



**ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING**

**Assessment of photo-Fenton process for the removal of
pesticide from wastewater**

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of Science in Environmental Engineering**

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Declaration

I declare that, this thesis for M.Sc. Degree at Addis Ababa University Institute of Technology, here by submitted by me, is my original work and it hasn't been submitted previously for the degree at this or any other university and that all resources of materials used in this thesis have been duly acknowledged.

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List of Acronyms

AOP: Advanced oxidation Process

BBD: Box-Benkhen design

BOD: Biological Oxygen Demand

COD: Chemical Oxygen Demand

DOC: Dissolved Organic Carbon

DOM: dissolved organic matter

EFSA European Food Safety Authority

EPA: Environmental protection agency

K : Equilibrium constant

k : Rate constant

MoA: Ministry of Agriculture

NPS: Non-point source

NTU: Nephelometric Turbidity Units

OCs: organochlorines

Ops: Organophosphates

POPs: persistent organic pollutants

Pow: partition coefficient octanol-water

PPPs: plant protective products

PS: Point source

RSM: Response Surface Methodology

TOC: Total Organic Carbon

UV/Vis: Ultraviolet/Visible

WWTP: Wastewater treatment plant

ABSTRACT

The main purpose of this work was to study assessment of photo-Fenton process ($Fe^{2+}/H_2O_2/UV$) for the removal of pesticide from wastewater. Synthetic wastewater from 2,4-Dichlorophenoxyacetic was prepared and characterized for its organic matter content and also its PH and turbidity which has a significant effect on the degradation process. Box-Benken design response-surface methodology was developed to optimize photo-Fenton degradation of 2,4-Dichlorophenoxyacetic in which UV light radiation was used as a source of light. The three variables considered in Box-Benken design model included initial 2,4-Dichlorophenoxyacetic [2,4-D], hydrogen peroxide [H_2O_2] and Ferrous iron [Fe^{2+}] concentrations. The removal efficiency was expressed in terms of total organic carbon (TOC) and chemical oxygen demand (COD) percentage removal. The optimum values of 94.7 mg/L 2,4-D, 22.78 mg/L Fe^{2+} , 156.4 mg/L H_2O_2 were obtained by optimizing the variables using Box-Benken design that the data was analyzed after carrying out each experiment for 2 hours at room temperature. The photo-Fenton process led to 85% TOC removal and 96% COD removal thereby showing the effectiveness of using photo-Fenton process for the removal of pesticide from wastewater.

1. INTRODUCTION

1.1. Background of the study

A wide range of xenobiotic compounds are detected in industrial and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in biological treatment systems due to their resistance to biodegradation or/and toxic effects on microbial processes (Stasinakis, 2008). They are sourced by industrial and domestic wastewaters, hospital effluents, landfill leachates, runoff from agriculture, livestock and aquaculture. The water and wastewater treatment processes are hampered since wastewater treatment plants (WWTPs) using conventional physicochemical and biological treatments are not specifically designed to eliminate such compounds. The potential contamination of the main environmental compartments, such as surface water, groundwater and soils, which are constantly interconnected, may cause cumulative negative effects along multigenerational exposure in aquatic organisms and micro-pollutants can even end up in drinking water (Ana R. Ribeiro O. C., 2015).

Biocides are one of the most important classes of compounds used in agriculture and introduced into surface waters by human activities and can contaminate rivers and other water bodies due to transport from cultivated areas and can pose considerable toxicity risks to operators, consumers, and the wider environment (Thiago et al., 2012). Pesticides is one of the most common groups of pollutants found in wastewater effluents due to their widespread use in agriculture in order to protect and treat crops and fruits from insects, pests and microbial infestation so as improve the quality and quantity of production. These micro-pollutants are usually detected in trace concentrations (ng L^{-1} or $\mu\text{g L}^{-1}$) and are resistant to conventional wastewater treatment systems of urban wastewater treatment plants (WWTP) such as biological processes (secondary treatment) (A.S., 2017).

Pesticide exposure may pose a potential risk to humans, causing neuritis, psychiatric manifestations, and hepatorenals disorders, neurological, immunological, metabolic and endocrine. It has also been linked to increased incidence of leukemia and bladder cancer in farmers, following genotoxic effects of some pesticides(Prieto Garcia et al., 2012).

Globally, an alarming level of pesticides concentration has been reported in air, water and soil as well as in foods and biological materials. Some of these pesticides have been reported to be persistent, toxic, mutagenic and carcinogenic. Pesticide contamination of water systems is a major concern as residues reach the aquatic environment through manufacturing plants, direct surface run-off, leaching, careless disposal of empty containers, equipment washings, spray-drift, soil erosion, volatilization, etc. (Yusoff, 2013).

In Ethiopia a major increase in pesticides mainly herbicide use is shown among teff growers, from around 30 percent applying ten years ago to over 60 percent now (Megan Sheahan, 2017). Recently, Ethiopia has been considered as having the largest accumulations of absolute pesticides in Africa. It is estimated that there were 1,500 tonnes of absolute pesticides (Mengistie, 2016).

Ethiopia has no industry to produce active ingredients and only one local pesticide formulating company, Adami Tullu Pesticide Processing Share Company in the Adami Tulu Woreda near Ziway. Between 2000 and 2012, the company produced 17,155.52 metric tons of insecticides for agricultural and public health purposes (Central Statistical Agency, 2013/2014). The other types of pesticides produced by the company are Acaricide and fungicide which are produced in lesser amount compared to insecticides.

The company has not yet started the production of herbicides despite there is a demand in greater amount for the agricultural productions. The company has planned the production of 2,4-D at its new factory which has been under construction in Butajira town, around 110Km from Addis Ababa on 3.4ht of land. The new factory will have the capacity to produce 500,000lt of 2,4-D, reaching 1.5 million litres in two years.

The wastewater coming from usual sources like private households can be treated in ordinary two phases wastewater treatment plants. The physical (mechanical) part combined with the activated sludge (biological) treatment is sufficient to treat all biodegradable wastewater. To cope with the large and still growing the types of anthropogenic pollutants in number which are non-biodegradable, there exist and newly develop different technologies of treatment. Technologies like phase-transfer, air stripping, adsorption or extraction are already established and applied, however, these technologies have drawbacks to remove the contaminant to the standard. Considering the toxic nature of pesticides, it is clear to have low biodegradability and, in most

cases, are highly refractory organic compounds. For organic pollutants in general but especially for toxic pesticides the Advanced Oxidation Processes (AOPs) seem to be a promising technology regarding to the potential of mineralizing most of the contaminants (Hilgert, 2009).

The use of photo-Fenton process is gaining momentum in recent years, and even experiments at industrial plant scale have been performed. The photo-Fenton is able to achieve complete elimination of the active ingredients in a shorter time than other types of oxidation processes (Vicente Candela, et al., 2014). The photo-Fenton reaction typically gives enhanced rates and a faster mineralization of recalcitrant organics than the dark reaction (Fenton reaction) and can take the advantage of UV irradiation from the solar light. In the reaction of the photo-Fenton process Fe^{2+} ions are oxidized by H_2O_2 to Fe^{3+} and one equivalent $\text{HO}\cdot$ is produced. In aqueous solutions the resulted Fe^{3+} act as the light absorbing species that produce another radical while the initial Fe^{2+} is reproduced (Alalm & Tawfik, 2013).

Moussavi (2017) has clearly indicated that among the main reasons for the huge popularity and widespread applicability of Photo-Fenton oxidation processes are includes the high efficiency of mineralization enables the transformation of organic pollutants into non-toxic CO_2 ; Owing to the rapid reaction between iron and H_2O_2 , the activation of H_2O_2 and the subsequent generation of hydroxyl radicals are completed in the shortest reaction time among all other AOPs; Oxidizing radicals are generated at ambient pressure and temperature, which avoids the requirement of complicated reactor facilities; The use of cheap, moderately reactive, easy to handle reagents (iron and H_2O_2) and use of irradiation from sunlight makes the Photo-Fenton process cost effective and practically viable; and the simple and flexible nature enables easy implementation as a stand-alone or hybrid system and also facilitates easy integration in existing water treatment processes like coagulation, filtration and biological oxidation. Therefore, the objective of the present study is to assess the efficiency of photo-Fenton process on the degradation of 2,4-dichlorophenoxyacetic acid from wastewater.

1.2. Statement of the problem

It is well known that almost all the Ethiopian industries (Pesticide, textile, paper, plastic, leather, food, cosmetic, etc.) release their untreated or partially treated wastewaters into municipal sewers or directly into nearby drains, rivers, ponds, lagoons, or lakes. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at

large. Although some of these industries dilute the wastewater that discharged to the environment with clean water, it does not prevent the pollutant from reaching and pollute the environment.

From the pesticides import data to Ethiopia (from 200 to 2017) three major categories of pesticide chemicals arranged from the higher volume to the lower are herbicides (56.4%), insecticides (19.8%) and fungicides (16.4%) respectively (Central Statistical Agency, 2013/2014). The increase in imports and use of herbicides has followed the expansion of the crop production area in Ethiopia and contributed to yield increases and expansion of large-scale floriculture industries, has resulted in an increased use of herbicides. The herbicide is effective in broadleaf weed control in the agricultural industry and is one of the most widely used herbicides in the world. The 2,4-D is the most commonly used herbicide in Ethiopia and applied for weed control on various crops including teff, sugar cane and wheat.

The pesticides, retained in wastewater, are resistant to conventional biological treatment owing to their high toxicity and biological persistence. It was reported that no significant decrease in pesticide content occurred after the biological treatment and remaining recalcitrant organic carbon mainly due to pesticide molecules(Cheng et al., 2015).

The types of herbicides used in Ethiopia (and perhaps elsewhere) really do have toxicity levels harmful to humans; chemicals banned or replaced in high-income countries are often sold and used in Sub-Saharan Africa (SSA). For example, both Dichlorophenoxyacetic acid (commonly known as 2,4-D) and Trifluralin are used in Ethiopia; these compounds are 10 and 140 times more toxic for humans than glyphosate, the most commonly used herbicide in the United States, which replaced these more toxic herbicides (Megan Sheahan, 2017).

According to the type of toxicity, these chemicals affect the growth and survival of reproductive factors and in the case of acute toxicity may cause death of exposed organisms. These substances have been considered as potential mutagens because they contain ingredients to cause changes in deoxyribonucleic acid (DNA). According to estimates by the World Health Organization (WHO) each year between 500,000 and 1 million people are poisoned by pesticides and between 5,000 and 20,000 die(Prieto Garcia et al., 2012).

As these contaminants are not biodegradable and can risk the effectiveness of conventional treatment plants, their removal from wastewaters requires non-conventional water treatment

technologies. Advanced Oxidation Processes (AOPs) which uses strong chemical oxidants and/or the presence of an irradiation source have been studied for that aim, with promising results over the years (Turbay, 2013).

1.3. Objective of the study

1.3.1. General Objective

The objective of this thesis is to study the assessment of photo-Fenton process for the removal of pesticide in wastewater.

1.3.2. Specific Objectives

- To study the characteristics of the wastewater prepared for the experimental work.
- To study the effect of experimental factors such as concentrations of 2,4-D, H₂O₂ and Fe²⁺.
- To analyze the efficiency of photo-Fenton process in terms of the removal of total organic carbon (TOC) and chemical oxygen demand (COD) from waste water.
- To make optimization of experimental factors and responses using Box–Benkhen Design (BBD), Response Surface Methodology of Design Expert 11.1 software.

1.4. Significance of the study

- This work investigates the use of AOPs (photo-Fenton process in particular) for the removal of recalcitrant pesticide substances from wastewater. The study conducted assessment on the efficiency of the photo-Fenton process for the degradation of 2,4-dichlorophenoxyacetic acid in terms of the percentage removal of TOC and COD.
- The study creates awareness on the treatment of wastewater using photo-Fenton process to reduce the concentration of pesticide residue from drinking water and surface water.
- The photo-Fenton technology has the potential to be used in the future for the factories in our country that produce wastewater containing organic pollutants in general and for Adami Tulu Pesticides Processing Share Company that produces wastewater contaminated with pesticides mixture that was collected at Adami Tulu Pesticide processing evaporation pond in particular.
- The removal of such recalcitrant pollutant from aqueous effluents is of significant environmental importance.

2. LITERATURE REVIEW

2.1. Water pollution and water pollutants

Water pollution refers to the presence of chemical, physical or biological species which change the quality of water and are able to produce harmful effects on ecosystems. It affects surface water, groundwater and even drinking water with serious consequences to human health (Turabay, 2013).

Polluted drinking water is usually present in less-developed countries and in time of war and it is a threat to public health because of the transmission of bacterial waterborne disease. Surface water pollution is harmful to aquatic organisms and causes public health problems, while groundwater pollution is a source of serious health risks (Turabay, 2013).

Prior to discussing water treatment and reclamation, one should be aware about the qualitative and quantitative nature of water pollutants. Many pollutants are present in wastewater but toxicity is only observed beyond a certain limit called the permissible limit. The type of pollutants present in the waste water depends upon the nature of the industrial, agricultural and municipal wastewater releasing activities. The different types of water pollutants may be categorized as inorganic, organic, and biological in nature. The most common inorganic water pollutants are heavy metals, which are highly toxic and carcinogenic in nature. Additionally, nitrates, sulphates, phosphates, fluorides, chlorides and oxalates also have some serious hazardous effects. The toxic organic pollutants are from pesticides which includes insecticides, herbicides, fungicides, polynuclear hydrocarbons (PAHs), phenols, polychlorinated biphenyls, halogenated aromatic hydrocarbons, formaldehyde, polybrominated biphenyls, biphenyls, detergents, oils, greases etc. In addition to these, normal hydrocarbons, alcohols, aldehydes, ketones, proteins, lignin, pharmaceuticals etc. are also found in wastewater. Different types of microbes thriving in wastewater may be responsible for different type of diseases. The harmful microbes include bacteria, fungi, algae, plankton, amoeba, viruses and other worms. These water pollutants remain either in solvated, colloidal or in suspended form (Vinod Kumar Gupta, 2012).

2.2. Pesticides – general overview

As the Food and Agriculture Organization of the United Nations (FAO) defined, pesticide is any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, including vectors of human or animal disease, unwanted species of plants or animals causing

harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. A pesticide may be a chemical substance, biological agent (such as a virus or bacteria), antimicrobial, disinfectant or device used against any pest. Basically, agricultural pesticides are divided into five categories, depending on the target pest: insecticides, herbicides, fungicides, rodenticides, and fumigants (Žabar, 2012).

Recently, the European Food Safety Authority (EFSA) tried to replace the expression “pesticide” due to its negative connotation, with the new the term - “plant protective product - PPP” (Žabar, 2012).

For more than six decades synthetic pesticides or PPPs have been used and their consumption increases constantly worldwide. In the past, several different types of insecticides were synthesized and put into application; starting with organochlorine insecticides at the beginning of the last century, through organophosphorus pesticides after the Second World War. However, over the past twenty five years, neonicotinoids have gained increasing interest in the agricultural sector (Žabar, 2012).

2.3. Water Pollution by pesticides

The worldwide consumption of pesticide is about two million tons per year. Of which 24% is consumed in the USA alone, 45% in Europe and the rest is in other countries. The pesticide consumption in the agriculture sector showed that herbicides are the leading category followed by insecticide and fungicide as the weeds produced the highest potential crop loss (34%), with animal pests (18%) and pathogens (16%) being less important (Yusoff, 2013).

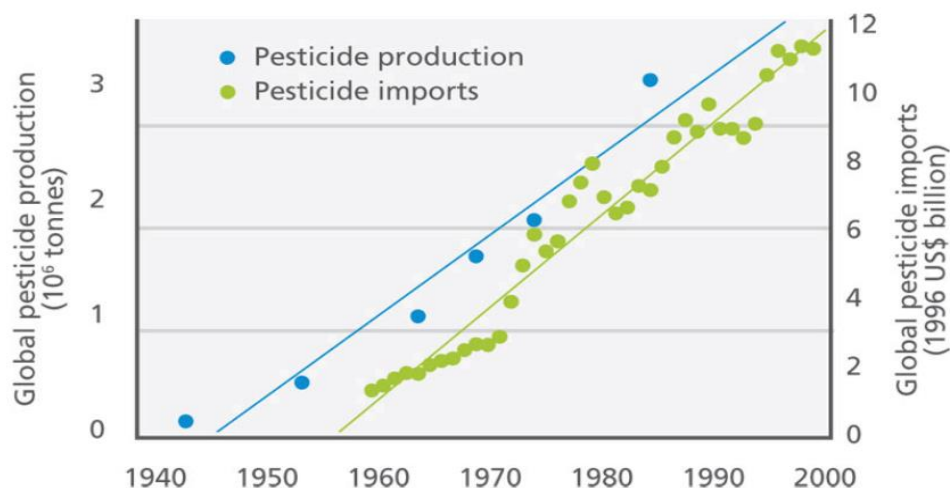


Figure 2. 1. Global Pesticides production (Yusoff, 2013)

There are various groups of pesticides such as carbamate, pyrethroid, organochlorine and organophosphate. Organophosphate pesticides (OPs) are widely used in modern agriculture as an alternative and effort to substitute the organochlorines (OCs) for pest control because of the longevity and toxicity of the organochlorines pesticides. Regardless of the pesticides' group, it has been reported that pesticides manufacturing industries and specifically their use over a long period in agricultural and non-agricultural area can reach the water resources which then influences the quality of groundwater and surface water (Yusoff, 2013).

The widespread use of pesticides in the past decades represents serious water pollutants. Various types of pesticides residues were frequently detected in surface water and aroused great public concern. The pesticides will cause potential adverse health risks even at low concentration (pg/L to ng/L). These pesticides, retained in agrochemical wastewater, are resistant to conventional biological treatment owing to their high toxicity and biological persistence. It was reported that no significant decrease in pesticide content occurred after the biological treatment and remaining recalcitrant organic carbon mainly due to pesticide molecules (Cheng, et al., 2015).

Globally, an alarming level of pesticides has been reported in air, water and soil as well as in foods and biological materials. Some of these pesticides have been reported to be persistent, toxic, mutagenic and carcinogenic. Pesticide contamination of water systems is also a major concern as residues reach the aquatic environment through manufacturing plants, direct surface run-off,

leaching, careless disposal of empty containers, equipment washings, etc. Apart from surface water, pesticides can also contaminate groundwater from both point sources and non-point sources. From nonpoint sources, pesticides typically enter surface water when rainfall or irrigation exceeds the infiltration capacity of soil and resulting runoff then transports pesticides to streams, rivers, and other surface-water bodies. Contamination of groundwater may result directly from spills and from pesticide applications. Groundwater contamination also may come indirectly by the percolation of agricultural and urban irrigation water through soil layers and into groundwater as shown on figure 2.2 below (Yusoff, 2013).

