1.79\,AD+0.9500\,BC-1.49\,BD-1.94\,CD-10.03\,A^2-5.48\,B^2-16.03\,C^2-10.53\,D^2 \ldots\ldots (38)$$

$$\text{Color removal (\%)} = +95.87+8.70\,A+4.17\,B-6.74\,C+4.19\,D+0.9750\,AB-2.40\,AC+1.79\,AD+0.9500\,BC-1.49\,BD-1.94\,CD-10.03\,A^2-5.48\,B^2-16.03\,C^2-10.53\,D^2 \ldots\ldots (39)$$

Turbidity removal (%) = $+96.16+8.72\ A+4.14\ B-6.76\ C+4.21\ D+0.9937\ AB-2.38\ AC+1.77\ AD+0.9312\ BC-1.47\ BD-1.92\ CD-10.00\ A^2-5.60\ B^2-16.00\ C^2-10.50D^2$………..……………………………………..(40)

Table 4.3 ANOVA for Quadratic model of COD

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	**Remark**
Model	13283.83	14	948.84	50.16	< 0.0001	Highly significant
A-H_2O_2	1362.42	1	1362.42	72.02	< 0.0001	Highly significant
B-Fe^{2+}	313.33	1	313.33	16.56	0.001	Highly significant
C-pH	818.78	1	818.78	43.28	< 0.0001	Highly significant
D-RT	315.84	1	315.84	16.7	0.001	Significant
AB	15.21	1	15.21	0.8041	0.384	
AC	92.16	1	92.16	4.87	0.0433	Significant
AD	51.12	1	51.12	2.7	0.121	
BC	14.44	1	14.44	0.7633	0.3961	
BD	35.4	1	35.4	1.87	0.1914	
CD	60.06	1	60.06	3.18	0.095	
A^2	260.78	1	260.78	13.79	0.0021	Significant
B^2	77.88	1	77.88	4.12	0.0606	
C^2	665.97	1	665.97	35.21	< 0.0001	Highly significant
D^2	287.42	1	287.42	15.19	0.0014	Significant
Residual	283.75	15	18.92			
Lack of Fit	207.54	10	20.75	1.36	0.3858	
Pure Error	76.21	5	15.24			
Cor Total	13567.58	29				

Table 4.4 Fit Statistics of COD removal

Std. Dev.	4.35	R^2	0.9791
Mean	66.23	Adjusted R^2	0.9596
C.V. %	6.57	Predicted R^2	0.8939
		Adeq. Precision	19.907

Table 4.5 ANOVA for Quadratic model of Color

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	**Remark**
Model	13283.83	14	948.84	50.16	< 0.0001	Highly significant
A-H_2O_2	1362.42	1	1362.42	72.02	< 0.0001	Highly significant
B-Fe^{2+}	313.33	1	313.33	16.56	0.001	significant
C-pH	818.78	1	818.78	43.28	< 0.0001	Highly significant
D-RT	315.84	1	315.84	16.7	0.001	significant
AB	15.21	1	15.21	0.8041	0.384	
AC	92.16	1	92.16	4.87	0.0433	significant
AD	51.12	1	51.12	2.7	0.121	
BC	14.44	1	14.44	0.7633	0.3961	
BD	35.4	1	35.4	1.87	0.1914	
CD	60.06	1	60.06	3.18	0.095	
A^2	260.78	1	260.78	13.79	0.0021	significant
B^2	77.88	1	77.88	4.12	0.0606	
C^2	665.97	1	665.97	35.21	< 0.0001	Highly significant
D^2	287.42	1	287.42	15.19	0.0014	significant
Residual	283.75	15	18.92			

Lack of Fit	207.54	10	20.75	1.36	0.3858	
Pure Error	76.21	5	15.24			
Cor Total	13567.58	29				

Table 4.6 Fit Statistics of color removal

Std. Dev.	4.35	R^2	0.9795
Mean	70.63	Adjusted R^2	0.9598
C.V. %	6.16	Predicted R^2	0.8942
		Adeq Precision	20.056

Table 4.7 ANOVA for Quadratic model of Turbidity

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	Remark
Model	13284.39	14	948.89	50.22	< 0.0001	Highly significant
A-H_2O_2	1367.64	1	1367.64	72.38	< 0.0001	Highly significant
B-Fe^{2+}	308.35	1	308.35	16.32	0.0011	Significant
C-pH	822.83	1	822.83	43.54	< 0.0001	Highly significant
D-RT	318.36	1	318.36	16.85	0.0009	Significant
AB	15.8	1	15.8	0.8362	0.375	
AC	90.73	1	90.73	4.8	0.0446	Significant
AD	50.06	1	50.06	2.65	0.1244	
BC	13.88	1	13.88	0.7343	0.405	
BD	34.52	1	34.52	1.83	0.1966	
CD	58.91	1	58.91	3.12	0.0978	
A^2	258.86	1	258.86	13.7	0.0021	Significant

B^2	81.12	1	81.12	4.29	0.0559	
C^2	662.91	1	662.91	35.08	< 0.0001	Highly significant
D^2	285.41	1	285.41	15.1	0.0015	Significant
Residual	283.45	15	18.9			
Lack of Fit	207.24	10	20.72	1.36	0.3864	
Pure Error	76.21	5	15.24			
Cor Total	13567.84	29				

Table 4.8 Fit Statistics of Turbidity removal

Std. Dev.	4.35	R^2	0.9797
Mean	70.91	Adjusted R^2	0.9599
C.V. %	6.13	Predicted R^2	0.8944
		Adeq. Precision	20.064

4.3 Effect of operating parameters and optimization

4.3.1 The effect of hydrogen peroxide (H_2O_2)

The dosing rate of H_2O_2 is considered to be one of the most important factors which should be considered in the solar photo Fenton process. It was found that COD, color and turbidity removal efficiency increases with increasing the dosing rate of hydrogen peroxide from 0.5g/L to 0.75g/L. The highest percentage removal of COD was attained at time 118.478 min, iron concentration of 63mg/L and initial effluent pH of 3.619 when using a H_2O_2 dosing rate of 781mg/L so further addition of H_2O_2 is not necessary. Excessive H_2O_2 reacts with $OH^\bullet$ (Equation

(41)) competing with organic pollutants and consequently reducing treatment efficiency. Excessive of H_2O_2 may cause unutilized of hydroxyl radical.