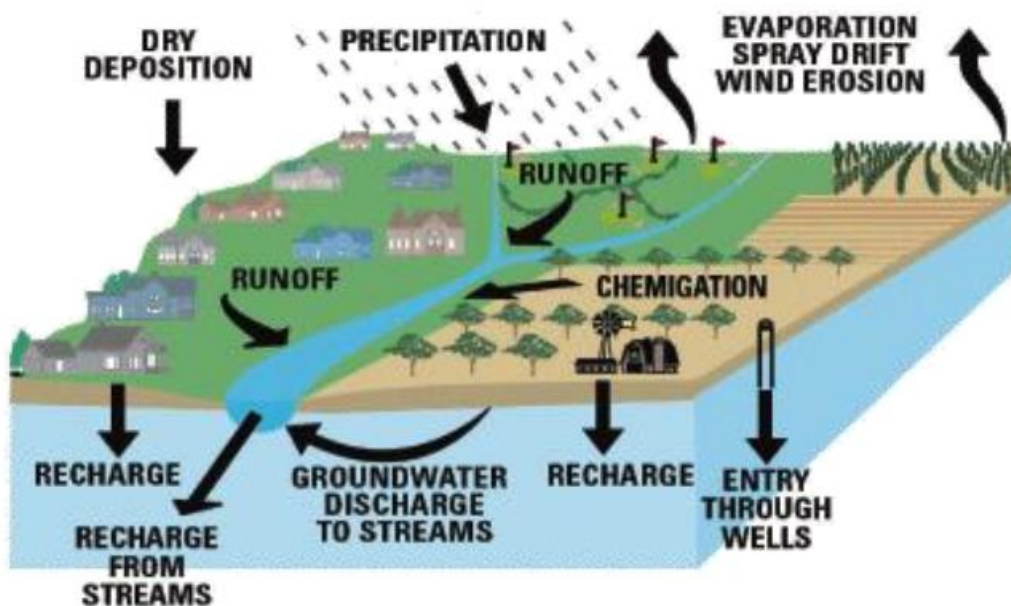


Figure 2. 2. Schematic diagram illustrating routes of pesticides into streams and groundwater (Yusoff, 2013)

Based on different physical and chemical characteristics and due to several features of the pesticide industry these substances should be considered as a major threat to the ecosystem. The pesticide production, transport, application and finally the recycling of the containers stand for many opportunities where the environment is consciously or unconsciously exposed to these contaminants. For instance the residual water of the washing facilities of pesticide containers comprises a high concentration of pesticides and is not always well treated. General problems in this product chain are the diffuse sources of contaminants and the large amounts of pesticides being

deployed in the ecosystem. A major problem is the complexity of the composition of these chemicals due to varying compounds and concentrations. A big part of these compounds exhibit a high persistence in the ecosystem and are called “persistent organic pollutants” (POPs). Further important attributes which affect the behavior of the contaminants in the environment are the solubility in water the absorption coefficient, ionization constant, stability and volatility. Concerning the solubility some of the pesticides represent a threat to the surface water as well as to the groundwater (Hilgert, 2009).

Wastewater containing pesticides have been reported to be treated using conventional wastewater treatment processes such as coagulation, filtration, trickling filters and conventional activated sludge (AS). Conversely, these processes do not provide reliable effective treatment against pesticides. For instance, many studies have reported biological processes to be challenging when treating high strength wastewater due to pollutants showing toxicity and resistance towards the microorganisms. The chlorinated herbicides 2,4-D, 2,4-DCP, 2,4,6-TCP, MCPA and MCPP will be challenging to remove using biological processes due to the structure, chemical groups and significant half-lives, therefore a pre/post treatment option would ensure that these chlorinated herbicides would be removed prior to been discharged (Lindsey Goodwin, 2017).

2.4. Pesticides in Ethiopia

Pesticides in agricultural sector were introduced in Ethiopia in the 19640s. Different types of pesticides were imported by both private and public companies for agricultural uses. Since then, the use of pesticide has increased rapidly for crop protection. Throughout the world overuse and misuse of pesticides in agriculture cause environmental and health effects and Ethiopia is no exception. Recently, Ethiopia has been considered as having the largest accumulations of absolute pesticides in Africa. It is estimated that there were 1,500 tonnes of absolute pesticides (Mengistie B. T., 2016).

The pesticides import data from Ministry of Agriculture (MoA) indicated that pesticides usage in Ethiopia was increased over the last 15 years (1996 - 2011). The table below shows the amount of pesticides imported to the country in tonnes over the specified time interval (Mengistie B. T., 2016).

Table 2. 1. Amount of pesticides imported over the specified time interval (Mengistie B. T., 2016)

Item	Time interval				
	1996-1998	1999-2001	2002-2004	2005-2006	2006-2011
Amount of pesticides imported in tonnes	2,973	3,670	5,079	8,302	27,268.73

Ethiopia is net importer of the agrochemicals the country demand for agrochemicals is dependent on international producers with the exception of one factory which formulates pesticides using imported active ingredients and solvents from foreign countries, mostly from Italy and Israel within the country. The implication is that there is total reliance on imports for consumption needs. These indicate that private investors wishing to invest on production of agrochemicals in the country have a clear advantage to fulfill the local demand and can exporting the manufactured agrochemicals to other African countries. Recognizing the potential vulnerably to global economic shocks from a heavy reliance on imports goods, Ethiopia is moving towards producing its own fertilizer during the next few years (Mengistie B. T., 2017).

Ethiopia is dependent for much of its demand on imported pesticides, although some are manufactured in recent decades within the country. The largest share of all pesticides used in Ethiopia is imported from abroad. According to the data from central statistical agency, a general trend of pesticide importation is found to be an increasing trend for the last 17 years (Table 2.2).

The data from Ethiopian central statistical agency indicates that large amount of pesticides are being imported to the country every year. Table 2.2 shows the amount of pesticides in Metric Tons imported between 2000 and 2017 years. On the other hand, Adami Tulu Pesticides Processing Share Company synthesizes different types of pesticides which contributes to large amount of pesticides accumulation in the country.

Table 2. 2. Pesticide and herbicide import to Ethiopia from 2000 to 2017 years in Metric Tons (MT)

Year	Insecticides (MT)	Herbicides (MT)	Fungicides (MT)	Others (MT)	Total (MT)
2000	160.7	805.9	46.8	2.5	1,015.9
2001	462.6	760.7	36.0	177.5	1,436.8
2002	706.0	1136.0	71.0	171.0	2,084.0
2003	359.0	868.5	77.0	323.0	1,627.0
2004	407.0	915.7	114.0	322.8	1,759.5
2005	455.6	1197.6	146.6	423.8	2,223.7
2006	569.3	1821.1	135.7	801.6	3,327.7
2007	595.7	1687.9	153.7	594.4	3,031.7
2008	453.1	1634.9	141.7	212.7	2,442.4
2009	376.8	3105.8	223.1	12.6	4,718.3
2010	651.9	3146.8	387.3	25.4	4,211.5
2011	431.0	973.0	337.0	0	1,741.8
2012	1212.0	1992.0	355.0	52.0	3,647.7
2013	1751.04	2877.95	512.89	75.13	5,217.01
2014	1617.287	5826.535	282.631	272.9854	7999.438
2015	1487.546	4758.079	454.675	629.3918	7329.692
2016	2150.791	6987.437	579.9951	854.7547	10572.98
2017	2018.787	3295.598	9058.1412	1220.534	15593.06
Average	881.453	2505.523	728.513	342.894	4,443.34
Share in %	19.838	56.388	16.395	7.717	-

Source: (Central Statistical Agency, 2018)

From the above table the three major categories of pesticide chemicals arranged from the higher volume to the lower are herbicides, insecticides and fungicides respectively. The increase in imports and use of agrochemical inputs has followed the expansion of the crop production area in Ethiopia and contributed to yield increases and expansion of large-scale floriculture industries, has resulted in an increased use of pesticides.

The types of herbicides used in Ethiopia (and perhaps elsewhere) really do have toxicity levels harmful to humans; chemicals banned or replaced in high-income countries are often sold and used in Sub-Saharan Africa. For example, both Dichlorophenoxyacetic acid (commonly known as 2,4-

D) and trifluralin are used in Ethiopia; these compounds are 10 and 140 times more toxic for humans than glyphosate, the most commonly used herbicide in the United States, which replaced these more toxic herbicides (Megan Sheahan, 2017).

Ethiopia has no industry to produce active ingredients and only one local pesticide formulating company, Adami Tulu Pesticide Company. A limited amount of the pesticides are produced in Ethiopia, by the Adami Tullu Pesticide Processing Share Company in the Adami Tulu Woreda near Ziway.

This company uses imported active ingredients and solvents to formulate a portion of the pesticides required in Ethiopia. Between 2000 and 2012, the company produced 17,155.52 metric tons of insecticides for agricultural and public health purposes. Of this production, public health products for vector control accounted for a significant share: 8,858.26 metric tons (Central Statistical Agency, 2013/2014).

Table 2. 3. Production by Adami Tulu pesticide processing S.C 2000-2012 (years).

Year	Insecticide for Agriculture(A)	Insecticide for public health (B)	Acaricide	Fungicide	Total(tones)
2000	106.46	-	2.50	-	108.96
2001	293.75	93.65	3.03	-	390.43
2002	319.71	60.34	2.00	-	382.05
2003	545.50	157.78	7.42	-	710.70
2004	397.17	475.25	12.42	-	884.84
2005	327.54	565.41	70.31	-	963.26
2006	792.07	764.46	22.42	-	1,578.95
2007	767.92	616.47	50.59	-	1,434.98
2008	560.93	785.23	34.79	1.84	1,382.79
2009	773.18	1561.58	28.52	0.07	2,363.35
2010	1,110.50	1959.84	65.28	21.50	3,157.12
2011	1,093.02	862.18	67.70	36.57	2,059.47
2012	1,209.51	956.07	71.71	8.44	2,245.73
Share %	48.36	51.64	100	100	-
Total(A+B)	17,155.52				

Source: (Central Statistical Agency, 2013/2014)

2.5. Chemical and physical properties of the chlorinated aromatic herbicides in pesticide production wastewater

The chlorinated aromatic herbicides present in the pesticide production wastewater have different chemical and physical characteristics meaning they have different environmental fates (Table 2.3). To understand and predict the most efficient processes to remove pollutants from wastewater, it is key to correlate the chemical and physical characteristics of the pollutants with their environmental fate such as solubility, molecular weight, structure octanol/water coefficient (Log K_{ow}), sludge distribution coefficient (Kd), Henry's coefficient (Hc) and compounds reactivity to hydroxyl radicals (KoH) (Table 2.3). Furthermore, these characteristics can help design suitable treatment processes using one or a combination of these: sorption, volatilization, biodegradation and transformation or chemical conversion (Lindsey Goodwin, 2017).

Table 2. 4. Interpretation of the physical and chemical characteristics of pollutants

Solubility (mg/ L)	<2 poor solubility	2-100 average solubility	>100 high solubility
Log Kow	0.5-2.5 Very hydrophilic & bioavailable	2.5-4.0 Average hydrophobic	>4.0 Very hydrophobic
Log Hc (atm/mol.m3)	<10 ⁻³ Volatilize	>10 ⁻³ Poor volatilization	
Log Kd	<0.7-1.5 Poor sorption to solids	0.1-10 Average sorption to solids	3.0-3.9 Strong sorption to solids
Log KOH (1/M.S)	<10 ⁹ Poor reactivity with hydroxyl radicals	>10 ⁹ Good reactivity with hydroxyl radicals	

➤ Physical and Chemical Properties of 2,4-D

The 2,4-D is a white crystalline salt. It possesses an aromatic ring to which are attached two chlorine atoms at the ortho and para positions as shown in Figure 2.3 (Mangat, 1997).

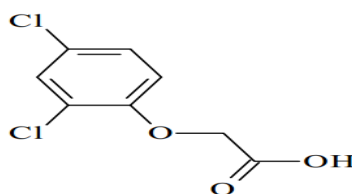


Figure 2.3: Structure of 2,4-D Molecule

This herbicide behaves as an organic anion in aqueous solutions. The solubility of 2,4-D in water is 0.9 g/L. The low solubility in water of the parent compound can be altered by using appropriate salt forms. For example, the sodium, potassium, and amine salts of 2,4-D are highly soluble in water. However, there is a controversy about the low solubility of calcium and magnesium salts in water. 2,4-D is far more soluble in other liquid solvents such as ethanol, ether, and acetone. The solubility values in these three solvents are 13 g/L, 8.5 g/L, and 12.7 g/L respectively. The melting point of 2,4-D is 140.5°C. A vapor pressure of 8×10^{-6} mmHg suggests a low volatilization potential. The polarity of a compound is directly related to the sorption into solid surfaces, which also dictates the mobility in the environment and the bioconcentration potential. 2,4-D with a K_{ow} (octanol/water) value in the 2.81-20.0 range possesses no major bioconcentration threat. On the other hand, DDT with a K_{ow} of about 10^6 exhibits a very high bioconcentration potential (Mangat, 1997).

2.6. Environmental fates of pesticides

The pesticides, when applied onto a surface, they travel outside their intended area of use by air, soil or water. This is one common way in which chemical pesticides cause collateral damage, beyond their intended use. Pesticides can also be found in rain, ground water, streams, rivers, lakes and oceans. There are four major ways that pesticides can reach the water, it can drift outside of the area of where was sprayed, it may leach through the soil, it could be carried as runoff, or it may be spilled accidentally. Pesticides are one of the causes of water pollution, air pollution and soil (Bashour, 2008).

Pesticides in agriculture and urban settings have the potential to contaminate our air, affecting human, animal and plant health. Some pesticide ingredients stay in the atmosphere for only a short period of time, while others can last longer. Pesticides released into the air can settle to the ground, be broken down by sun light and water in the atmosphere, or dissipate into the surrounding air (Tadeo, Analysis of pesticides in food and environmental samples, 2008).

Soil can be degraded and the community of organisms living in the soil can be damaged by the misuse or over use of pesticides. Some pesticides are more toxic to soil organisms than others. Some pesticides may break down quickly when applied to soils, while others may

persist for longer periods. The type of soil and the type of pesticide can also affect pesticide persistence. The use of pesticides decreases the general biodiversity in the soil. If there is no chemicals in the soil there is a higher soil quality, and this allows for higher water retention, necessary for plants to grow (Ghalwa A, 2015).

2.6.1. Environment fates of 2, 4-D

The 2,4-Dichlorophenoxyacetic acid (2,4-D) may reach both surface and subsurface water by several routes including runoff, erosion, leaching, spray drift, improper disposal of containers, and accidental spills. Fate studies explore a variety of interrelated factors such as the degradation of a compound or its persistence and formation of potentially harmful metabolites that may be destructive to the ecological system. Low degradation potential can result in high persistence values for a given compound. In addition, 2,4-D degradation byproducts can also exhibit toxicological properties in the environment (Mangat, 1997).

Once a particular pesticide is released into the environment several physical, chemical and biological factors can influence its behavior. In order to generate photo induced transformation of the phenoxy herbicides, 280-290nm ultraviolet radiation (UV) wavelengths are required. Sunlight falling on the earth's surface is composed of wavelengths greater than 280nm, which facilitate the naturally occurring photochemical degradation of phenoxy acids (Mangat, 1997).

According to the National Library of Medicine (1902) there have been over 200 independent studies that link 2,4-D with various diseases. This general-use chemical is known to produce skin and eye irritation problems. Prolonged breathing of 2,4-D causes coughing, burning, dizziness, and temporary loss of muscle coordination. The 2,4-D is readily absorbed through the skin and lungs in mammals and is excreted through urine. There have been indications of reproductive problems with moderate exposures. However, in a mutagenic effect study, 2,4-D cultured with human cells showed a potential for mutational changes. Several studies have linked 2,4-D exposure to cancer in humans (Mangat, 1997).

2.7. Effects of Pesticides on Human Health

According to a WHO and UNEP report, there are more than 26 million human pesticide poisonings worldwide, with approximately 340,000 deaths per year (Y. S . Yildiz, 2008). A recent study by PAN International assumes that currently, among the total of 1.3 billion farm workers

worldwide, approximately 41 million suffer from pesticide poisoning each year with an average poisoning rate of 32% (B. T. Zhu, 2005). In Africa, PAN-Africa and Pan-UK documented 16 suicide cases in Benin, Senegal, Ghana and Ethiopia in the years 2002-2006 (Fossen, 2006).

A World Bank (2008) report estimates that 355,000 people worldwide die each year from unintentional pesticide poisoning. 25 million agricultural workers in the developing world suffering some form of occupational pesticide poisoning each year, though most incidents are not recorded and most patients do not seek medical attention. Acute pesticide poisoning may in some developing countries be as serious a public health concern as are communicable diseases (S. Tchamango, 2010).

Among the typical symptoms of acute (short-term) poisoning in humans are fatigue, headaches and body aches, skin irritation, eye irritation, irritation of the nose and throat, feelings of weakness, dizziness, nausea, vomiting, excessive sweating, impaired vision, tremors, panic attacks and cramps. Chronic (long-term) poisoning leads to severe health problems, such as cancer, damage to the reproductive system, the liver, the brain, and other parts of the body (M. Y. A. Mollah, 2004).

2.7.1. Short-term Health Effects of Pesticides

Among the typical symptoms of poisoning in humans that are relatively easy to diagnose as acute pesticide poisoning are fatigue, headaches and body aches, skin discomfort, skin rashes, poor concentration, feelings of weakness, circulatory problems, dizziness, nausea, vomiting, excessive sweating, impaired vision, tremors, panic attacks, cramps, etc., and in severe cases coma and death (Middain, 1994). Diagnosis of acute pesticide poisoning generally occurs when one or more of these symptoms, which appear a short time after contact with pesticides, are detected, so that patients or physicians can link them to pesticide exposure. However, these symptoms can also frequently be attributed to other illnesses. Analysis of blood, urine, or stomach content to detect pesticide residues can lead to an unequivocal diagnosis (Tadeo, 2008).

2.7.2. Long-term Health Effects of Pesticides

When a person is exposed to pesticides over a long period of time, it is hard to know if his health problems are caused by pesticides. Long-term exposure may cause long-term harm,

such as cancer and damage to the reproductive system, the liver, the brain, and other parts of the body.

Many long-term effects of pesticides are hard to see because people in farming areas are exposed to many different chemicals and because farm workers may move from place to place. When people get cancer and other diseases, doctors and scientists may say the illness is due to chance, or to problems other than pesticides or contamination. They may tell us we cannot blame pesticides or other toxic chemicals. And sometimes people who sell pesticides or promote pesticide use will lie about it because they do not want to be responsible for other people's health problems. They can say this because it is often impossible to prove without a doubt that an illness which takes a long time to develop was caused by a particular pesticide or other toxic chemical. Pesticides and other toxics can cause many long-term (chronic) illnesses. Some signs of chronic illness are: weight loss, constant weakness, constant or bloody cough, wounds that do not heal, no feeling in the hands or feet, poor balance, loss of vision, very fast or very slow heartbeat, sudden mood changes, confusion, memory loss, and trouble concentrating (Hamada, 2002).

The connection between pesticide exposure and common diseases affecting the public's health continues to strengthen causing more and more concern for individuals directly and indirectly exposed to pesticides. Farm workers are directly exposed to and work with pesticides on a daily basis. Diseases that are most linked to pesticide exposure are asthma, autism and learning disabilities, birth defects and reproductive dysfunction, diabetes, Parkinson's and Alzheimer's diseases, and several types of cancer (Lobe, 2006).

2.8. Methods for the pesticides removal

There are four major causes of pesticide water pollution (Žabar, 2012):

- Pesticide treatment as a consequence of agricultural practices (in concentration range of few ppb),
- Rinse water from containers and spray equipment (10-100 ppm),
- Wastewater from agricultural industries (10-100 ppm),
- Wastewater from formulating or manufacturing pesticide plants (1-1000 ppm).

As every year more and more xenobiotics are released into the environment, a pathway for their efficient degradation or removal should be implemented. Various techniques are reported, such as microbial degradation of pesticides, constructed wetlands, biological waste water treatment plants and sonochemical degradation. Moreover, photodegradation studies were efficiently used for various pesticide degradation sequences during last decade and revealed diverse kinetics, mechanisms and the formation of by-products (Žabar, 2012).

A promising way for decreasing pesticides' concentration, or even complete removal, is the application of advanced oxidation processes (AOPs). Heterogeneous TiO₂ photocatalysis and photo-Fenton's reagent are the most intensively applied techniques. However, the efficiency of applied AOPs was mostly evaluated through the mineralization rate and the degradation of an initial compound (Žabar, 2012).

2.8.1. Photodegradation of pesticides

According to the literature, the degradation of pesticides can be classified into a few broad categories such as (Žabar, 2012):

- Direct photodegradation,
- Photosensitized degradation,
- Advanced Oxidation Processes (AOPs).

Most of the photodegradation experiments under natural conditions or laboratory conditions are performed in water (natural waters or deionized water) and in soil. Some of them are carried out in field while others are performed under laboratory conditions. The main procedure for these methods is to prepare a known concentration of selected pesticides in a certain matrix and within defined time intervals the sampling was carried out. (Žabar, 2012)

2.8.1.1. Direct photodegradation

Almost all pesticides show absorbance in UV-Vis spectrum, however at short wavelengths. On the other hand, light from the Sun reaches the Earth' surface, but with the small amount of UV irradiation, mostly UV-A ($\lambda = 320 - 400$ nm) and the small part of UV-B ($\lambda = 280 - 320$ nm). Therefore, the direct photodegradation of the pesticides was expected to be very limited. In the

literature, the direct photodegradation was mostly studied through laser-pulsed UV radiation (Žabar, 2012).

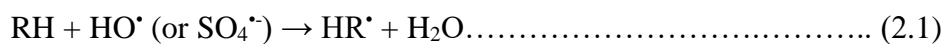
2.8.1.2. Photosensitized degradation

This specific degradation depends on the absorption of light by another molecule. Moreover, this process can transfer energy from its excited state to the pesticides and again as a consequence, pesticides can undergo different processes following direct photodegradation (Žabar, 2012).

2.8.1.3. Advanced Oxidation Processes (AOP)

The various currently used chemical oxidation processes for pesticide elimination are reported. Heterogeneous TiO₂ photocatalysis, ozonation and photo-Fenton's reagent are the most intensively applied technologies. A promising way for decreasing pesticides' concentration, or even complete removal, is the application of the so called advanced oxidation processes (AOP) (Žabar, 2012).

Advanced oxidation processes (AOPs) are technologies with significant importance in environmental restoration applications. The AOPs concept was established by Glaze et al., who defined AOPs as processes involving the generation of highly reactive oxidizing species able to attack and degrade organic substances. Nowadays AOPs are considered high efficiency physical-chemical processes due to their thermodynamic viability and capable to produce deep changes in the chemical structure of the contaminants via the participation of free radicals. These species, mainly hydroxyl radicals (HO[•]), are of particular interest because their high oxidation capability. However, other studies have suggested that, besides hydroxyl radicals, AOPs can also generate other oxidizing species. Generated radicals are able to oxidize organic pollutants mainly by hydrogen abstraction (eq. 2.1) or by electrophilic addition to double bonds to generate organic free radicals (R[•]) which can react with oxygen molecules forming peroxyradicals and initiate oxidative degradation chain reactions that may lead to the complete mineralization of the organics, as proposed in eq. (2.1) (Marco A. Quiroz, 2011).



AOPs are considered clean technologies for the treatment of polluted waters that apply the concept of producing hydroxyl radicals ($\text{HO}\cdot$), which will attack the organic pollutants. The efficiency of AOPs is based on the generation of these highly reactive radicals that are unselective and powerful oxidizing species ($E^0 = 2.80 \text{ V}$), which can degrade indiscriminately micro pollutants with reaction rate constants usually around $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, yielding CO_2 , H_2O and eventually, inorganic ions as final products. After fluorine, hydroxyl radical is the strongest oxidant and its production can be achieved by many pathways (i.e., by different AOPs based on different fundamentals), which allows one to choose the appropriate AOP according to the specific characteristics of the target water or wastewater and treatment requirements (Ana R. Ribeiro O. C., 2014).

When the contaminants and their reaction intermediate products are completely destroyed by the chemical process (mineralization), critical secondary wastes are not generated and, thus, post-treatment or final disposal is not required. However, when complete mineralization is not achieved or requires too long reaction periods, a post-treatment may be necessary before final disposal. A higher biodegradability and/or lower toxicity of the reaction byproducts, in comparison with the parent compounds, are desirable benefits of applying AOPs to treat wastewaters; but in some cases these byproducts can be less biodegradable and/or more toxic than the parent pollutants. AOPs can be applied as post-treatment or pre-treatment of biological processes. The integration of different AOPs in a sequence of complementary processes is also a common approach to achieve a biodegradable effluent that can be further treated by a cheaper and conventional biological process, reducing the residence time and reagent consumption in comparison with AOPs alone. However, it is important to completely eliminate the oxidizing agents before any biological treatment, since they can inhibit the growth of microorganisms (Ana R. Ribeiro O. C., 2014).

Diverse classifications of the AOPs can be done depending on different aspects of the process, the inclusion of light, the use of precursors for $\text{HO}\cdot$ production, etc. Table 2.2 shows a classification of the most common AOPs evaluated for water and wastewater according to its photochemical nature (Gonzalo, 2017).

Table 2. 5. Most common AOPs evaluated for water and wastewater treatment.

Advanced oxidation Processes	
Photochemical processes	Non-photochemical processes
UV oxidation process	Ozonation (O ₃)
UV/H ₂ O ₂	Fenton
UV/O ₃	Ultrasound (US)
UV/H ₂ O ₂ /O ₃	Us/H ₂ O ₂ , US/O ₃ , US/Fenton
UV/Ultrasound	Electrochemical Oxidation
Photo-Fenton	Supercritical water oxidation
Photo-Catalysis	Ionizing radiation
Vacuum UV (VUV)	Electron-beam irradiation
Microwave	Water-air oxidation
Sonophotocatalysis	Pulsed plasma

Source: (Gonzalo, 2017)

2.8.2. Implementation of AOPs

All advanced oxidation processes, when applied for the degradation of organic compounds, share the same reactions pattern (Figure 2.3). There are producing simultaneously the AOP reaction that generates the oxidative specie and the oxidation reactions that degrade the organic compounds (Gonzalo, 2017).

The first stage of the oxidative process involves the parameters affecting the AOP reaction rate and consequently the rate of production of the oxidative specie, which use to be the hydroxyl radical (HO·) (Gonzalo, 2017).

In the second stage, which is produced simultaneously to the first one, the oxidative species generated react with the recalcitrant organic compounds and oxidize them into biodegradable compounds or mineralize them into water, carbon dioxide and inorganic salts. The extent of these reactions is mainly controlled by parameters such as the amount and nature of the organic load in water, amount of oxidant produced, the presence of scavenging compounds or the amount of other organic compounds competitive for the oxidant species. According to these parameters, the

original recalcitrant organic compounds can be partially oxidized into biodegradable compounds or totally mineralized (Gonzalo, 2017).

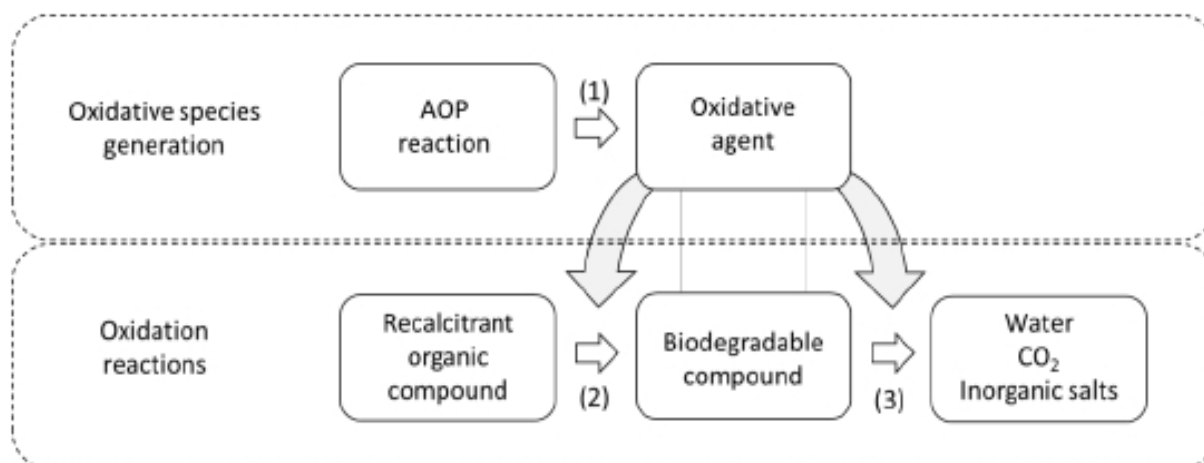


Figure 2. 3. Stages involved in the degradation of a recalcitrant organic compound by using an AOP.

To achieve the desired extent of pollutants removal, sometimes it is convenient to couple some processes to optimize the AOP performance (Gonzalo, 2017).

2.9. Degradation of 2,4-Dichlorophenoxy acid by Advanced Oxidation Process

The degradation of 2,4-D by previous researchers was reported. Different methods advanced oxidation processes were investigated and promising results were obtained. Some them were described as follows.

The chlorophenoxy herbicide, 2,4-D (2,4-dichlorophenoxyacetic acid) is one of the most widely used pesticides. Complete conversion and substantial mineralization (70% as TOC) of 2,4-D during degradation by H₂O₂/UV AOP ($\lambda = 185\text{--}254$ nm, 50 – 200 mg/L of H₂O₂, 41 mg/L of 2,4-D) (Alfano, 2001). The conversion was greatly enhanced from the direct UV photolysis alone (Kwan, 2003).

Varieties of Fenton-type processes have been evaluated for 2,4-D degradation. Slightly faster and higher conversion of 2,4-D was achieved by the classic Fenton reaction than by UV photolysis. 2,4-Dichlorophenol was detected as a degradation intermediate of the Fenton treatment. Although

the Fenton-type $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process (dark, oxygenated; 55.8 mg/L of Fe^{3+} , 340 mg/L of H_2O_2 , 22.1 mg/L of 2,4-D, PH 2.7) was slower than the classic Fenton, a higher degree of mineralization was achieved with the former process. Nearly quantitative (90–100%) decolorization was observed in the oxygenated 2,4-D solution treated by the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process (Pignatello, 1992).

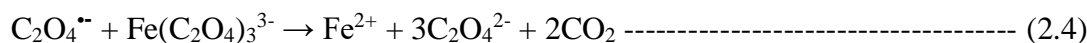
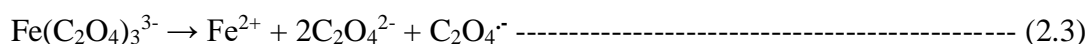
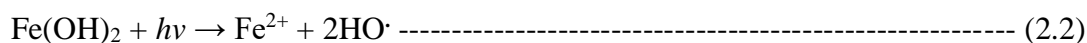
The optimization of 2,4-D degradation and mineralization by oxalate-mediated photo-Fenton process using the response surface methodology. Up to 93% of TOC from 0.1 mM 2,4-D was mineralized under the optimized reaction condition involving 0.6 mM ferrioxalate, 8 mM H_2O_2 , and 10 min of irradiation with a 15 W black light lamp (Paterlini, 2005).

The degradation of several chlorophenoxy herbicides by an electrochemical Fenton process generating H_2O_2 and reducing Fe^{3+} with continuous bubbling of O_2 and electrolysis (60 mA) was investigated. Ferrous ammonium sulfate, $(\text{NH}_4)_2\cdot\text{Fe}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$, was supplied as a source of ferric ions (55.8 mg/L of Fe^{3+}). More than 75% TOC reduction (220 mg/L of 2,4-D) was achieved by the electro-Fenton treatment after 6 h (Oturán, 2000).

2.10. The Photo-Fenton Process

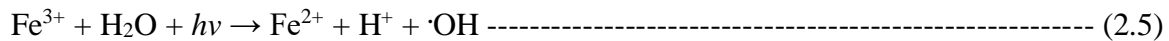
Photo-Fenton process is the combination of Fenton's reaction with UV light (180-400 nm) and as a result additional $\cdot\text{OH}$ is produced. Some decades ago, it was found that the illumination of Fenton reaction systems with UV or visible light accelerated the rate of degradation of a number of pollutants (Virkus, 2016).

It is well accepted that in the photo-Fenton process the irradiation with UV–vis light accelerates the regeneration rate of Fe^{2+} from Fe^{3+} complexes (Eq. (2.2)), and also the photo-decarboxylation of ferric carboxylates. As alternative, the Fe^{3+} oxalate complexes are used (Fe^{3+} -oxalate-induced photolysis or photo-Fenton-like oxidation), which have an extended absorption range (up to 570 nm) and give a higher quantum yield of Fe^{2+} as compared to the Fe^{2+} hydroxyl complexes (Eqs. (2.3) and (2.4)) (Ana R. Ribeiro O. C., 2014).

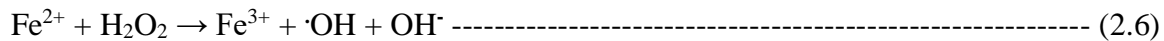


The photo-Fenton process is more efficient in the generation of hydroxyl radicals when compared to the conventional Fenton process or to photolysis alone, so the degradation rate of organic compounds is expected to be higher. The great advantage of lowering the amount of catalyst needed leads to a compensation in the higher costs of UV as well as to a decrease of the final sludge volume, making the photo-Fenton process competitive with the classical Fenton process regarding the overall treatment costs (Ana R. Ribeiro O. C., 2014).

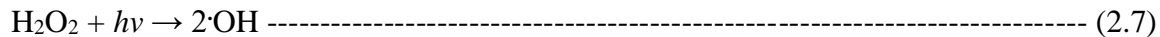
Fe(III) can catalyze the formation of hydroxyl radicals when irradiated with light (wavelength 180-400 nm), that is, ultraviolet and some visible light. This process can be illustrated with following reactions (Virkus, 2016):



It is called photo-Fenton reaction and is followed by



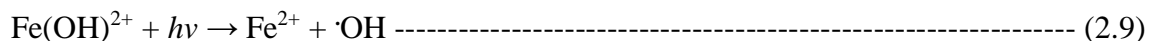
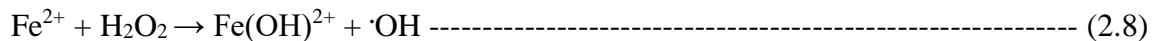
Hydrogen peroxide photolyzes with UV light



Iron starts to cycle between the 2+ and 3+ oxidation states. As long as H₂O₂ is available, the continuous recycle of ferrous iron reduces the amount of iron salts required for the Fenton's reaction (Virkus, 2016).

The production of hydroxyl radicals is determined by the availability of light and H₂O₂. In theory, by combination of these two reactions, one mole of H₂O₂ consumed should produce two moles of •OH (Virkus, 2016).

Photo-Fenton process can also be explained with the following reactions:



Studies have shown that the photo-Fenton reaction is optimum at PH 2.8. Under such conditions, half of the Fe(III) is present as Fe³⁺ ion and half as Fe(OH)²⁺ ion, the photo-active species. If PH

is lower than 2.8, the concentration of $\text{Fe}(\text{OH})^{2+}$ decreases and if PH is higher, the $\text{Fe}(\text{III})$ precipitates as oxyhydroxides (Virkus, 2016).

The $\text{Fe}(\text{OH})^{2+}$ ion absorbs light at wavelengths up to 410 nm. Thanks to that, the reaction can be carried out with longer wavelength light than other advanced oxidation processes like O_3/UV or H_2O_2 (wavelengths <300 nm) (Virkus, 2016).

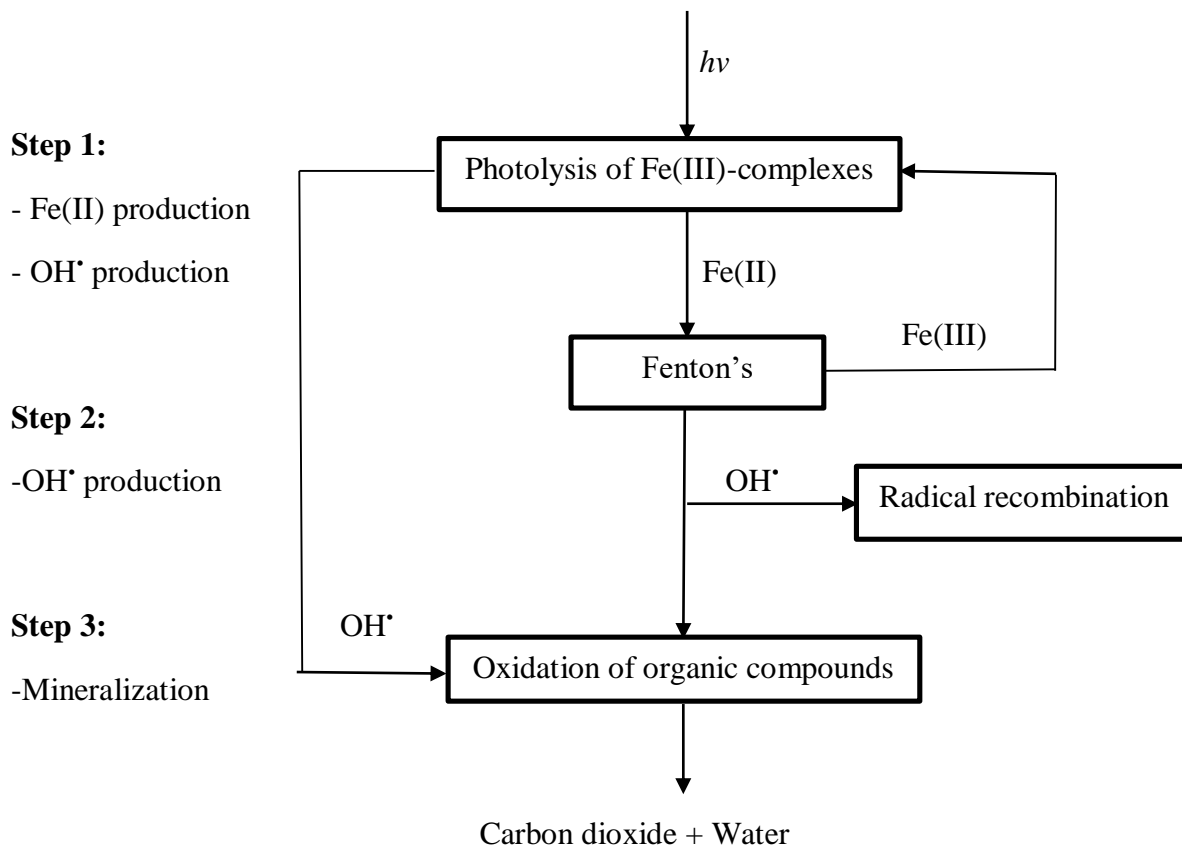


Figure 2. 4. Reaction pathways of the Photo-Fenton process

Figure 2.4 shows the reaction pathways for the process starting with the primary photo-reduction of the dissolved $\text{Fe}(\text{III})$ complexes to $\text{Fe}(\text{II})$ ions followed by the Fenton's reaction and the subsequent oxidation of organic compounds. Additional hydroxyl radicals generated in the first step also take part in the oxidation reaction (Parag R. Gogate, 2004).