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (41)$$

The H_2O_2 is the main source of $^{\bullet}OH$ in the SPF process. H_2O_2 is an oxidant widely used for water treatment due to its oxidation potential of around 1.4 V at near-neutral pH(Spuhler and Antonio, 2016). Moreover, it is cheap, safe, easy to handle and does not generate residues as it easily decomposes to water and oxygen. As a matter of fact, H_2O_2 alone (even at non-toxic microbial concentration, lower than 50 mg/L) in combination with natural sunlight can promote very high microbial inactivation rates (Ferro et al., 2015).

In order to find out the optimum condition in solar photo Fenton reaction different dosage of hydrogen peroxide were added to the solution. All experiments were exposed to different duration of solar radiation.

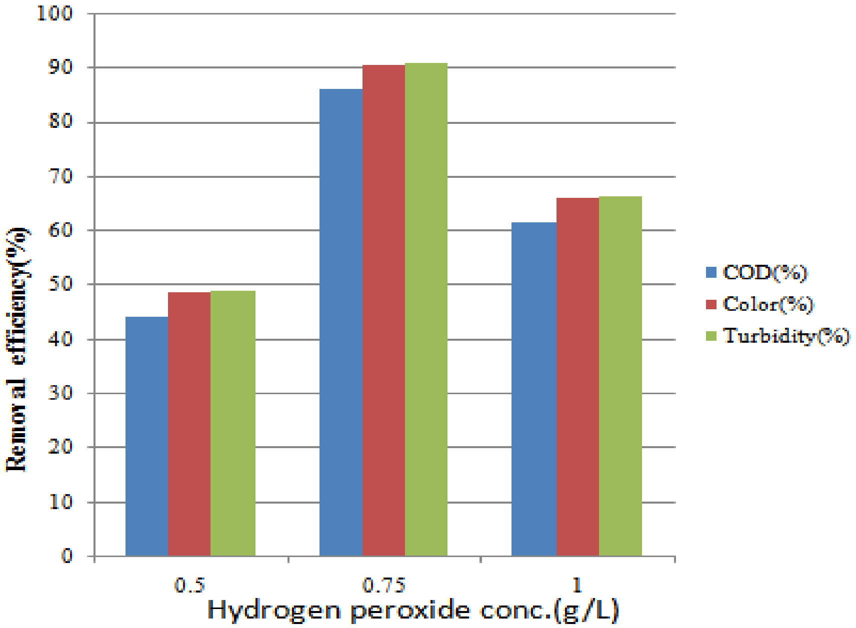


Figure: 4.4 Effect of Hydrogen peroxide concentration on removal efficiency of COD (%), Color (%) and Turbidity(%)

4.3.2 The effect of ferrous salt (Fe^{2+})

The amount of ferrous ion is one of the main parameters which influence the solar photo-Fenton processes. In this study, to obtain the optimal initial Fe^{2+} concentration, the investigation was carried out in the range of 0.01-0.08 g/L Fe^{2+}, at different pH, solar radiation and hydrogen peroxide concentration. The result was shown in Fig 4.2.

The ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was introduced into the solution at start-up. The solutions were continuously stirred using a magnetic stirrer. This is due to the fact that increasing Fe^{2+} produces more quantity of hydroxyl radical with solar radiation. This hydroxyl radical enhances the oxidation of pollutant and the removal of COD, color and turbidity. It can be seen that the removal rate of COD clearly increased with the increasing amount of Fe^{2+}, in the range of 0.01g/L to 0.045g/L. It was known that Fe^{2+} had a catalytic decomposition effect on H_2O_2. When the Fe^{2+} concentration increased, the catalytic effect increased accordingly. However, for Fe^{2+} doses higher than 0.045g/L, the COD, color and turbidity percent removal decreased slightly. This decrease was essentially due to competitive consumption of $^{\cdot}OH$ radicals (equation 41). The amounts of Fe^{2+} ions should be as low as possible for economic and environmental reasons; high amounts of Fe^{2+} ions might produce a larger quantity of Fe^{3+} sludge. The removal/treatment of the sludge containing Fe^{3+} at the end of the wastewater treatment is expensive and requires a large amount of chemicals and manpower (Ramirez et al., 2007). As shown in the inset of Figure 4.3, 0.063g/L Fe^{2+} can be used as an optimum dosage in this study. Solar radiation was used as alternative to tackle this problem in degradation of pollutants and molecules. Fe^{2+} has relatively high solubility at acidic or neutral conditions and can be oxidized easily into Fe^{3+} by dissolved oxygen in water(Faiqun *et al.*, 2007).

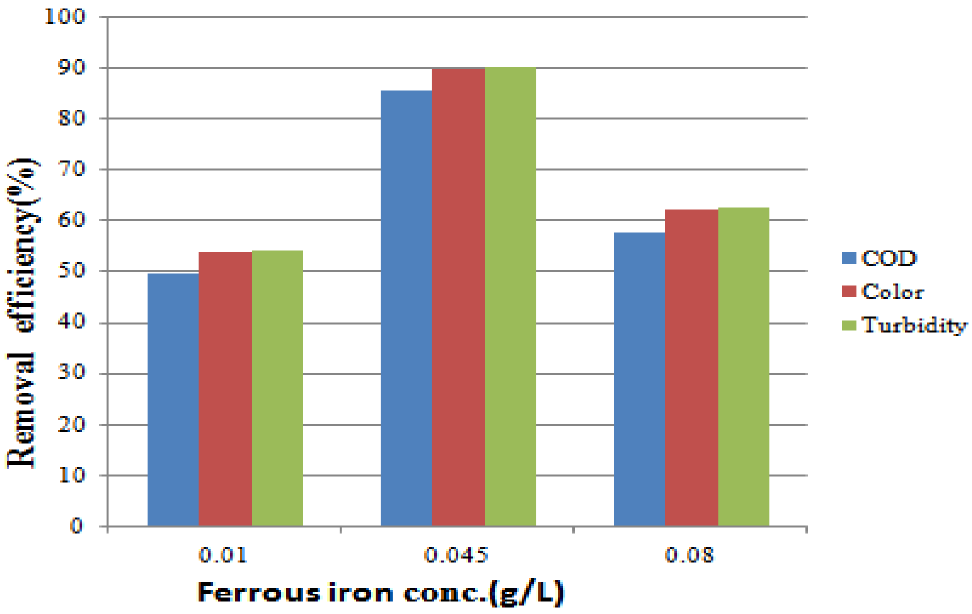


Figure: 4.5 Effect of ferrous salt on removal efficiency of COD(%), Color(%) and Turbidity(%)

4.3.3 The Effect of Initial Effluent pH

The pH affects the oxidation of organic substances both directly and indirectly. The solar photo-Fenton reaction was strongly pH-dependent. The pH value influences the generation of hydroxyl radicals and thus the removal efficiency. The experiments were carried out at a pH within the range of 2-6. The optimum pH was found to be about 3.619, as optimized in the response surface methodology of central composite design. It can be seen that the removal rate of COD, color and turbidity clearly increased with the pH, in the range of 2 to 4 and decreases to 6. The degradation decreased at pH values higher than 3.619, because iron precipitated as hydroxide. Additionally, the oxidation potential of the hydroxyl radical was known to decrease with increasing pH. Another reason for the inefficient degradation at pH > 3.619 is the dissociation and auto-decomposition of H_2O_2. For pH values below 2.5, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected causing reduction in hydroxyl radical production, due to hydroxyl-radical scavenging by H^+ ions.

Solution pH is an important operating parameter that can influence the solar photo Fenton process. To study the effects of effluent pH on the treatment efficiency, the initial pH of the wastewater was adjusted to between 2 and 6. The removal efficiency of COD, color and turbidity as a function of initial pH is presented in the table 4.4. When the initial pH was changed from 2 to 4, the COD, color and turbidity removal efficiencies increased. However, when the initial pH was changed from 4 to 6, the removal efficiencies decreased.

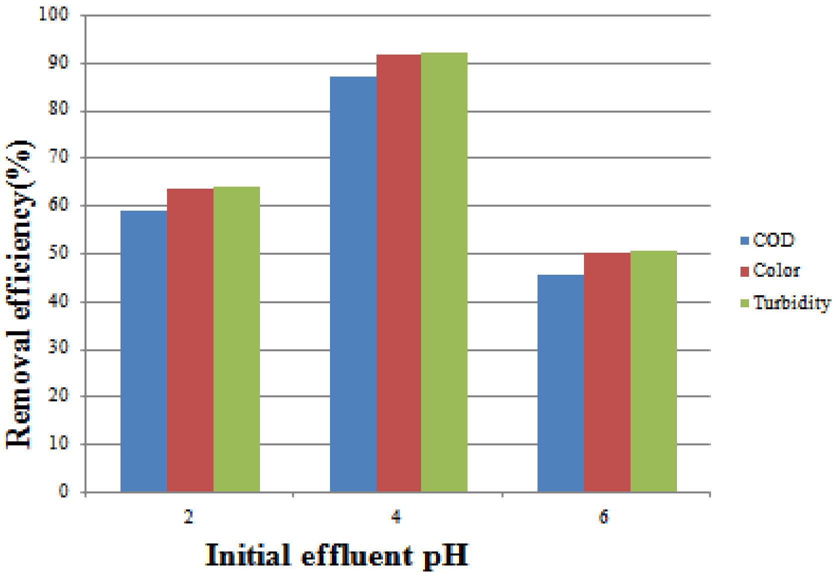


Figure: 4.6 Effect of initial effluent pH on removal efficiency of COD (%), Color(%) and Turbidity(%)

4.3.4 The Effect of reaction time (RT)

Solar radiation is the main factor that influences degradation during the different time interval of exposed solution due to the generation of hydroxyl radicals. At the start the molecular reaction mechanism between H_2O_2 and Fe^{2+} was predominant and decreases after catalyzing some hydrogen peroxide in the reaction. Solar radiation is required for further degradation of pollutants and splitting of hydrogen peroxide. The regeneration of Fe^{2+} from photo reduction of Fe^{3+} by solar radiation increases the degradation of pollutants from wastewater. In the presence of sufficient hydrogen peroxide (H_2O_2) and Fe concentrations, the exposure to solar radiation increases the amount of degradation in wastewater due to the continuous regeneration of Fe^{2+}

from the photo-reduction of Fe^{3+} by solar light (according to Reactions 42 and 43) and the generation of extra free radicals (mainly $^{\cdot}OH$) due to ferrioxalate ($Fe^{3+}(OH)^{2+}$) photochemistry as commented in the following section

$$Fe(III)+H_2O \longrightarrow Fe(III)(OH)^{2+}+H^{+} \quad (42)$$

$$Fe\,(III)(OH)^{2+}+hv \longrightarrow Fe(II)+{}^{\cdot}OH \quad (43)$$

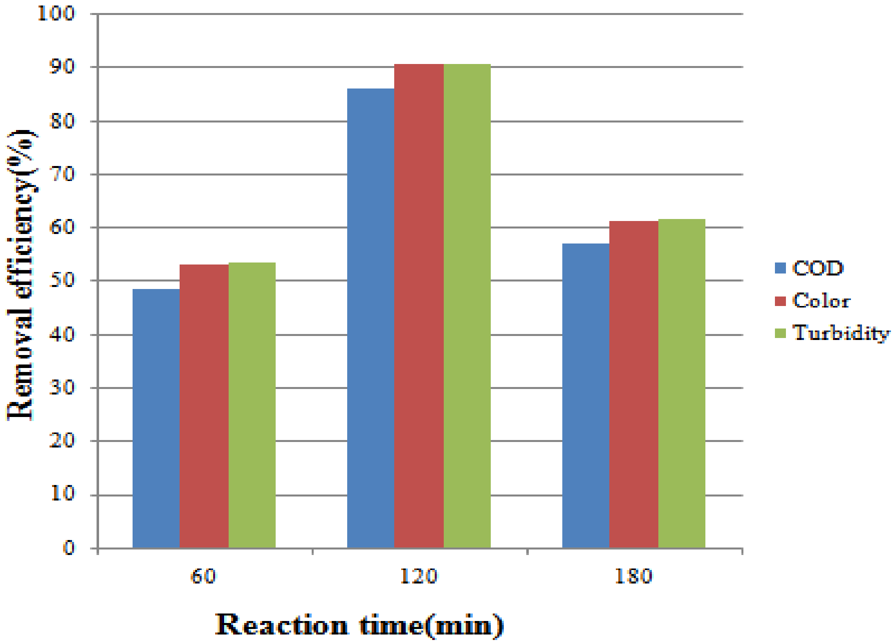


Figure: 4.7 Effect of reaction time on removal efficiency of COD(%), Color (%) and Turbidity(%)