The photo-Fenton process has many advantages. It gives higher degree of mineralization and faster reaction rates than Fenton reaction. The photo-Fenton does not produce new pollutants and small

amount of iron salt is needed. Remaining hydrogen peroxide that is not used in photo-Fenton process will decompose into water and molecular oxygen (Virkus, 2016).

2.11. The radiation sources of the Photo-Fenton process

Using UV or solar light can increase the mineralization degree and make dark Fenton process more efficient by the photo-reduction of $\text{Fe}(\text{OH})^{2+}$ which leads to additional $\cdot\text{OH}$ production and continuous regeneration of Fe^{2+} (Virkus, 2016).

In homogeneous and heterogeneous Photo-Catalysis, radiation is identified as a very important supply to the overall process. Two main radiation sources have been used to promote these processes: artificial radiation and solar radiation. The use of artificial radiation sources has been widely applied for pesticide degradation by mean of different photochemical processes, among them homogeneous or heterogeneous Photo-Catalysis. In recent years, application of photo-catalytic processes using solar radiation has increased as a cost-effective alternative for these technologies. It is interesting note that, actual industrial or commercial applications developed recently are related to solar enhanced processes (Marco A. Quiroz, 2011).

Several different solar collector geometries have been tested for application to solar photo-catalytic processes (both, homogeneous and heterogeneous) and a wide number of works dealing with the comparison between all these experimental results have been reported. From all these information, the actual consensus is that low concentration collectors seems to be the best technological option instead of earlier high concentration designs. In particular, compound parabolic concentrators (CPCs) have been identified as very promising technological approach to industrial application of solar Photo-Catalysis. CPCs combine the characteristics and advantages of high range concentrators and static flat systems. Among their main advantages are use of global solar radiation, absence of tracking systems, low evaporation of volatile compounds, low cost and high optical and quantum (Marco A. Quiroz, 2011).

2.12. Effects of factors on Photo-Fenton process

Based on several studies, there are a number of indicators that affect the efficiency of photo-Fenton process and they must be considered when doing experiments or using it for the clarification of wastewaters.

2.12.1. The pH

The pH affects the oxidation of organic substances both directly and indirectly. The Fenton and photo-Fenton reactions are strongly pH-dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. The experiments were carried out at a pH within the range of 2.5-4.0. The degradation decreased at pH values higher than 3.5, because iron precipitated as hydroxide (Youssef Samet, 2012).

Additionally, the oxidation potential of the hydroxyl radical was known to decrease with increasing pH. Another reason for the inefficient degradation at $\text{pH} > 3$ 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 (Youssef Samet, 2012).

Fenton and photo-Fenton processes are dependent of the solution pH because of iron and hydrogen peroxide is used in this systems. Optimal pH for photo-Fenton process is considered to be around 3. If the pH is higher than 3, Fe (III) catalyst starts to precipitate. pH also affects the decomposition of H_2O_2 . Sulphuric acid and hydrogen peroxide are used to control the pH in photo-Fenton process (Virkus, 2016).

Usually, neutral pH causes decomposition of hydrogen peroxide, which leads to extension of the degradation reaction. That is why acidic pH is more favourable for the decomposition of H_2O_2 and reaction between H_2O_2 and Fe^{2+} , resulting in the generation of hydroxyl radicals. Photo-Fenton process was efficient when pH was between 2 and 4 (Virkus, 2016).

Photo-Fenton process is strongly dependent on the solution pH mainly due to iron and hydrogen peroxide speciation factors. The optimum pH for the Photo-Fenton reaction was found to be around 3, regardless of the target substrate. The activity of Photo-Fenton reagent is reduced at higher pH due to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate. In this situation, less hydroxyl radicals are generated due to the presence of less free iron ions. The oxidation potential of hydroxyl radicals decreases with increasing pH. In addition, auto-decomposition of hydrogen peroxide is accelerated at high pH. In general higher-than-optimum pH values disturb Photo-Fenton efficiency through (Moussavi, 2017):

- Prevention of H_2O_2 decomposition to generate $\cdot\text{OH}$ s due to the deficiency of H^+ ions,

- Accelerated decomposition of H_2O_2 to water and oxygen at PH values above 5,
- Decline in oxidation potential of hydroxyl radicals ($E^0 = 2.8\text{-}1.95\text{ V}$ at pH 0-14),
- Possible generation of more selective ferric species other than hydroxyl radicals at PH above 5 and
- Development of ferric oxyhydroxide (Fe-OOH) at PH above 4 that reduces degradation rate. At PH values above 4, iron precipitates as ferric hydroxide.

At PH below 3, decrease in degradation efficiency was observed. At very low PH values, iron complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ exists, which reacts more slowly with hydrogen peroxide than other species. In addition, the peroxide gets solvated in the presence of high concentration of H^+ ions to form stable oxonium ion $[\text{H}_3\text{O}_2]^+$. Oxonium ions make hydrogen peroxide more stable and reduce its reactivity with ferrous ions. Therefore, the efficiency of the Photo-Fenton process to degrade organic compounds is reduced both at high and low PH. Thus an adequate control of PH would increase process efficiency (Moussavi, 2017).

2.12.2. The Ferrous ion concentration

Iron dosage is a crucial parameter for design of large scale wastewater treatment plants. The concern is not only for the cost of iron salt, but also for its influence on the needed irradiation time which affects the reactor size. Moreover, the residuals of iron in treated effluent and settled sludge is very harmful to the environment, and needs further treatment to be separated. Therefore, the dosage of iron should be optimized according to the initial concentration of pesticides and the desired degree of pesticides elimination. The relatively high dosage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is attributed to the consuming of some Fe^{+2} ions in coagulation of fine suspended particulates existing in the wastewater. The photo-degradation of pesticides was poor when the process was free from Fe^{+2} . This could be explained by the increasing of hydroxyl radicals produced from photo-Fenton reaction (Mohamed Gar Alalm A. T., 2015).

The Photo-Fenton reaction begins by producing hydroxyl radicals from the reaction between ferrous ion and hydrogen peroxide. Usually the rate of degradation increases with an increase in the concentration of ferrous ion. However, the extent of increase is sometimes observed to be marginal above a certain concentration of ferrous ion. Also, an enormous increase in the ferrous ions will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the total dissolved solids content of the effluent stream and this is not permitted. Thus,

laboratory scale studies are required to establish the optimum loading of ferrous ions to mineralize the organics (Moussavi, 2017).

Higher amount of Fe^{2+} can inhibit UV radiation penetration because of the production of brown turbidity in the photo-Fenton system. Through photolysis, Fe^{2+} is regenerated and due to that, the amount of Fe^{2+} can be reduced. If there is not enough H_2O_2 , concentration of Fe^{2+} can increase 30% because of the photolytic regeneration (Virkus, 2016).

2.12.3. The Hydrogen peroxide concentration

The use of hydrogen peroxide as an oxidant has a number of advantages over other chemical treatments such as chlorination and ozonation; its commercial availability, thermal stability and storage on-site, infinite solubility in water, no mass-transfer problems associated with gases, minimal capital investment, and no formation of disinfection by-products such as halogenated hydrocarbons and bromate ion (El-Din, 2006).

Concentration of hydrogen peroxide plays a crucial role in deciding the overall efficiency of the degradation process. It has been observed that the degradation percent of the pollutant increases with an increase in the dosage of hydrogen peroxide. However, care should be taken while selecting the operating oxidant dosage. The unused portion of hydrogen peroxide during the photo-Fenton process contributes to COD and hence excess amount is not recommended. Also, the presence of hydrogen peroxide is harmful to many of the organisms and will affect the overall degradation efficiency significantly, where photo-Fenton oxidation is used as a pretreatment to biological oxidation (Moussavi, 2017).

When H_2O_2 or Fe^{2+} is overdosed for making enough hydroxyl radicals available for the oxidation, then the best efficiency is achieved. Mineralization is not complete if the hydrogen peroxide dosage is decreased. If the H_2O_2 dosage is higher, then the degradation percentage increases. Extra amount of hydrogen peroxide can cause iron sludge flotation or sedimentation (Virkus, 2016).

It is important to determine an optimal ratio of hydrogen peroxide and iron to increase COD removal. The ratio of H_2O_2 and Fe^{2+} should be as low as possible to reduce the amount of final sludge and to avoid recombination of hydroxyl radicals (Virkus, 2016).

As the optimal ratio of hydrogen peroxide and iron depends not only on the concentration of organic contaminants, but is influenced by other constituents present in the wastewater, the hydrogen peroxide and iron dosages and the optimal ratio should be determined experimentally for every specific case (Virkus, 2016).

2.12.4. The Temperature

Temperature has a small positive effect on the treatment efficiency in photo-Fenton process compared to the other factors. Too low and too high temperatures usually decrease the process efficiency, so the suitable temperature is between 20°C and 30°C (Virkus, 2016).

2.12.5. The Contaminant concentration

Regarding wastewater treatment plants, the influent water usually contains high organic matter load, which produces a high competition for the oxidative species. Thus, the application of an AOP for the elimination of trace recalcitrant compounds would be not economically viable to be applied to raw water. In this case, the AOPs are usually applied as tertiary treatments, once the secondary biological treatment have already removed the higher amount of organic matter and allows a more efficient removal of trace refractory compounds. Even so, if the organic load in the influent is low, AOPs could eventually be applied after primary treatment, which also would enhance wastewater biodegradability (Gonzalo, 2017).

In the case of drinking water treatments, the influent coming from surface and groundwater use to contain a very low load of organic matter. The low competition for the oxidant species allow to apply AOPs as a pre-oxidation as the initial treatment to remove these refractory trace organic compounds or also as a post-treatment after the process, which could remove the trace organic compounds and act as disinfection process at the same time (Gonzalo, 2017). Several studies have shown that if the initial contaminant concentration is higher, then the degradation of pollutant decreases. It can be said, that lower concentrations are preferred.

2.12.6. The Turbidity

This water property also affects the HO \cdot production reaction in photochemical based AOPs. A high turbidity lowers water transmittance, what consequently reduces the penetration of light into the source water. Thus, the production of \cdot OH will be drastically reduced and so the global efficiency on target compounds removal (Gonzalo, 2017).

2.12.7. The Irradiation time

The rate of pesticides degradation was higher during the first 90 min of effective irradiation time. In the second 90 min, the degradation rate of pesticides gradually decreased. This was probably due to the consumption of hydroxyl radicals and the low remaining concentration of pesticides. After 120 min of irradiation the degradation of pesticides was limited. Hence, the optimum irradiation time is considered to be 120 min (Mohamed Gar Alalm A. T., 2015).

The optimum normalized illumination time is 120 minutes, which achieved 91% removal of COD and 78% degradation of Chloropyrifos. Increasing the illumination time more than 120 min gave slight improvement on the removal efficiency of pesticides and COD because most of H_2O_2 and Fe^{+2} were consumed, which detract the rate of organic matter degradation (Mohamed Gar Alalm A. T., 2013).

2.13. Advantages and Disadvantages of Advanced Oxidation Processes

2.13.1. Advantages of Advanced Oxidation Processes

- Rapid reaction rates.
- Small foot print.
- Potential to reduce toxicity and possibly complete mineralization of organics treated.
- Does not concentrate waste for further treatment with methods such as membranes.
- Does not produce materials that require further treatment such as "spent carbon" from activated carbon absorption.
- Does not create sludge as with physical chemical process or biological processes (wasted biological sludge).

2.13.2. Disadvantages of Advanced Oxidation Processes

- Capital Intensive.
- Complex chemistry must be tailored to specific application.
- For some applications quenching of excess peroxide is require (Sandip Sharma, 2011).

3. MATERIALS AND METHOD

3.1. Materials

3.1.1. The 2, 4-Dichlorophenoxyacetic acid (2,4-D)

The most commonly used herbicide in Ethiopia, 2,4-D (2,4-dichlorophenoxyacetic acid), was used to prepare synthetic pesticide wastewater solution. The 2,4-Dichlorophenoxyacetic acid (commonly 2,4-D) is an organic compound with the chemical formula $C_8H_6Cl_2O_3$. It is a systemic herbicide which selectively kills most broadleaf weeds by causing uncontrolled growth in them, but thin leaves like grasses, cereals, lawn turf, and grassland relatively unaffected. It acts by mimicking the action of the plant growth hormone auxin, which results in uncontrolled growth and eventually death in susceptible plants.

Table 3. 1. General Characteristic of 2,4-dichlorophenoxyacetic acid

Chemical Name	Synonyms	Color	Form	Molecular Formula	Molecular Weight
2,4-Dichlorophenoxyacetic acid	2,4-D; 2,4 Dichlorophenoxyacetic acid; 2,4-Dichlorophenoxyacetic acid	White to yellow : yellow color is phenolic impurities	Crystalline powder	$C_8H_6Cl_2O_3$ or $Cl_2C_6H_3OCH_2COOH$	221.03 g/mol

The Structural formula of 2,4-dichlorophenoxyacetic acid is shown below

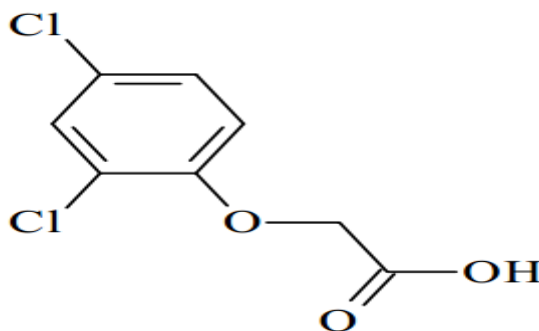


Figure 3. 1. Structural Formula of 2,4-dichlorophenoxyacetic acid

3.1.2. Analytical Instruments

Laboratory equipment such as UV lamp, measuring cylinder, magnetic mixer, 250 ml and 50ml beakers, analytical balance, oven, BOD incubator, turbidity meter, COD digester, COD vials with stand, TOC analyzer and personal protective equipment were used. UV lamp was used as a light radiation source and digital pH meter for pH measurement were used.

3.1.3. Chemicals

The herbicide (2,4-Dichlorophenoxyacetic acid) in the form of crystalline powder was bought from private distributors' shops found around Merkato. Fenton's reagent such as hydrogen peroxide (H_2O_2), hydrated ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and to adjust the PH of the wastewater sample, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were bought from private importers' shops found around kirkos. At the end of the experiments the pH was stabilized (between 6 and 8) by drops of a sodium hydroxide solution (2M) to precipitate the iron.

3.2. Methods

3.2.1. Wastewater preparation

The pesticide wastewater was synthetically prepared to from a stock solution using commercial formulations of 2,4-D (2,4-dichlorophenoxyacetic acid) imported to Ethiopia. The RICHWAY®750 WDG, the commercially available type of 2,4-dichlorophenoxyacetic acid was diluted with distilled water to simulate the wastewater from formulating or manufacturing pesticide plants. The 200 mg/L concentration of pesticide wastewater which was used in this study confirms with the concentration in the wastewater from formulating or manufacturing pesticide plants (1-1000 ppm) as expressed in section 2.8. It is also made to confirm with concentration used for treatment of pesticides as expressed in a number of literatures.

The stock solution preparation of wastewater for the 200 mg/L of 2,4-D was conducted as follows:

- 200 mL of distilled water was filled to the 250 ml beaker.
- 40mg of 2,4-D (2,4-dichlorophenoxyacetic acid) was added to the distilled water to prepare stock solution of a desired concentration.
- The content of the reactor was mixed with magnetic mixer to obtain homogenous solution.

3.2.2. Analytical Methods

The synthesized wastewater was characterized in terms of parameters such as chemical oxygen demand (COD, mg/l), biochemical oxygen demand (BOD, mg/l), total organic carbon (TOC, mg/l), turbidity (NTU) and pH. The experiment was conducted according to procedures given in standard methods for the examination of water and wastewater. Some of the experimental procedures which are relevant with the objectives of this work are described in the following sections. The final result describing the extent of pesticide removal from wastewater is expressed in terms of chemical oxygen demand (COD, mg/l) and total organic carbon (TOC, mg/l).

3.2.2.1. Five Days Biochemical Oxygen Demand (BOD₅) Test

BOD of wastewater is the amount of oxygen required for the biological decomposition of dissolved organic matter to occur under slandered condition at standardized time and temperature. Usually the time is taken as 5 days and the temperature is 20 °C. The BOD test is among the most important method in sanitary analysis to determine the polluting power or strength of industrial wastewater.

Procedure for BOD test

Wastewater sample was collected in two BOD bottles. One BOD bottle was incubated in BOD incubator for five days at 20°C while DO of another was determined on the first day. After five days, another BOD bottle was removed from the incubator and DO was determined. Difference in DO was calculated which gave the measure of BOD. When seed is not used:

$BOD\text{ mg/l} = (\text{Initial DO} - DO_5) * \text{Dilution Factor}$

$$\text{Dilution Factor} = \frac{\text{Bottle Volume (300 ml)}}{\text{Sample Volume}}$$

Where, Initial DO = DO of diluted sample before incubation, mg/L

DO₅ = DO of diluted sample after 5 days incubation at 20°C, mg/L

BOD₅ analysis is usually performed in a 300 mL sample bottle

Note: If initial DO is less than 1 mg/L or initial (DO – DO₅) is less than 2 mg/L, the

BOD result is invalid and should not be used for reporting purposes.