4.3.5 Optimization

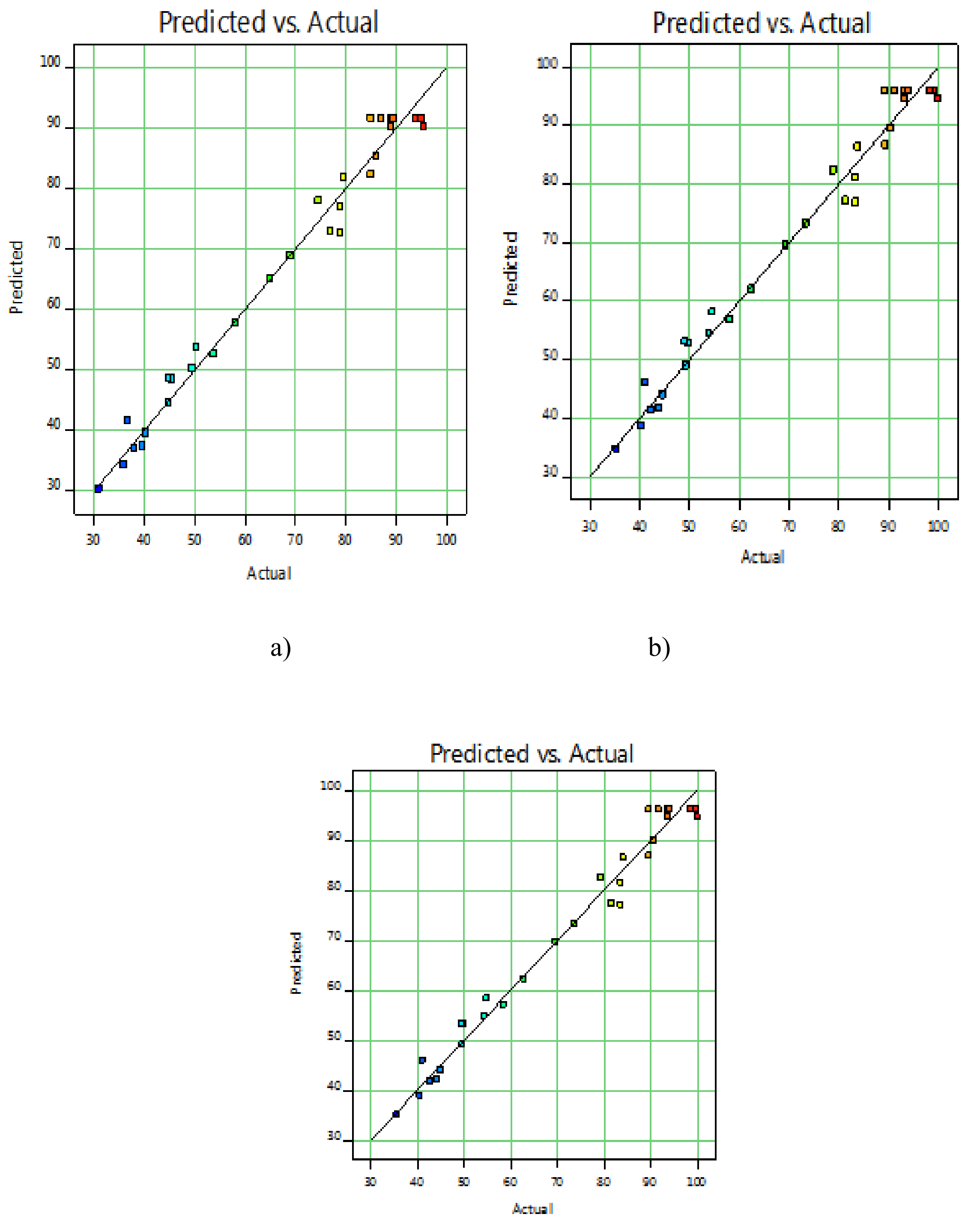
The other crucial study part of this investigation is to get an optimum conditions on the removal percentage of COD, color and turbidity from institutional wastewater through the application of solar photo-Fenton process by considering different operational factors and that was implemented Central Composite Design from Response Surface Methodology.

One of the main purposes of this investigation was to obtain the optimal conditions for the removal of COD, color and turbidity from institutional wastewater using solar photo Fenton process. The results were optimized using the regression equation of RSM based on the CCD. In the optimization of hydrogen peroxide (A), ferrous salt (B), initial effluent pH(C) and reaction time (D) were selected as within range and the responses such as COD, color and turbidity removal efficiency were maximized.

Under these optimum of experimental conditions such as hydrogen peroxide (A) 781mg/L, ferrous salt (B) 63mg/L, initial effluent pH(C) 3.619 and with reaction time (D) 118.478min and the percentage COD, color, and turbidity removal were 99.776%, 100% and 100% respectively and desirability of 1 was selected. The good correlation between these actual and predicted results indicate that the reliability of central composite design incorporate desirability function method and it could be effectively used to optimize the solar photo Fenton process parameters for institutional wastewater.

4.4 Three-dimensional plots of the regression and optimization process

As shown in Figures 4.7, 4.8 and 4.9, the response surfaces plots were created by Design Expert version 11.1.2.0 provided a three-dimensional view of the COD, Color and Turbidity removals surface over the independent variables. The main factors of this process that improved the COD, Color and Turbidity removal were H_2O_2 dosages, Fe^{+2} dosages, pH and contact time. Design Expert 11.1.2.0 was used to determine optimization of removal efficiency for COD, Color and Turbidity. The pH, H_2O_2 dosage, Fe^{+2} dosages, and reaction time were chosen as ‘‘within’’ the range in the software optimization step. The responses (COD, Color and Turbidity removals) were defined as ‘‘maximum’’ to achieve the highest performance. The program combined individual desirability into a single number and then search to optimize this function based on the response goal. It was showed that the COD, color and turbidity removal by solar photo Fenton oxidation and the corresponding pH variation over time under the optimal conditions a rapid degradation up to 118.478 min followed a slow degradation. The rapid degradation was attributed to high hydroxyl radical ($^{\cdot}OH$) concentrations which it exhibited reactivity toward organic compounds as a result of amounts of Fe^{2+} catalyst in solution that reacts with H_2O_2 that was regenerated from Fe^{3+}. At the second stage, after 118.478 min, Fe^{2+} ions were decreased and the excess of H_2O_2 reacted with hydroxyl radical ($^{\cdot}OH$) in result to slower rate of production hydroxyl radical ($^{\cdot}OH$).



a) b)

c)

Figure: 4.8 Adjustment of curvature of actual Vs predicted of a) COD, b) Color and c) Turbidity

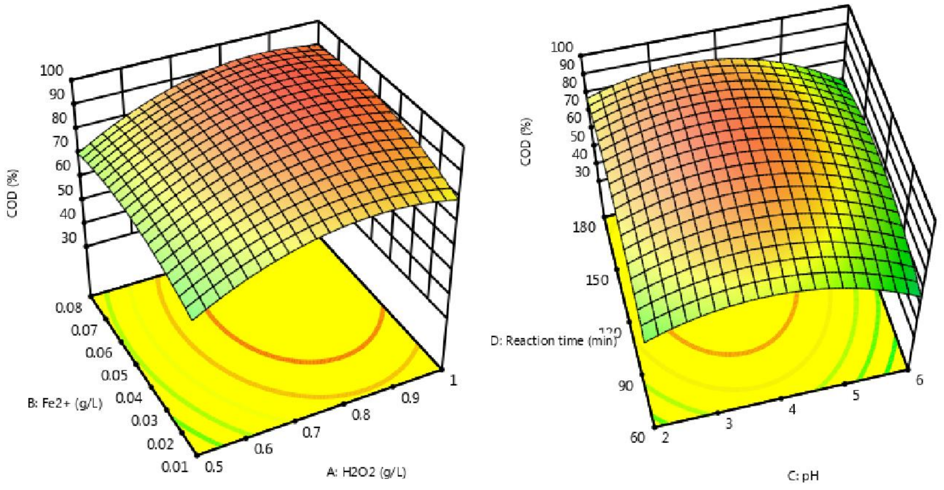


Figure 4.9 COD Removal efficiency

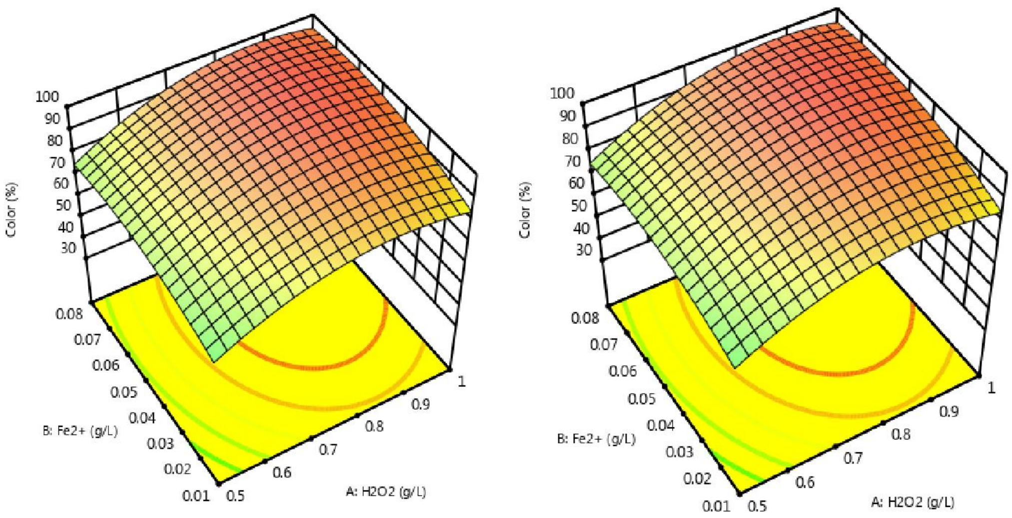


Figure 4.10 Color Removal efficiency

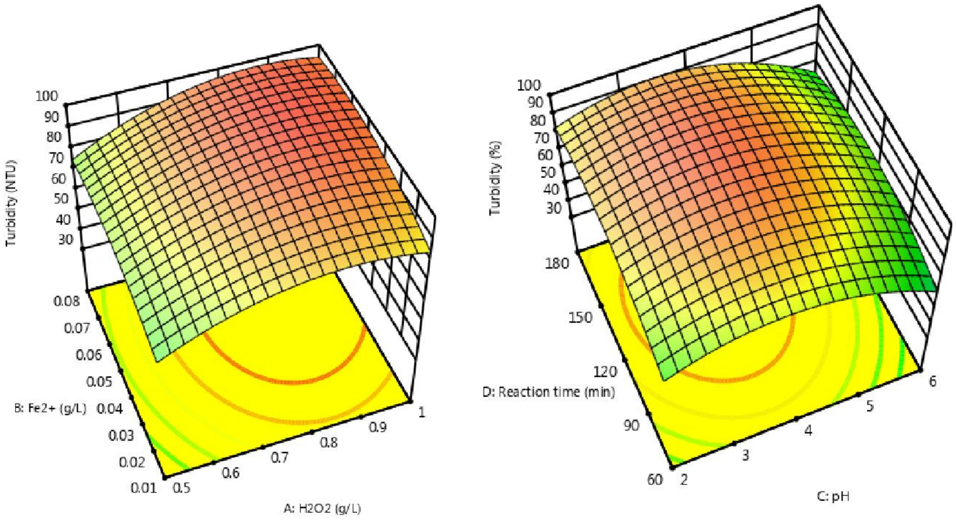


Figure: 4.11 Turbidity Removal efficiency

Table 4.9 Selected results from thirty experiments by optimization

H_2O_2	Fe^{2+}	pH	RT	COD	Color	Turbidity	Remark
781mg/L	**63mg/L**	**3.619**	**118.478min**	**99.776%**	**100%**	**100%**	**selected**

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 **CONCLUSIONS**

From this research study, the following conclusions were drawn. The literature review of electrochemical treatment, electrocoagulation, UV-ozone process and Fenton process for the treatment of wastewater were successfully carried out and the results were compared in terms of, COD removal, color removal and turbidity removal. The results showed that the solar photo Fenton process was more effective than the listed advanced treatment processes in the literature part of the study.