When seed is added directly to the sample or seed control bottle:

$$\frac{mg}{L} \text{ of BOD} = \frac{(D1 - D2) - (B1 - B2)F}{P}$$

Where: D1 = DO of diluted sample before incubation, mg/L

D2 = DO of diluted sample after 5 days incubation at 20°C, mg/L

P = decimal volumetric fraction of sample used (mL sample/300)

B1 = DO of seed control before incubation, mg/L

B2 = DO of seed control after 5 days incubation at 20°C, mg/L

$$F = \frac{\text{Volume of seed in diluted sample}}{\text{Volume of seed in seed control}}$$

Note: If D2 is less than 1 mg/L or (D1 - D2) is less than 2 mg/L, the BOD result is invalid and should not be used for reporting purposes. Dilution Water Blank should not deplete more than 0.2 mg/L. Each sample should deplete at least 2 mg/L. Final DO should not be less than 1.0 mg/L.

3.2.2.2. Chemical Oxygen Demand (COD) Test

COD is the measurement of the amount of oxygen in water consumed for chemical oxidation of pollutants. COD determines the quantity of oxygen required to oxidize the organic matter in water or waste water sample, under specific conditions of oxidizing agent, temperature, and time. For domestic and some industrial wastewater, COD value is about 2.5 times BOD value. COD values are always greater than BOD values.

Procedure for COD test

Take three COD vials with stopper (two for the sample and one for the blank). Add 2.5 mL of the sample to each of the two COD vials and the remaining COD vial is for blank; to this COD vial add distilled water. Add 1.5 mL of potassium dichromate reagent - digestion solution to each of the three COD vials. Add 3.5 mL of sulphuric acid reagent - catalyst solution in the

same manner. Cap tubes tightly. Switch on the COD Digester and fix the temperature at 150° C and set the time at 2 hours. Place the COD vials into a block digester at 150°C and heat for two hours. The digester automatically switches off. Then remove the vials and allow it to cool to the room temperature. Meanwhile, get ready with the burette for the titration. Fill the burette with the ferrous ammonium sulphate solution, adjust to zero and fix the burette to the stand. Transfer the contents of the blank vial to conical flask. Add few drops of ferroin indicator. The solution becomes bluish green in color. Titrate it with the ferrous ammonium sulphate taken in the burette. End point of the titration is the appearance of the reddish brown color. Transfer the contents of the sample vial to conical flask. Add few drops of ferroin indicator. The solution becomes green in color. Titrate it with the ferrous ammonium sulphate taken in the burette. End point of the titration is the appearance of the reddish brown colour. Note down the volume of ferrous ammonium sulphate solution added for the blank (A) and ferrous ammonium sulphate solution added for the sample (B).

$$\text{Chemical oxygen demand} = \frac{A - B * N * 8 * 100}{\text{Volume of sample taken}}$$

Where, A = Volume of ferrous ammonium sulphate for blank

B = Volume of ferrous ammonium sulphate for sample

N = Normality of ferrous ammonium sulphate

3.2.2.3. TOC Analysis

To control the general degree of mineralization of the pesticides during the photo-Fenton process the TOC was measured. The sample is homogenized and diluted as necessary and a micro portion is injected into a heated reaction chamber packed with an oxidative platinum catalyst supported on aluminium oxide spheres thereby converting all carbon into CO₂. The combustion chamber has a temperature of 680°C. The water is vaporized and the organic carbon is oxidized to CO₂ and H₂O. The CO₂ from oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a non-dispersive infrared analyzer.

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

Experimental procedure

- ✓ Adjust to optimum combustion temperature to 680 °C.
- ✓ Homogenize the sample until satisfactory replication is obtained. Transfer a representative portion (15 ml) to a 30 ml beaker, add acid to reduce PH to 2 and purge with gas for 10 min to remove inorganic carbon before analysis.
- ✓ Withdraw a portion of prepared sample using a syringe fitted with a blunt tipped needle. Stir samples containing particulates with a magnetic stirrer. Inject samples and standards into analyzer and record response. Repeat injection until consecutive measurement is obtained, that is reproducible to within $\pm 10\%$.
- ✓ Prepare standard organic and inorganic carbon series by diluting stock solutions to cover the expected range in samples within the linear range of the instrument. Dilute samples higher than the linear range of the instrument in reagent water. Inject and record peak height or area of these standards and a dilution water blank.
- ✓ Plot carbon concentration in milligrams per liter against corrected peak height or area on rectangular coordinate paper.

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

2.1.1.1. pH Measurements

The pH meter was calibrated as follows:

- The pH mode was selected and the temperature control knob was set to 25°C.
- The electrode was rinsed with deionized water and blot dried using piece of tissue.

- The electrode was placed in a solution of pH 7 buffer and the display was allowed to stabilize and then, the display was set to read 7 by adjusting cal.1. And the electrode was removed from the buffer.
- The electrode was rinsed with deionized water and blot dried by a piece of tissue.
- And then the electrode was placed in a solution of pH 2 buffer, the display was allowed to stabilize and the display was set to read 2 by adjusting cal.2. Then the electrode was removed from the buffer.
- The electrode was rinsed with the deionized water and blot dried with piece of tissue.

Measuring pH

- The pH meter was set to pH mode and the temperature was adjusted to 25°C.
- The electrode was placed in the sample to be tested.
- The pH of the solution was appeared in the display.
- The electrode was rinsed and placed in the storage solution.

3.2.2.4. Turbidity Test

Turbidity is the technical term referring to the cloudiness of a solution and it is a qualitative characteristic which is imparted by solid particles obstructing the transmittance of light through a water sample. Turbidity often indicates the presence of dispersed and suspended solids like clay, organic matter, silt, algae and other microorganisms. Turbidity is based on the comparison of the intensity of light scattered by the sample under defined conditions with the intensity of the light scattered by a standard reference suspension under the same conditions. The turbidity of the sample is thus measured from the amount of light scattered by the sample taking a reference with standard turbidity suspension.

Procedure for turbidity measurement

Switch on the turbidity meter at least 30 min before the test. Prepare 400 NTU solutions. Calibrate the turbidity meter to 400 NTU using the standard solution by adjusting the calibration knob. Calibrate the turbidity meter to 0.0 NTU using distilled water and by adjusting the calibration knob. Read the turbidity meter by inserting the sample.

3.3. Experimental procedures

The experiments for all photo-Fenton were carried out at laboratory scale in the 250 ml beaker. The beaker was cleaned and filled with 200 ml of distilled water to ensure that no other compounds were present in the beaker. The UV lamp was turned off and the beaker was covered with Aluminium sheets to prevent any photochemical reactions. The experiments were carried out using the following procedures:

- 200 ml of distilled water was filled to the beaker.
- The required amount of pesticides (2,4-D) was added to the distilled water in the beaker.
- Perfect homogenization and dilution of the pollutants was achieved by mixing the solution with magnetic mixer until the homogenous solution is obtained.
- The pH of the solution was adjusted to a value close to 2.8, immediately afterwards using sulphuric acid (2N, 98% purity). The sample was taken for further homogenization.
- The second sample was drawn (to control the pH value) and immediately afterwards the calculated amount of ferrous sulphate heptahydrate was added to the reactor, in order to achieve the desired concentration of $[mg L^{-1}]$ of iron. One more time the process fluid was mixed for homogenization.
- Sample 3 was drawn to control the dissolved iron concentration and directly afterwards the calculated amount of H_2O_2 (30% w/v solution) was introduced to the system again followed by homogenization.
- The fourth sample was drawn to check the initial conditions for the photo-Fenton experiment. Immediately the content was placed in appropriate position to UV lamp. The Aluminium sheet was removed from the beaker and the UV lamp was turned on. The photo-Fenton degradation process was started.
- After 120 minutes the PH was increased to 7 using sodium hydroxide and the process was allowed to continue for additional 5 minutes.
- The stirrer speed was reduced and the process proceed for 15 minutes and allowed to settle for 30 minutes then the sample was analysis.

During the photo-Fenton experiments regular samples was drawn (each 15-30 minutes) to measure the main process variables. The process fluid was adjusted to the constant temperature of 25°C.

Some Lists of laboratory works were available in Appendix B

3.4. Experimental design of process variables

To determine the effect of main parameter on the removal of 2,4-Dichlorophenoxyacetic acid (2,4D) as well as to optimize all the affecting parameters collectively by statistical experimental design, Response surface methodology was used in this work. Box–Benkhen statistical experiment design (BBD) of the RSM, consisting of a three-factor and three-level pattern was used to conduct the experiment. The factors and the experimental levels for each factor were based on values found in the literature, available resources and preliminary experiments’ results. The result of the experimental design were studied and interpreted by Design expert 11.1 statistical software to estimate the response of the dependent variable.

- i) Selection of response variable
 - ✓ Percentage total organic carbon (%TOC) removal &
 - ✓ Percentage chemical oxygen demand (%COD) removal
- ii) Choice of factors, levels and range
 - ✓ Factors:

The potential design factors that have prime effect on the oxidation of the 2,4-D wastewater are:

1. Initial pesticide (2,4-D) concentration
2. Concentration of Fe^{2+}
3. Concentrations of H_2O_2

Table 3. 2. Experimental range and levels of independent variables

Factor	Unit	Amount		
		Low	Medium	High
[2,4-D]	mg/L	30	115	200
[H_2O_2]	mg/L	30	115	200
	mL	0.018	0.069	0.12
[Fe^{2+}]	mg/L	5	17.5	30
	Mg	4.94	17.29	29.64

The initial 2,4-D concentration selected for the experiments was in compromise to within the range experimented in the literature. The $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ is based on most literature values.

Design comprised of 17 runs in random order; all points in coded factor levels. The center point (0, 0, 0) was replicated five times. The combination of the three factors (initial pesticide concentration, $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$) studied in the response surface experiment and optimization was based on the +1 and -1 variable levels of the experimental design.

3.5. Experimental Approach

To determine the effect of main parameter on the removal of the 2,4-D as well as to optimize all the affecting parameters collectively by statistical experimental design, Response surface methodology was used in this work. **Box–Benkhen** statistical experiment design and the RSM, consisting of a three-factor and three-level pattern was used to conduct the experiment. The result of the experimental design were studied and interpreted by DESIGN EXPERT 11.1 statistical software to estimate the response of the dependent variable.

4. RESULTS AND DISCUSSION

This chapter deals with the results obtained from the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using photo-Fenton method under different experimental conditions. The percentage degradations of these organic pollutant was studied in terms of the percentage removal of total organic carbon (TOC) and chemical oxygen demand (COD).

Model solution containing known concentration of the organic pollutant (2,4-D) was prepared and the photodegradation of this pollutant was optimized by studying the effects of 1) hydrogen peroxide concentration, 2) Ferrous ion concentration and 3) initial concentration of the organic pollutant. Those factors that have no significant effect on the photodegradation of organic pollutant were kept constant during the experiment.

4.1. Wastewater Characteristics

Physical/chemical characteristics of fresh wastewater and the bio treated wastewater were showed in Table 4.1.

Table 4. 1. Characteristics of the wastewater sample

Parameters	Value	EPA Limit Value
BOD ₅ (mg/L)	212	6-9
COD (mg/L)	598	40
PH	5.5 – 5.8	6-8.5
TOC (mg/L)	185	-
Turbidity (NTU)	118	-

The results in Table 4.1 shows that the pesticide wastewater is highly contaminated which can be hazardous to the environment if it is disposed untreated. All the values of the parameters are higher than the limit values for discharge to in land water granted by Addis Ababa city government environmental protection authority ((EPA), 2004). Generally, the result of the characterization shows that pesticide wastewaters are hazardous and have to be treated before discharge.

4.2. Degradation of 2,4-D Using Photo-Fenton Method

The results obtained from this experiment were illustrated in Table 4.2. The maximum TOC and COD removal efficiency was found to be 83% and 95%, respectively at PH = 2.8.

Table 4. 2. Experimental results for Box–Benkhen design applied to 2,4-D oxidation using photo-Fenton degradation.

Run Number	H ₂ O ₂ [mg/L]	Fe ²⁺ [mg/L]	2,4-D [mg/L]	%TOC Removal	%COD Removal
1	30	30	115	59	75
2	30	17.5	200	57	73
3	115	17.5	115	83	94
4	200	17.5	200	77	90
5	200	17.5	30	78	92
6	115	17.5	115	81	93
7	115	17.5	115	82	94
8	115	17.5	115	81	92
9	200	30	115	83	95
10	115	30	200	74	91
11	30	5	115	55	72
12	115	17.5	115	82	93
13	115	5	30	75	87
14	115	30	30	78	89
15	200	5	115	62	78
16	30	17.5	30	72	84
17	115	5	200	60	74

The results in table 4.2 indicated that the method of treatment of pesticide waste water using Photo-Fenton method are effective to remove TOC and COD which can be reduced to greater amount. So by applying AOP it is possible to change harmful organic compounds in to harmless inorganic species such as CO₂ and H₂O. As a result of this latest approach it is possible to protect the environment from being polluted and prevent public exposure to the hazardous pesticide.

The values of the dependent and independent variables and the experimental data are presented in Table 4.2 for every experiment. The center point (115, 17.5, 115) was repeated five times and nearly the same results were obtained indicating the reproducibility of the data.

4.2.1. The response function coefficients

The application of the Response Surface Method (RSM) offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function Y_1 (% TOC removal) and Y_2 (% COD removal) and the independent variables A ($[H_2O_2]$), B ($[Fe^{2+}]$) and C ($[2,4-D]$) can be approximated by a quadratic polynomial equation as follows:

$$Y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \text{ ----- (4.1)}$$

The coefficients of the response functions for different dependent variables were determined correlating the experimental results with the response functions by using a Stat-Ease Design Expert 11 regression program. The response functions with the determined coefficients for percent TOC (Y_1) and COD (Y_2) removals are presented by Equations (4.2) and (4.3).

Final Equation in Terms of Actual Factors

$$Y_1 = +54.65195 + 0.241436 A + 1.48795 B - 0.091990 C + 0.004000 AB + 0.000484 AC + 0.002588 BC - 0.001232 A^2 - 0.052160 B^2 - 0.000263 C^2; \quad R^2 = 0.9908 \text{ ----- (4.2)}$$

$$Y_2 = +71.74639 + 0.199602 A + 1.02769 B - 0.081938 C + 0.003294 AB + 0.000311 AC + 0.003529 BC - 0.000948 A^2 - 0.040640 B^2 - 0.000221 C^2; \quad R^2 = 0.9969 \text{ ----- (4.3)}$$

On the basis of the coefficients in Equations. (4.2) and (4.3), it can be said that percent TOC and COD removal decreases with the 2,4-D concentration (C) while increasing with hydrogen peroxide (A) and Fe(II) (B) doses. The Fe^{2+} dose has a more profound effect on degradation as compared to H_2O_2 .

The negative quadratic factors for hydrogen peroxide, iron concentration and pesticide concentration in the polynomial expression corroborated the fact that these concentrations' load was an intermediate value in the range being tested. Higher 2,4-D concentration values reduced its degradation as time elapsed whereas greater amounts of hydrogen peroxide and iron led to more successful 2,4-D degradation (Hernández-Shek, 2012).

4.3. Total Organic Carbon (TOC) Removal

4.3.1. Analysis of variance for TOC removal of the surface Quadratic Model

Table 4.3 has indicated that A, B, C, AB, AC, BC, A², B², C² are significant model terms since the P-values of these models are less than 0.0500. The Model F-value of 83.34 implies the model is significant.

Table 4. 3. Analysis of variance Table for TOC removal

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	1612.71	9	179.19	83.34	< 0.0001	Significant
A-H ₂ O ₂	406.13	1	406.13	188.90	< 0.0001	
B-Fe ²⁺	220.50	1	220.50	102.56	< 0.0001	
C-2,4-D	153.13	1	153.13	71.22	< 0.0001	
AB	72.25	1	72.25	33.60	0.0007	
AC	49.00	1	49.00	22.79	0.0020	
BC	30.25	1	30.25	14.07	0.0072	
A ²	333.52	1	333.52	155.12	< 0.0001	
B ²	279.67	1	279.67	130.08	< 0.0001	
C ²	15.20	1	15.20	7.07	0.0325	
Residual	15.05	7	2.15			
Lack of Fit	12.25	3	4.08	5.83	0.0607	not significant
Pure Error	2.80	4	0.7000			
Cor Total	1627.76	16				

Factor coding is **Coded**.

Sum of squares is **Type III – Partial**

The **Model F-value** of 83.34 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 5.83 implies there is a 6.07% chance that a Lack of Fit F-value this large could occur due to noise. Lack of fit is bad -- we want the model to fit. This relatively low probability (<10%) is troubling.

4.3.2. The Fit Statistics

Table 4. 4. Table of Fit Statistics for TOC removal

Std. Dev.	1.47	R²	0.9908
Mean	72.88	Adjusted R²	0.9789
C.V. %	2.01	Predicted R²	0.8769
		Adeq Precision	22.9417

The **Predicted R²** of 0.8769 is in reasonable agreement with the **Adjusted R²** of 0.9789; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 22.942 indicates an adequate signal. This model can be used to navigate the design space.

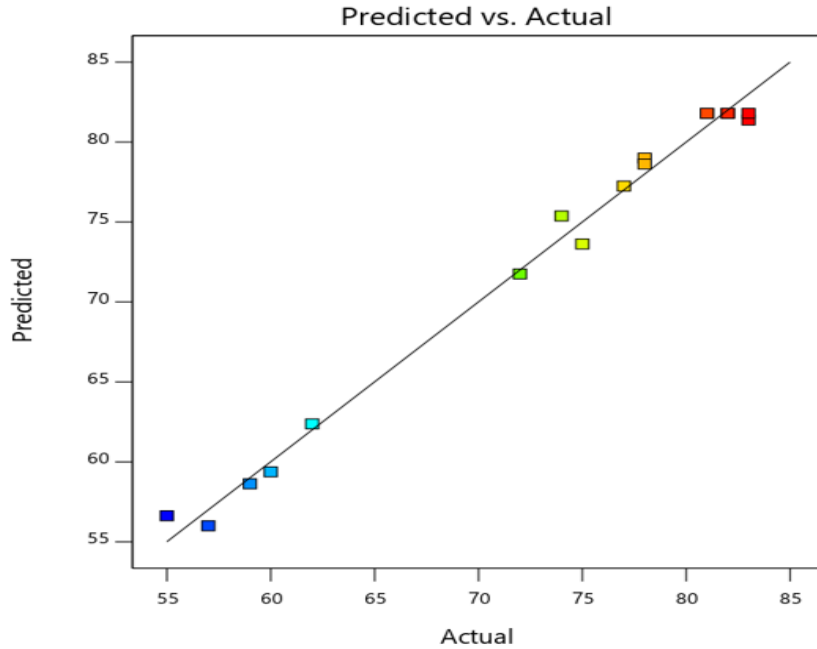
4.3.3. Diagnostics Plots

Externally Studentized residuals are the default with Internally Studentized and raw residuals as options. Externally Studentized residuals based on a deletion method are the default due to being more sensitive for finding problems with the analysis. Internally Studentized residuals are also available but are less sensitive to finding such problems.

i. Predicted vs. Actual

A graph of the observed (actual) response values versus the predicted response values. It helps to detect observations that are not well predicted by the model.