The effects of various operating parameters such as hydrogen peroxide (H_2O_2), ferrous salt (Fe^{2+}), initial effluent pH and reaction time (RT) by the solar photo-Fenton process were studied. The solar photo-Fenton process was optimized to maximize pollutant removal of institutional wastewater (COD, Color and turbidity). The maximum COD, color and turbidity removal of 99.776%, 100% and 100% respectively were observed at the hydrogen peroxide of 0.781 g/L, initial effluent pH of 3.619, ferrous salt concentration of 0.063 g/L, and reaction time of 118.478 minutes. The solar photo-Fenton process described in this study was suitable to be applied for the treatment of institutional wastewater as it has higher treatment efficiency compared to the conventional treatment systems and advanced treatment processes.

The general results of this study indicated that the solar photo-Fenton was a practical method to treat institutional wastewaters, allowing achieved well removal of COD, color and turbidity. Quadratic models for the following three responses proved to be significant with very low probabilities (<0.0001): Chemical oxygen demand (COD), Color and turbidity. The obtained optimum conditions included H_2O_2 dosage (0.781 g/L), Fe^{+2} dosage (0.063 g/L), pH (3.619) and reaction time (118.478 min). COD, Color and turbidity removal rates were 99.776%, 100% and 100% respectively. The predictions correspond well with experimental results. The current study revealed that the solar photo-Fenton process in an advanced oxidation process was well efficient in the institutional wastewater treatment, achieving a 99.776% COD removal at conditions; pH=3.619, H_2O_2/Fe^{+2} ratio =12.4.

5.2 RECOMMENDATIONS

- The development of solar photo Fenton process effectively works in tropical zone of the globe thus it is better to the implementation of the method in large scale to the treatment of wastewater.
- Different institution that discharging large amount of institutional wastewater to the environment should recommended to implement this system to better removal of the pollutants.
- Solar photo-Fenton process requires clear sun light so; seasons should be tested before the execution of this study.
- The availability of sunlight throughout the year may vary through seasons therefore it is recommended to store energy in solar panel for better implementation of this study (not to stop the process).

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APPENDICES

Appendix A: Laboratory procedure

a) Determination of COD

Procedure

1 Wash 25 mL of COD vials.

2 In COD vials put 0.05 g of $HgSO_4$ + 2.5 mL sample + 1.5mL $K_2Cr_2O_7$ + 3.5 mL concentrated H_2SO_4.

3 Add small amount of silver sulphate.

4 Shake well and reflux for 2 hr.

5 Cool and add little amount of distilled water to the flask through the condenser.

6 Titrate the solution in the flask against FAS using Ferron indicator

7 End point green color to reddish brown








b) Determination of pH

Procedure:

1. Switch on the pH meter.

2. Prepare buffer solution of 4.0, 7.0 and 9.2.

3. Calibrate the pH meter using buffer solution and adjust the calibration knob.

4. Read the pH meter by inserting the sample.

5. By adjust the pH using 0.1M solution of NaOH and H_2SO_4.

c) Determination of Turbidity

Procedure:

1. Switch on the turbidity meter.

2. Prepare 400 NTU solution.

3. Calibrate the turbidity meter to 400 NTU using the standard solution by adjust the calibration knob.

4. Calibrate the turbidity meter to 0 NTU using the distilled water by adjust the calibration knob.

5. Read the turbidity meter by inserting the sample.

D) **Determination of Dissolved oxygen**

E) Determination of pH, ORP, ION, Conductivity, TDS, Salinity, Resistivity, Dissolved oxygen, and Temperature

Appendix A: 100 Solutions found of numerical optimization

№	H_2O_2	Fe^{2+}	pH	RT	COD	Color	Turbidity	Desirability	Remark
1	**0.781**	**0.063**	**3.619**	**118.478**	**99.776**	**100**	**100**	**1**	**Selected**
2	1	0.01	2	60	53.641	58.041	58.37	1	
3	0.5	0.045	4	120	72.742	77.142	77.444	1	
4	0.75	0.045	4	180	85.131	89.531	89.866	1	
5	0.75	0.045	4	120	91.475	95.875	96.156	1	