The difference between this graph and the one seen in Diagnostics is that models with transformations can be displayed in original scale.



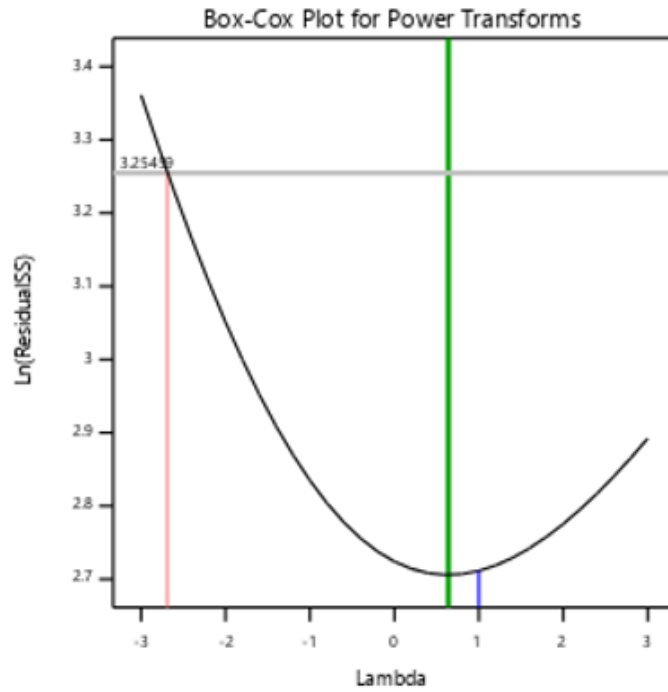
Plot 4.1. Predicted vs. Actual (model graphs)

This will usually result in more points towards the lower left than what is shown on the diagnostics version.

The data points should be split evenly by the 45 degree line in either scale.

ii. Box-Cox Plot for Power Transforms

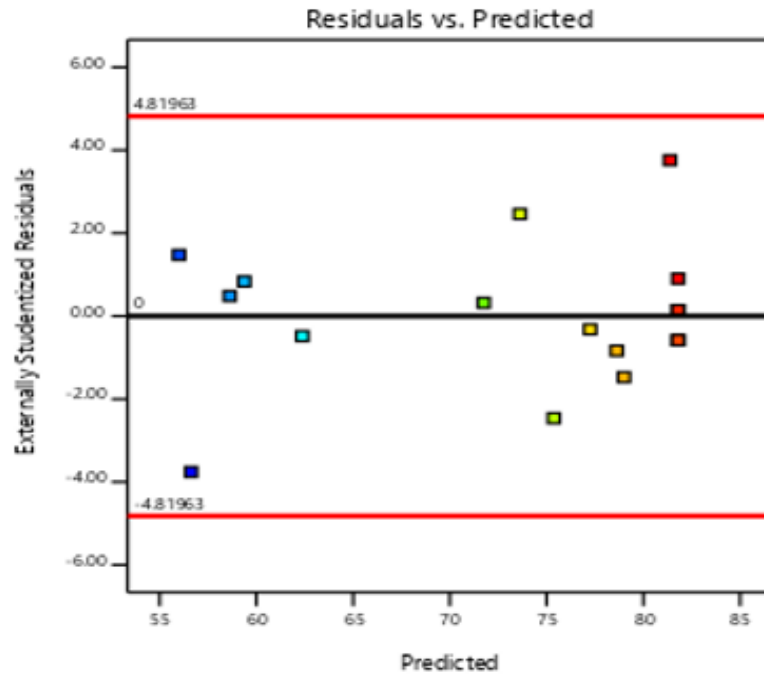
This plot provides a guideline for selecting the correct power law transformation. A recommended transformation is listed, based on the best lambda value, which is found at the minimum point of the curve generated by the natural log of the sum of squares of the residuals. If the 95% confidence interval around this lambda includes 1, then the software does not recommend a specific transformation. This plot is not displayed when either the logit or the arcsine square root transformation has been applied.



Plot 4.2 Box-Cox Plot for Power Transforms

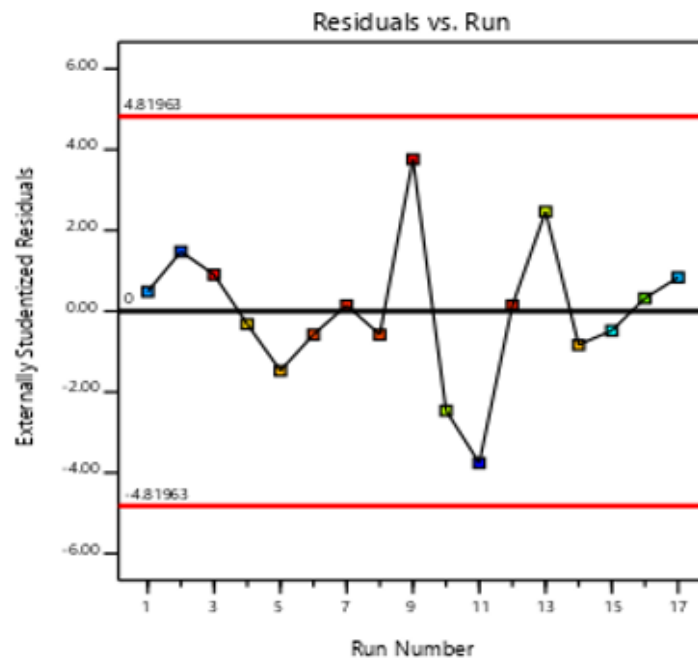
iii. Residuals vs. Predicted

This is a plot of the residuals versus the ascending predicted response values. It tests the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph). Expanding variance (“megaphone pattern <”) in this plot indicates the need for a transformation.



Plot 4.3 Residuals vs. Predicted

iv. Residuals vs. Run



Plot 4.4 Residuals vs. Run

This is a plot of the residuals versus the experimental run order. It checks for lurking variables that may have influenced the response during the experiment. The plot should show a random scatter. Trends indicate a time-related variable lurking in the background. Blocking and randomization provide insurance against trends ruining the analysis.

The rest of the diagnostic plots for TOC removal were listed on Appendix I

4.3.4. Effect of factors on the TOC removal

4.3.4.1. Effect of Single factor on TOC removal

a. Effect of H₂O₂ dosage

Effect of H₂O₂ dosage on TOC removal from 2,4-D containing wastewater using photo-Fenton method is shown in figure 4.1. As expected, the increase of H₂O₂ dosage from 30 to 160 mg/L accelerated TOC removal. The increased degradation efficiency can be attributed to the additional OH radicals produced from H₂O₂ decomposition. However, TOC removal could not be obviously improved by excessive addition of H₂O₂ (>160 mg/L). The results showed a negligible increase in removal efficiency when H₂O₂ dosage further increased from 160 to 200 mg/L.

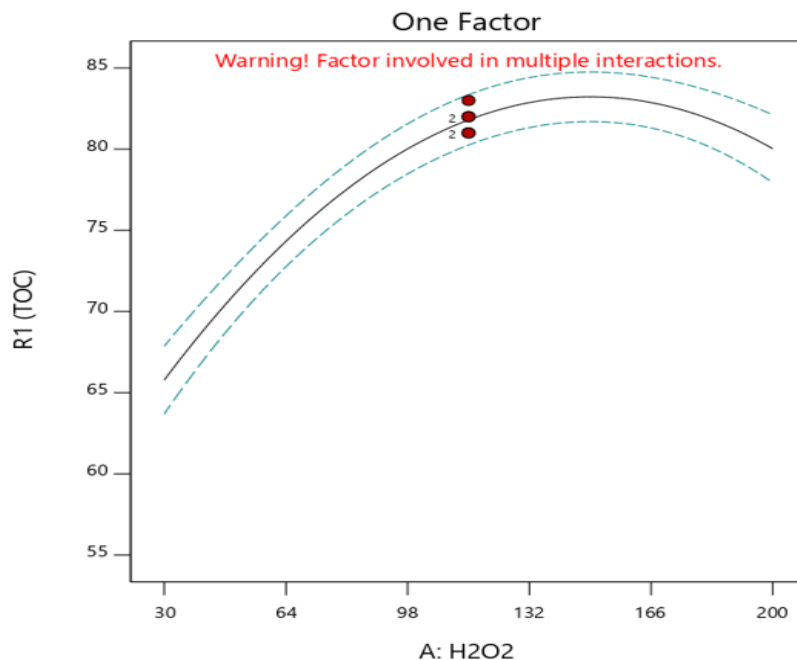
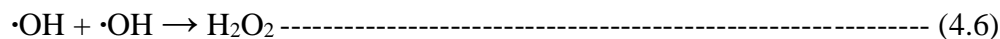
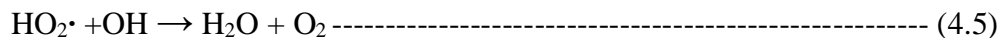
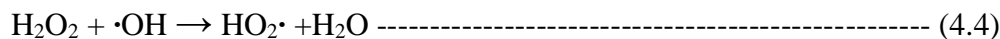


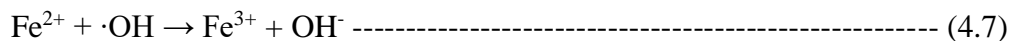
Figure 4. 1. Effect of H₂O₂ dosage on TOC removal

It can be interpreted that the excessive H₂O₂ acts as a scavenger of ·OH, but the produced HO₂· (Equations (4.4) – (4.6)) has much lower oxidation capacities (Cheng, et al., 2015). Therefore, the optimum H₂O₂ dosage was found to be 156.4 mg/L for advanced treatment of the pesticide-containing wastewater by the photo-Fenton method.



b. Effect of Fe²⁺ dosage:

To investigate effect of Fe²⁺ dosage on TOC removal, experiments were carried out at Fe²⁺ dosage ranging from 5 to 30 mg/L. Figure 4.2 showed a significant increase in TOC removal efficiency with the increasing Fe²⁺ concentration from 5 to 23 mg/L. Fe²⁺ is important for formation of photoactive ferric-hydroxyl complexes that absorb UV light to produce ·OH. However, further increases in Fe²⁺ concentration up to 30 mg/L only resulted in slight increases in degradation rate. Excessive ferrous ions may act as hydroxyl radical scavenger according to the following (Cheng, et al., 2015):



In addition, a deep color and high turbidity at high Fe²⁺ concentration reduced the transmission of UV light in solution, which inhibited the photolysis of H₂O₂ to produce OH radicals. Therefore, overdosed Fe²⁺ was inefficient for TOC removal by photo-Fenton process (Cheng, et al., 2015).

Therefore, the optimum Fe²⁺ dosage was found to be 22.79 mg/L for advanced treatment of the pesticide containing wastewater by the photo-Fenton method.

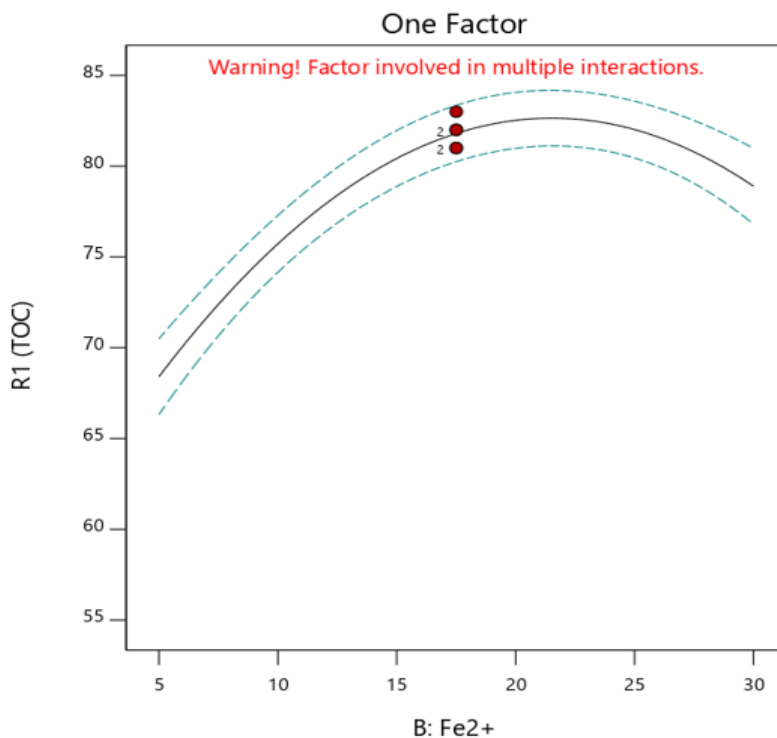


Figure 4. 2. Effect of Fe²⁺ dosage on TOC removal

c. Effect of 2,4-D concentration:

The efficiency of TOC removal slightly decreases as the concentration of 2,4-D increases significantly. This happens due to high organic matter load, which produces a high competition for the oxidative species. The establishment of competition for the oxidative species produced by AOPs consequently reduces their availability for the oxidation of the target recalcitrant compounds and the global efficiency of the process (Gonzalo, 2017).

Figure 4.3 showed that TOC removal efficiency was decreased slightly at the beginning and as the concentration started getting larger the removal efficiency significantly decreased beyond 100 mg/L of 2,4-D concentration. Excessive increment in 2,4-D concentration from up to 200 mg/L significantly reduced the removal efficiency of total organic carbon.

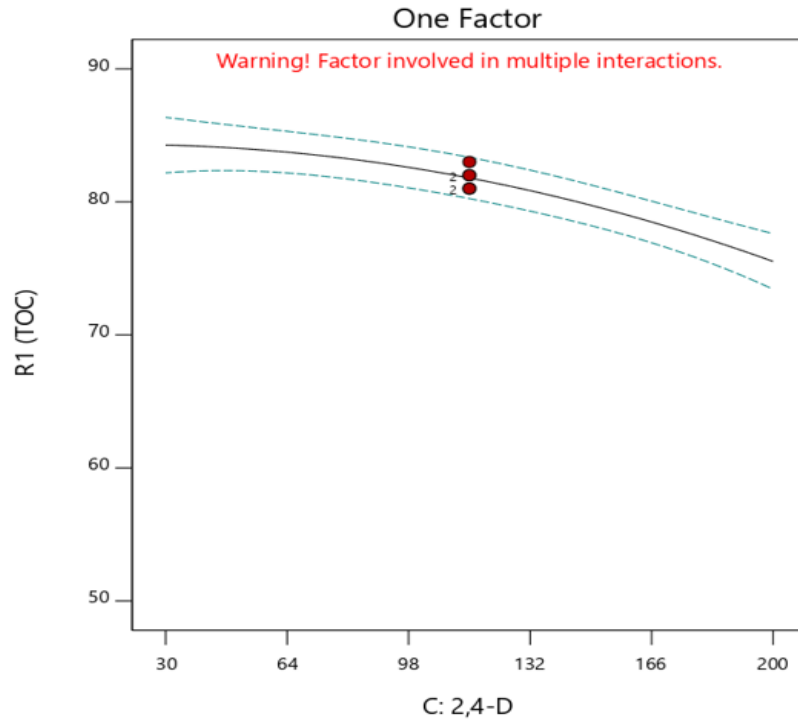


Figure 4. 3. Effect of 2,4-D concentration on TOC removal

4.3.4.2. Interaction Effects of factors on TOC Removal

a. Effect of H₂O₂ and 2,4-D concentrations

Figure 4.4. shows the response surface diagram for identifying the best H₂O₂ concentration required in photo-Fenton reaction to degrade a determined amount of 2,4-D with 17.5 mg/L Fe²⁺ in 120 minutes. It can be noticed in the experimental outcomes that 2,4-D degradation increased at higher H₂O₂ concentrations in the range studied here (30 - 200 mg/L) which was mainly due to greater •OH generation.

At low H₂O₂ and high 2,4-D concentration there is high competition for •OH due to its low availability resulting minimum efficiency in TOC removal. And also at high H₂O₂ and low 2,4-D concentration the excess H₂O₂ acts as a scavenger of •OH producing HO₂• which has much lower oxidation capacities (Cheng, et al., 2015). Moreover, HO₂• could further react with •OH and form water and oxygen.

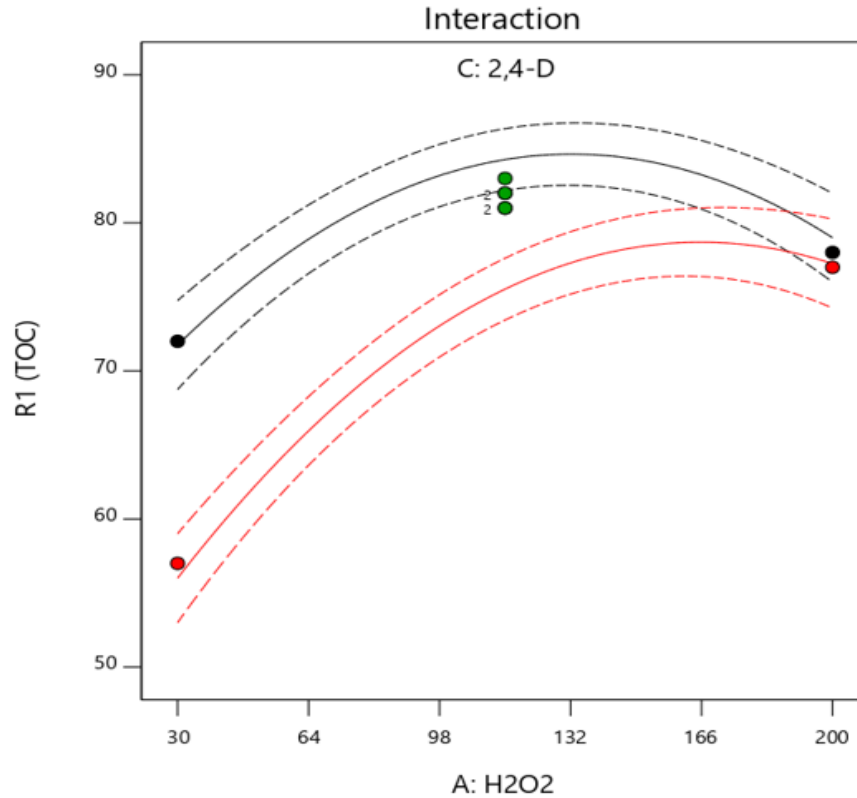


Figure 4. 4. Interaction effect of H₂O₂ and 2,4-D concentrations

Figure 4.5 below also indicated the 3-D diagram of the interaction effect of H₂O₂ and 2,4-D concentrations. It has shown the removal process is preferable at lower concentrations of 2,4-D as the removal efficiency was high at low concentration and then decreased with increased dosage of pesticide. However, the TOC removal efficiency increased with the increased dosage of H₂O₂ from 30 - 160 mg/L and then decreased with further increment in H₂O₂ dosage due its negative effects at high concentrations. As a result of the combining effects of these variables the values of 156.4 mg/L and 94.6 mg/L of H₂O₂ and 2,4-D respectively, were obtained using Box-Benkhen Design.