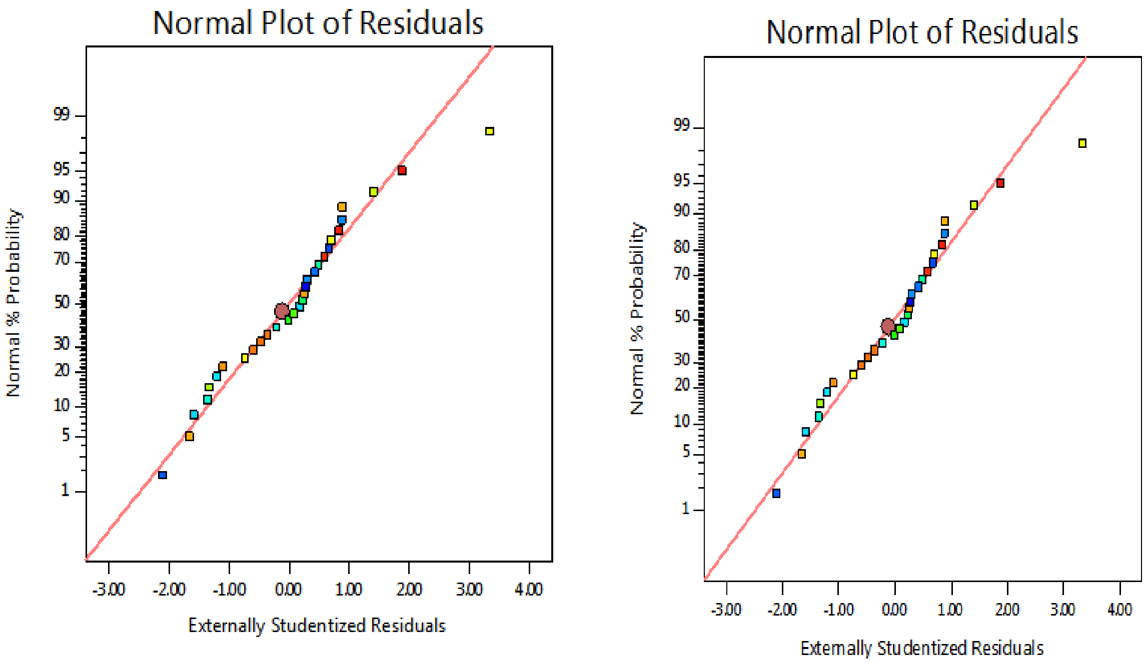
6	0.75	0.045	4	60	76.753	81.153	81.455	1	
7	0.5	0.01	6	60	30.252	34.652	34.914	1	
8	0.5	0.08	6	180	39.474	43.874	44.103	1	
9	0.75	0.045	2	120	82.187	86.587	86.922	1	
10	0.75	0.045	6	120	68.698	73.098	73.399	1	
11	1	0.01	2	180	72.443	76.843	77.093	1	
12	0.5	0.01	2	180	48.618	53.018	53.347	1	
13	1	0.01	6	180	48.379	52.779	53.108	1	
14	0.5	0.08	6	60	41.521	45.921	46.004	1	
15	0.5	0.01	2	60	36.966	41.366	41.699	1	
16	0.75	0.01	4	120	81.82	86.22	86.422	1	
17	1	0.01	6	60	37.327	41.727	42.06	1	
18	1	0.08	2	180	77.863	82.263	82.558	1	
19	0.75	0.08	4	120	90.164	94.564	94.699	1	
20	0.5	0.01	6	180	34.154	38.554	38.888	1	
21	1	0.08	6	60	52.496	56.896	57.125	1	
22	1	0.08	6	180	57.599	61.999	62.299	1	
23	1	0.08	2	60	65.01	69.41	69.71	1	
24	1	0.045	4	120	90.142	94.542	94.877	1	
25	0.5	0.08	2	180	50.138	54.538	54.838	1	
26	0.813	0.053	2.743	179.692	86.955	91.355	91.696	1	
27	0.787	0.053	3.358	133.907	94.343	98.743	99.029	1	
28	0.836	0.041	5.809	125.202	72.862	77.262	77.58	1	
29	0.588	0.033	2.218	82.99	64.668	69.068	69.416	1	
30	0.703	0.061	3.587	142.468	90.572	94.972	95.233	1	
31	0.575	0.033	3.756	102.236	76.935	81.335	81.625	1	
32	0.665	0.049	4.753	98.464	80.944	85.344	85.607	1	
33	0.649	0.011	5.032	102.573	67.852	72.252	72.472	1	
34	0.88	0.03	3.328	74.46	80.449	84.849	85.17	1	
35	0.679	0.025	4.503	69.56	70.705	75.105	75.382	1	

36	0.627	0.063	2.955	99.321	81.025	85.425	85.678	1	
37	0.943	0.065	2.998	83.967	86.038	90.438	90.734	1	
38	0.615	0.025	5.236	106.433	68.914	73.314	73.585	1	
39	0.553	0.079	5.681	141.362	60.491	64.891	65.041	1	
40	0.974	0.011	3.49	93.826	77.346	81.746	81.998	1	
41	0.528	0.076	4.842	152.582	67.181	71.581	71.769	1	
42	0.948	0.037	4.684	74.319	75.544	79.944	80.284	1	
43	0.528	0.011	5.329	158.423	54.01	58.41	58.686	1	
44	0.926	0.06	2.08	151.641	87.211	91.611	91.944	1	
45	0.915	0.025	5.942	75.185	55.54	59.94	60.276	1	
46	0.712	0.06	5.396	177.602	70.812	75.212	75.526	1	
47	1	0.032	2.865	157.052	88.439	92.839	93.173	1	
48	0.831	0.035	5.668	111.378	73.236	77.636	77.945	1	
49	0.846	0.011	5.356	124.787	70.789	75.189	75.424	1	
50	0.604	0.05	5.543	162.554	65.538	69.938	70.263	1	
51	0.748	0.068	2.633	155.997	87.403	91.803	92.075	1	
52	0.76	0.067	5.397	79.554	73.98	78.38	78.584	1	
53	0.55	0.036	4.947	109.957	70.265	74.665	74.953	1	
54	0.739	0.033	5.338	79.484	70.005	74.405	74.694	1	
55	0.811	0.018	5.933	148.426	62.964	67.364	67.658	1	
56	0.842	0.032	4.457	86.501	82.22	86.62	86.916	1	
57	0.513	0.019	3.129	163.303	65.653	70.053	70.371	1	
58	0.648	0.044	3.233	77.465	77.659	82.059	82.363	1	
59	0.996	0.055	4.336	150.753	89.318	93.718	94.05	1	
60	0.961	0.022	3.932	140.023	87.419	91.819	92.103	1	
61	0.644	0.062	5.491	168.202	67.886	72.286	72.577	1	
62	0.515	0.037	4.556	90.751	67.208	71.608	71.898	1	
63	0.694	0.046	4.505	167.262	82.569	86.969	87.288	1	
64	0.964	0.073	2.054	116.105	84.26	88.66	88.948	1	
65	0.795	0.061	5.997	85.184	66.207	70.607	70.857	1	

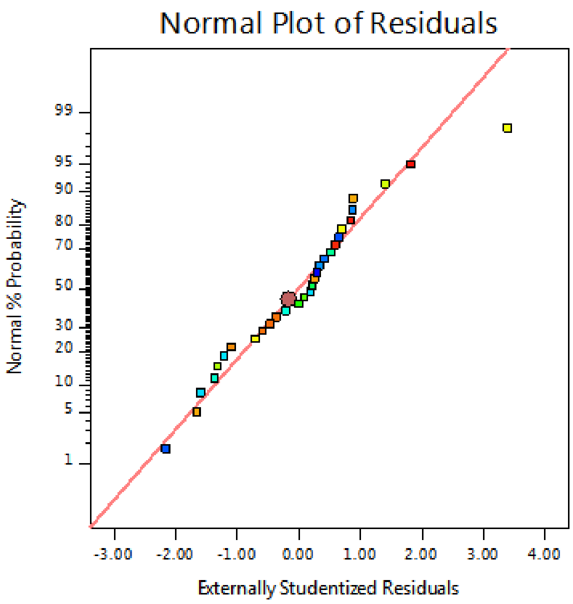
66	0.761	0.026	5.804	91.619	64.275	68.675	68.964	1	
67	0.781	0.055	2.729	105.267	89.091	93.491	93.785	1	
68	0.86	0.061	4.973	66.741	75.674	80.074	80.341	1	
69	0.974	0.066	3.92	158.515	91.429	95.829	96.127	1	
70	0.626	0.059	3.642	117.312	85.562	89.962	90.214	1	
71	0.65	0.061	3.484	153.498	85.908	90.308	90.586	1	
72	0.808	0.074	4.127	153.332	90.849	95.249	95.459	1	
73	0.782	0.04	2.927	102.716	88.386	92.786	93.092	1	
74	0.878	0.026	2.625	64.266	71.673	76.073	76.415	1	
75	0.745	0.054	4.872	98.222	83.71	88.11	88.365	1	
76	0.961	0.061	2.798	161.518	91.248	95.648	95.973	1	
77	0.705	0.029	2.039	66.245	63.675	68.075	68.431	1	
78	0.688	0.076	5.512	127.43	74.698	79.098	79.257	1	
79	0.994	0.01	2.626	122.331	79.514	83.914	84.153	1	
80	0.642	0.018	2.368	70.092	61.709	66.109	66.416	1	
81	0.59	0.053	2.785	166.347	76.167	80.567	80.91	1	
82	0.587	0.044	2.107	155.311	71.208	75.608	75.974	1	
83	0.718	0.061	2.646	75.092	78.282	82.682	82.966	1	
84	0.936	0.063	5.83	74.489	64.35	68.75	69.044	1	
85	0.799	0.077	5.238	159.584	78.816	83.216	83.418	1	
86	0.908	0.025	2.965	95.232	83.911	88.311	88.612	1	
87	0.593	0.019	3.408	86.13	70.572	74.972	75.241	1	
88	0.607	0.018	2.349	60.454	54.975	59.375	59.7	1	
89	0.745	0.046	2.575	137.816	88.756	93.156	93.472	1	
90	0.814	0.028	3.621	153.187	90.361	94.761	95.048	1	
91	0.565	0.05	5.522	83.781	62.431	66.831	67.091	1	
92	0.803	0.055	2.056	115.395	84.796	89.196	89.517	1	
93	0.946	0.068	4.55	105.796	88.06	92.46	92.713	1	
94	0.583	0.03	3.81	144.216	78.783	83.183	83.485	1	
95	0.648	0.018	4.716	119.258	75.512	79.912	80.157	1	

96	0.99	0.069	4.923	110.08	83.247	87.647	87.915	1	
97	0.572	0.021	4.744	134.635	70.931	75.331	75.604	1	
98	0.538	0.056	2.851	94.81	71.365	75.765	76.062	1	
99	0.894	0.028	4.682	177.61	80.002	84.402	84.73	1	
100	0.91	0.054	3.726	167.241	92.19	96.59	96.914	1	

Appendix B: Design expert plot, Normal probability plot of the studentized residuals for a) COD, b) Color and c) Turbidity removal



a) **b)**



c)

Appendix C: Fit Summary of experiments

a) Sequential Model Sum of Squares [Response 1: COD]

Source	Sequential p-value	Lack of Fit p-value	Adjusted R²	Predicted R²	
Linear	0.1972	0.0005	0.0803	-0.1434	
2FI	0.9975	0.0002	-0.1800	-2.0462	
Quadratic	**< 0.0001**	**0.3858**	**0.9596**	**0.8939**	**Suggested**
Cubic	0.4800	0.2690	0.9607	0.3610	Aliased

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Mean Vs Total	1.316E+05	1	1.316E+05			

Linear Vs Mean	2810.37	4	702.59	1.63	0.1972	
2FI Vs Linear	268.40	6	44.73	0.0810	0.9975	
Quadratic Vs 2FI	**10205.06**	**4**	**2551.27**	**134.87**	**< 0.0001**	**Suggested**
Cubic Vs Quadratic	154.89	8	19.36	1.05	0.4800	Aliased
Residual	128.86	7	18.41			
Total	1.451E+05	30	4838.22			

b) Sequential Model Sum of Squares [Response 2: Color]

Source	Sequential p-value	Lack of Fit p-value	Adjusted R²	Predicted R²	
Linear	0.1972	0.0005	0.0803	-0.1434	
2FI	0.9975	0.0002	-0.1800	-2.0462	
Quadratic	**< 0.0001**	**0.3858**	**0.9598**	**0.8942**	**Suggested**
Cubic	0.4800	0.2690	0.9607	0.3610	Aliased

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Mean vs Total	1.496E+05	1	1.496E+05			
Linear vs Mean	2810.37	4	702.59	1.63	0.1972	
2FI vs Linear	268.40	6	44.73	0.0810	0.9975	

Quadratic vs 2FI	**10205.06**	**4**	**2551.27**	**134.87**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	154.89	8	19.36	1.05	0.4800	Aliased
Residual	128.86	7	18.41			
Total	1.632E+05	30	5440.38			

c) Sequential Model Sum of Squares [Response 3: Turbidity]

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R^2**	**Predicted R^2**	
Linear	0.1960	0.0005	0.0809	-0.1426	
2FI	0.9976	0.0002	-0.1797	-2.0465	
Quadratic	**< 0.0001**	**0.3864**	**0.9599**	**0.8944**	**Suggested**
Cubic	0.4702	0.2767	0.9611	0.3796	Aliased

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	
Mean vs Total	1.508E+05	1	1.508E+05			
Linear vs Mean	2817.18	4	704.29	1.64	0.1960	
2FI vs Linear	263.88	6	43.98	0.0797	0.9976	
Quadratic vs 2FI	**10203.33**	**4**	**2550.83**	**134.99**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	156.04	8	19.50	1.07	0.4702	Aliased
Residual	127.41	7	18.20			

Total	1.644E+05	30	5480.02			

Appendix D: Thirty runs of the experiments


RUN-13
RUN-14
RUN-15
RUN-16
RUN-17
RUN-18


RUN-19
RUN-20
RUN-21
RUN-22
RUN-23
RUN-24


RUN-28
RUN-29
RUN-30
RUN-27
RUN-26
RUN-25