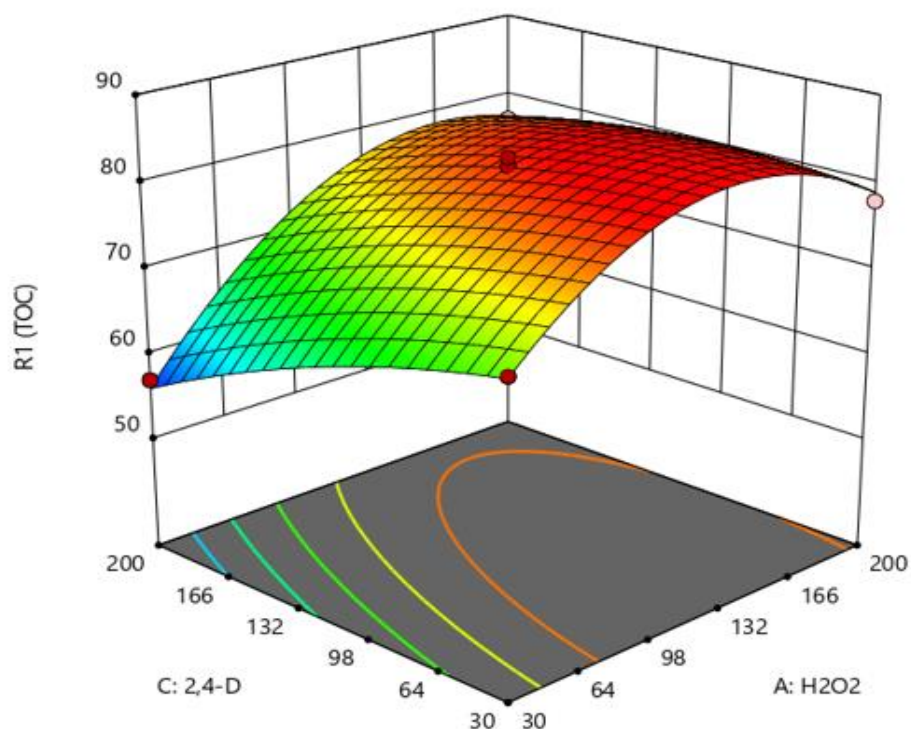


Figure 4. 5. 3D surface drawing indicating the effect of H₂O₂ and 2,4-D on percent TOC removal

b. Effect of Fe²⁺ and 2,4-D concentrations

Figure 4.6 has shown that Percent TOC removal increased with increasing Fe²⁺ doses up to nearly 23 mg/L and then decreased with further increase in Fe²⁺ dosage due to adverse effects of high Fe²⁺ doses yielding an optimal Fe²⁺ dose under the specified experimental conditions. At the same time the efficiency in TOC removal slightly decreased with increasing concentration of 2,4-D until it reaches 100 mg/L and then significantly decreases with further increment in concentration which results in high organic load existence. The optimum values of both Fe²⁺ and 2,4-D were found to be 22.79 mg/l and 94.8 mg/L respectively, which were described in the following section of this chapter using Box-Behnken Design.

Excessive ferrous ions and 2,4-D concentrations in the system resulted in decreases in mineralization yield due to radical scavenging effects of high Fe²⁺ doses as well as due to high organic load. The reduction in efficiency at high Fe²⁺ dosage can be due to the formation of deep

color and high turbidity that reduces the penetration of UV light in the solution (Cheng, et al., 2015).

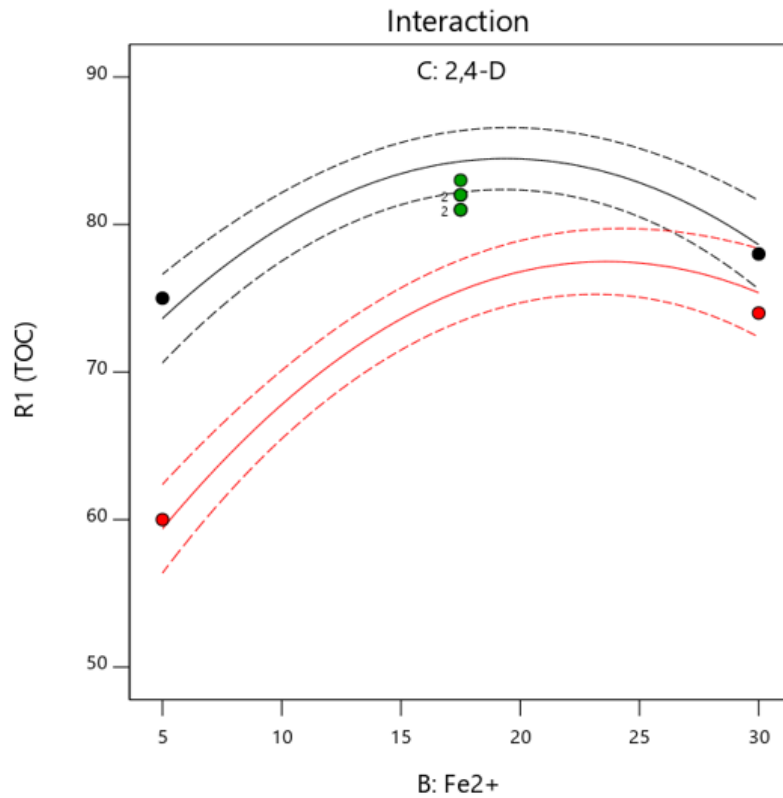


Figure 4. 6. Interaction effect of Fe²⁺ and 2,4-D concentrations

Figure 4.7 below also indicates the 3-D diagram of the interaction effect of Fe²⁺ and 2,4-D concentrations. It has shown that the TOC removal efficiency increased with the increased with increasing dosage of Fe²⁺. However, at high 2,4-D dosages the resulting efficiency was decreased due to the negative effects of high concentrations of Fe²⁺. It can be easily observed that TOC removal efficiency was higher at low concentrations of the pollutant. As a result of the combining effects of these variables the values of 22.79 mg/L and 94.6 mg/L of Fe²⁺ and 2,4-D respectively, were obtained using Box-Behnken Design.

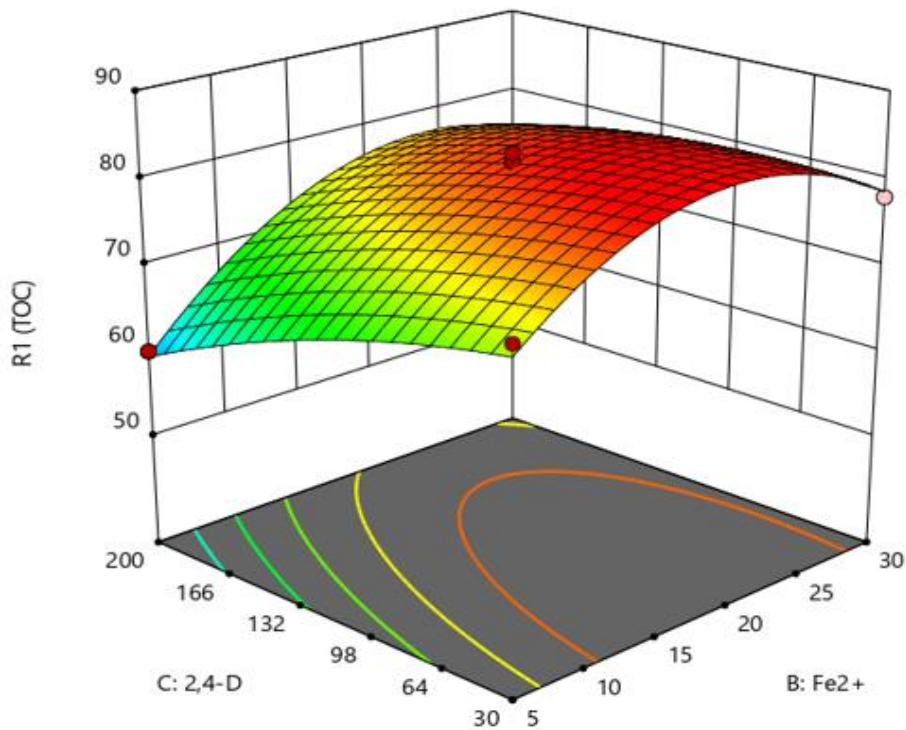


Figure 4. 7. 3D surface drawing indicating the effect of Fe²⁺ and 2,4-D on percent TOC removal

The rest of the Model Graphs for COD removal were listed on Appendix J.

4.4. Chemical Oxygen Demand (COD) Removal

4.4.1. Analysis of variance for COD removal of the surface Quadratic Model

The table 4.5 has indicated that A, B, C, AB, AC, BC, A², B², C² are significant model terms since the P-values of these models are less than 0.0500. The Model F-value of 246.15 implies the model is significant.

Table 4. 5. Analysis of variance Table for COD removal

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	1123.51	9	124.83	246.15	< 0.0001	significant
A-H ₂ O ₂	325.13	1	325.13	641.09	< 0.0001	
B-Fe ²⁺	190.13	1	190.13	374.89	< 0.0001	
C-2,4-D	72.00	1	72.00	141.97	< 0.0001	

AB	49.00	1	49.00	96.62	< 0.0001	
AC	20.25	1	20.25	39.93	0.0004	
BC	56.25	1	56.25	110.92	< 0.0001	
A ²	197.57	1	197.57	389.57	< 0.0001	
B ²	169.78	1	169.78	334.78	< 0.0001	
C ²	10.78	1	10.78	21.25	0.0025	
Residual	3.55	7	0.5071			
Lack of Fit	0.7500	3	0.2500	0.3571	0.7880	not significant
Pure Error	2.80	4	0.7000			
Cor Total	1127.06	16				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 246.15 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 0.36 implies the Lack of Fit is not significant relative to the pure error. There is a 78.80% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

4.4.2. The Fit Statistics

Table 4. 6. Table of Fit Statistics for COD removal

Std. Dev.	0.7121	R²	0.9969
Mean	86.24	Adjusted R²	0.9928
C.V. %	0.8258	Predicted R²	0.9855
		Adeq Precision	41.1947

The **Predicted R²** of 0.9855 is in reasonable agreement with the **Adjusted R²** of 0.9928; i.e. the difference is less than 0.2.

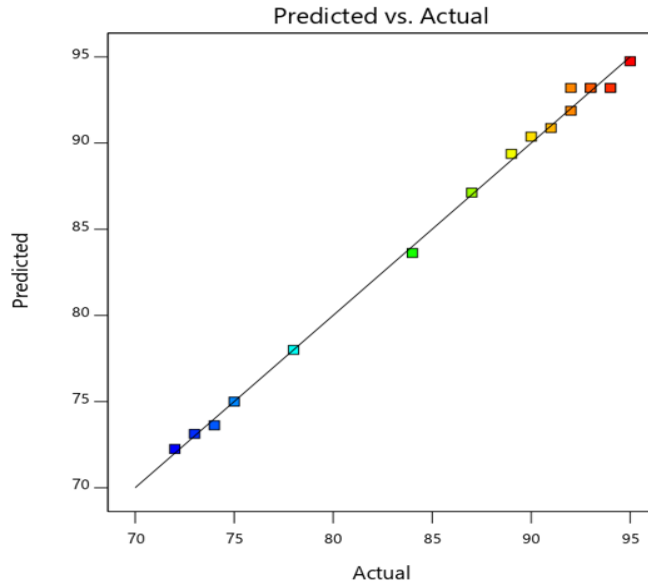
Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 41.195 indicates an adequate signal. This model can be used to navigate the design space.

4.4.3. Diagnostics Plots

Externally Studentized residuals are the default with Internally Studentized and raw residuals as options. Externally Studentized residuals based on a deletion method are the default due to being more sensitive for finding problems with the analysis. Internally Studentized residuals are also available but are less sensitive to finding such problems.

i. Predicted vs Actual

A graph of the observed (actual) response values versus the predicted response values. It helps to detect observations that are not well predicted by the model.



Plot 4.5. Predicted vs. Actual (model graphs)

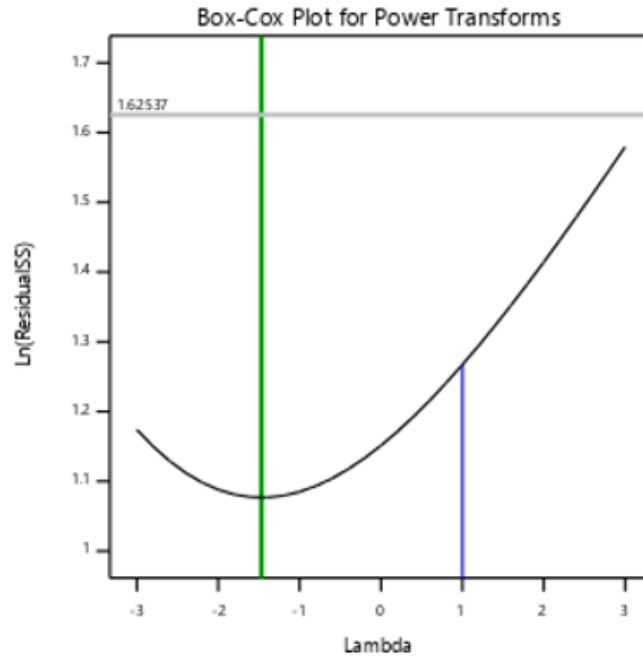
The difference between this graph and the one seen in Diagnostics is that models with transformations can be displayed in original scale.

This will usually result in more points towards the lower left than what is shown on the diagnostics version.

The data points should be split evenly by the 45 degree line in either scale.

ii. Box-Cox Plot for Power Transforms

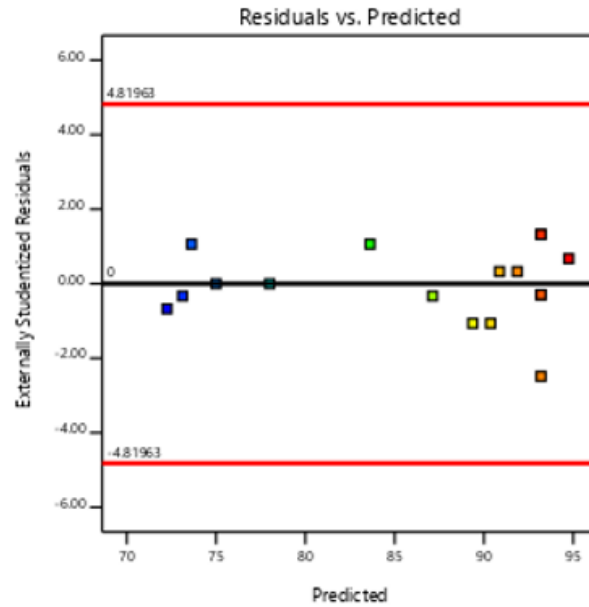
This plot provides a guideline for selecting the correct power law transformation. A recommended transformation is listed, based on the best lambda value, which is found at the minimum point of the curve generated by the natural log of the sum of squares of the residuals. If the 95% confidence interval around this lambda includes 1, then the software does not recommend a specific transformation. This plot is not displayed when either the logit or the arcsine square root transformation has been applied.



Plot 4.6 Box-Cox Plot for Power Transforms

iii. Residuals vs. Predicted

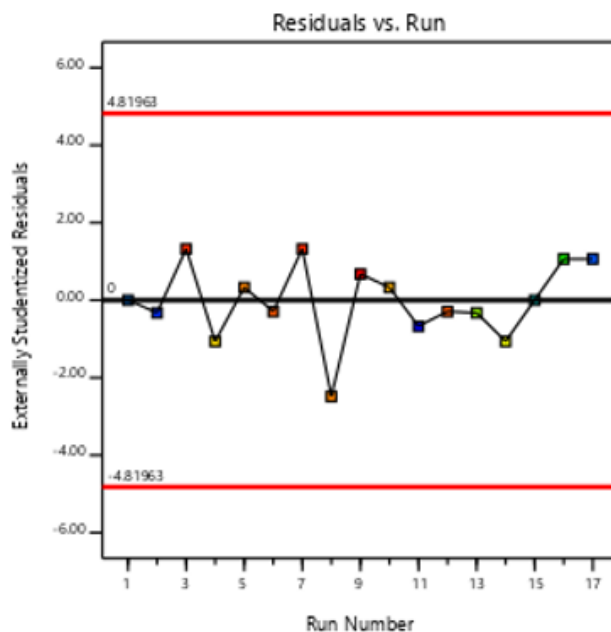
This is a plot of the residuals versus the ascending predicted response values. It tests the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph). Expanding variance (“megaphone pattern <”) in this plot indicates the need for a transformation.



Plot 4.7 Residuals vs. Predicted

iv. Residuals vs. Run

This is a plot of the residuals versus the experimental run order. It checks for lurking variables that may have influenced the response during the experiment. The plot should show a random scatter. Trends indicate a time-related variable lurking in the background. Blocking and randomization provide insurance against trends ruining the analysis.



Plot 4.8 Residuals vs. Run

The rest of the diagnostic plots for COD removal were listed in Appendix K.

4.4.4. Effect of oxidizing species on the COD removal

4.4.4.1. Effect of Single factor on COD removal

a. Effect of H₂O₂ dosage

It can be noticed in the experimental outcomes that 2,4-D degradation increased at higher H₂O₂ concentrations in the range studied here which was mainly due to greater •OH generation. Figure 4.8 has shown that the increased dosage of H₂O₂ from 30 to 160 mg/L accelerated COD removal. However, there exist the negative effect of H₂O₂ overdosed photo-Fenton system for the degrading a target compound.

At under-overdosed rate, H₂O₂ could react with •OH resulting in less powerful HO₂• being formed. Moreover, HO₂• could further react with •OH and form water and oxygen (Hernández-Shek, 2012).

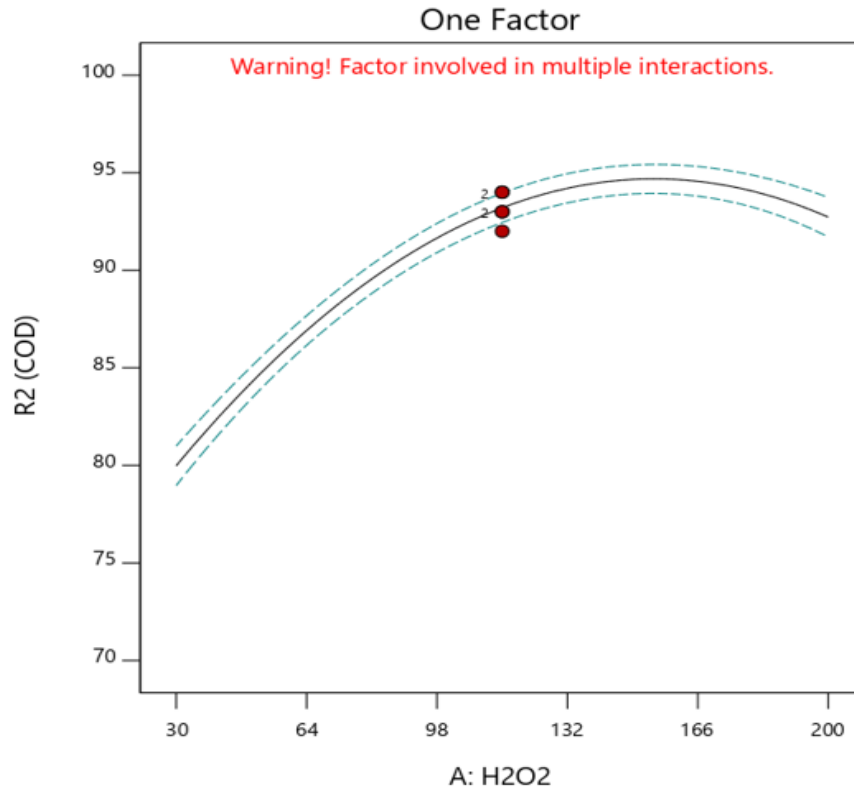
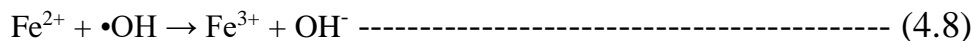


Figure 4. 8. Effect of H₂O₂ dosage on COD removal

b. Effect of Fe²⁺ dosage:

It can be seen from Fig. 4.9 that the removal rate of COD clearly increased with the increasing amount of Fe²⁺, in the range of 5–23 mg/L. It was known that Fe²⁺ had a catalytic decomposition effect on H₂O₂. When the Fe²⁺ concentration increased, the catalytic effect increased accordingly. However, for Fe²⁺ doses higher than 23 mg/L, the COD percent removal decreased slightly.

This decrease was essentially due to competitive consumption of •OH radicals (Eq. 4.8) (Cheng, et al., 2015).



In addition, a deep color and high turbidity at high Fe²⁺ concentration reduced the transmission of UV light in solution, which inhibited the photolysis of H₂O₂ to produce OH radicals. Therefore, overdosed Fe²⁺ was inefficient for COD removal by photo-Fenton process (Cheng, et al., 2015).

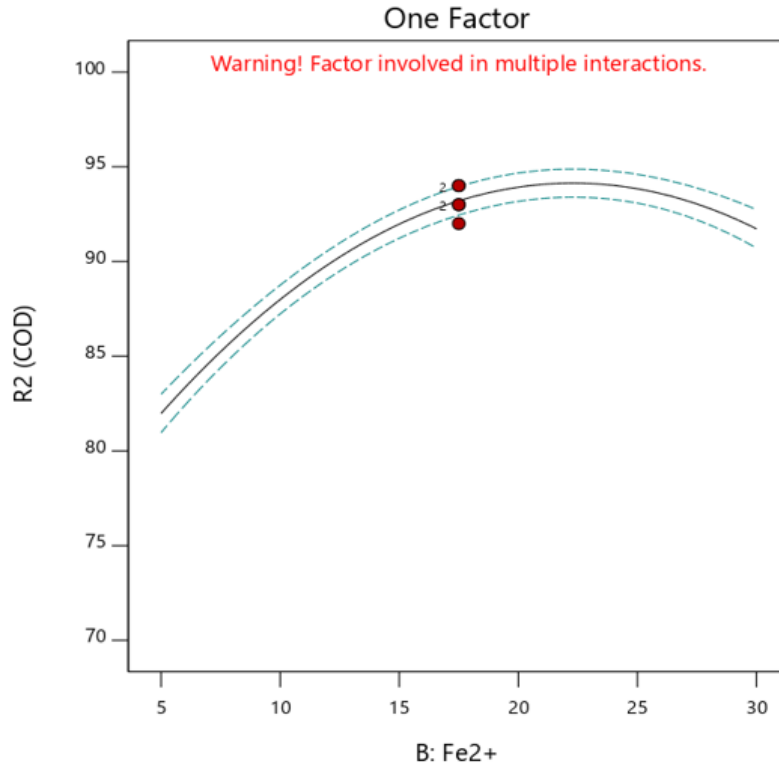


Figure 4. 9. Effect of Fe²⁺ dosage on COD removal

c. Effect of 2,4-D concentration:

The effect of 2,4-D concentration on the degradation efficiency was tested at different initial concentrations (5-30 mg/L), as presented in Fig. 4.10. It can be observed that the COD removal decreased with the increase of the initial concentration of the pollutant.

However, at high 2,4-D concentrations the removal of COD requires more time and thus greater quantities of H₂O₂. The reason for this is that when the concentration of 2,4-D increases, the quantity of hydroxyl radicals produced continuously with time does not increase accordingly; hence the removal rate decreases (Youssef Samet, 2012).

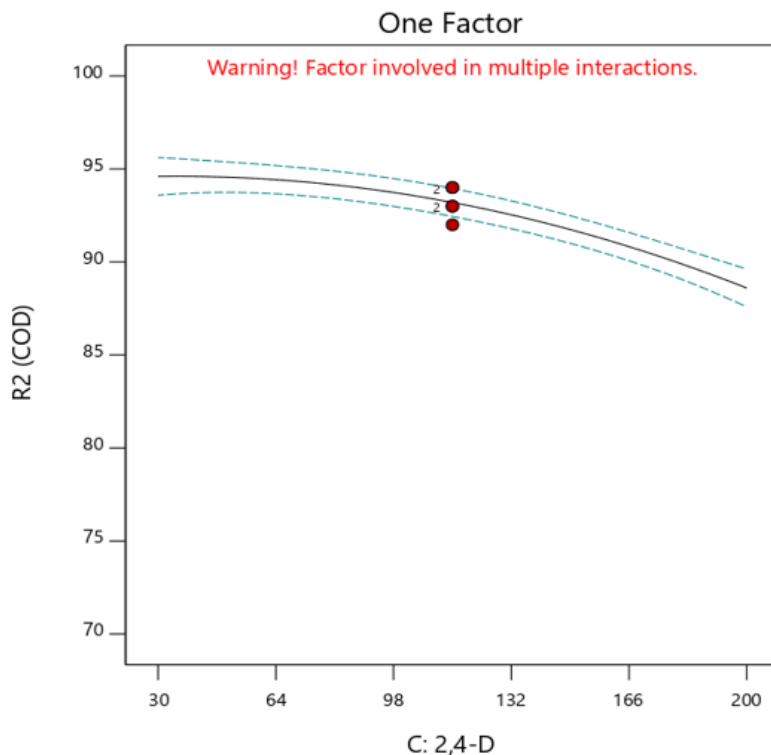


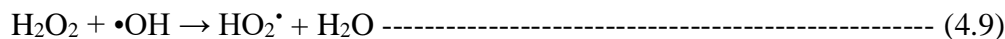
Figure 4. 10. Effect of 2,4-D concentration on COD removal

4.4.4.2. Interaction Effects of factors on TOC Removal

a. Effect of H₂O₂ and 2,4-D concentrations

Figure 4.11 shows the response surface diagram for identifying the best H₂O₂ concentration required in photo-Fenton reaction to degrade a determined amount of 2,4-D with 17.5 mg/L Fe²⁺ in 120 minutes. It can be noticed in the experimental outcomes that 2,4-D degradation increased at higher H₂O₂ concentrations in the range studied here (30 - 200 mg/L) which was mainly due to greater •OH generation.

Excess H₂O₂ dosage acts as a scavenger of •OH producing HO₂• which has much lower oxidation capacities. Moreover, HO₂• could further react with •OH and form water and oxygen (Hernández-Shek, 2012). Excessive H₂O₂ reacts with •OH (Eq. 4.9) competing with organic pollutants and consequently reducing treatment efficiency (Youssef Samet, 2012).



The percentage COD removal decreased with the increase of the initial concentration of the pollutant. The reason is that when the concentration of 2,4-D it requires high hydroxyl radicals and more time to be completely degraded. It can be said, that lower pollutant concentrations are preferred.

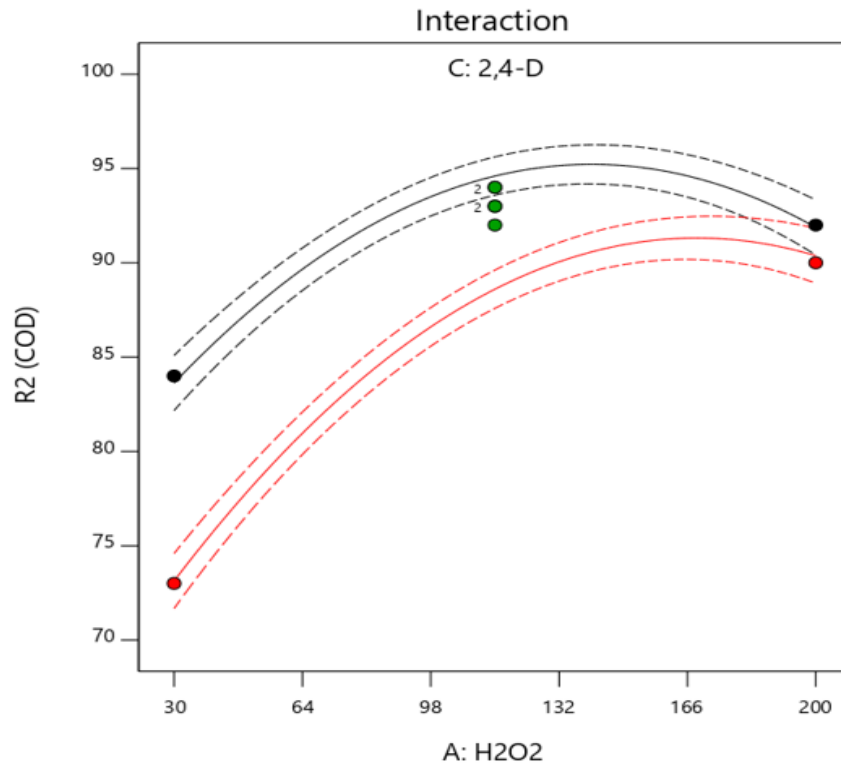


Figure 4. 11. Interaction effect of H₂O₂ and 2,4-D concentrations

Figure 4.12 below also indicated the 3-D diagram of the interaction effect of H₂O₂ and 2,4-D concentrations. It has shown the removal process is preferable at lower concentrations of 2,4-D as the removal efficiency slightly decreased from 30 - 125 mg/L and then decreased significantly with further increased dosage. However, the COD removal efficiency increased with the increased dosage of H₂O₂ from 30-160 mg/L and then decreased with further increment in H₂O₂ dosage due its negative effects at high concentrations. As a result of the combining effects of these variables the values of 156.4 mg/L and 94.6 mg/L of H₂O₂ and 2,4-D respectively, were obtained using Box-Benkhen Design.

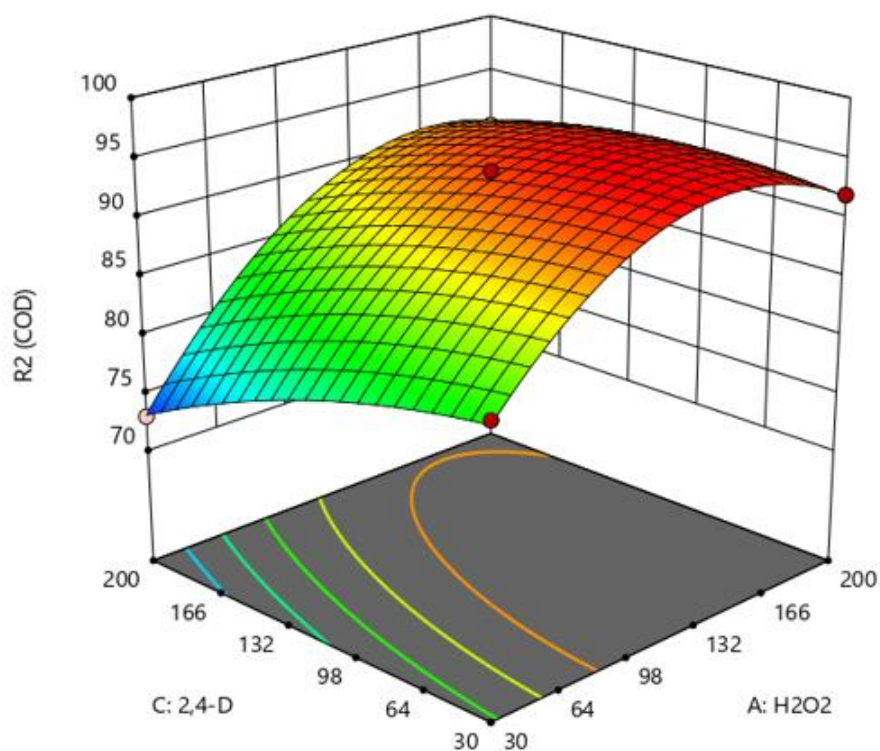


Figure 4. 12. 3D surface drawing indicating the effect of H₂O₂ and 2,4-D on percent COD removal

b. Effect of Fe²⁺ and 2,4-D concentrations

Figure 4.13 has shown that the efficiency of COD removal increased with increasing Fe²⁺ dosage and decreased with increasing 2,4-D concentration. Lower pollutant concentrations are preferred because at high concentrations large amount of reagents are required due high completion for oxidative species and also more time is needed for mineralization.

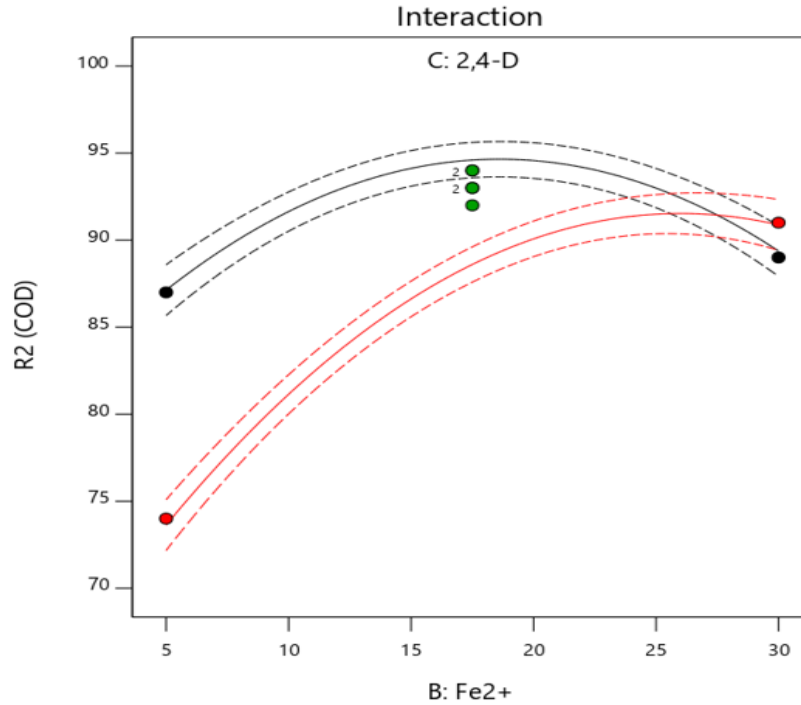


Figure 4. 13. Interaction effect of Fe²⁺ and 2,4-D concentrations

The 3-D diagram of the interaction effect of Fe²⁺ and 2,4-D also shows that excessive ferrous ions and 2,4-D concentrations in the system resulted in decreased mineralization yield due to radical scavenging effects of high Fe²⁺ doses as well as due to high organic load.

The reduction in efficiency at high Fe²⁺ dosage can be due to the formation of deep color and high turbidity that reduces the penetration of UV light in the solution (Cheng, et al., 2015). As a result of the combining effects of these variables the values of 22.79 mg/L and 94.6 mg/L of Fe²⁺ and 2,4-D respectively, were obtained using Box-Behnken Design.

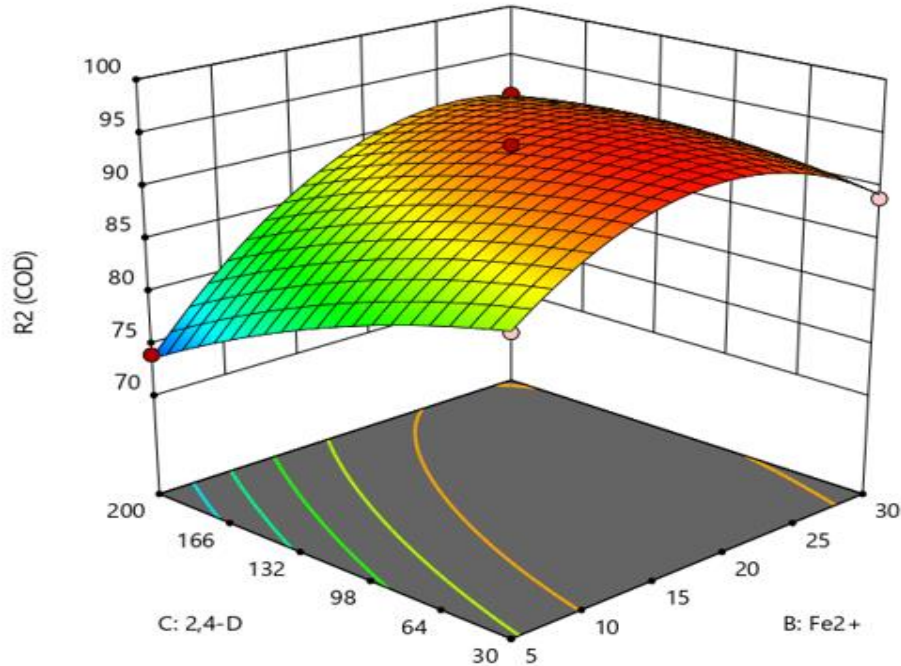


Figure 4. 14. 3D surface drawing indicating the effect of Fe^{2+} and 2,4-D on percent COD removal

The rest of the Model Graphs for COD removal were listed on Appendix L.

4.5. Optimization of process variables

The optimum conditions of factors and the optimized values of responses can be obtained using both Numerical Optimization and Graphical Optimization techniques by **Box-Benkhen Design**, response surface methodology. In order to determine the optimum processing conditions, the factors were set to be in the range and the responses were to be maximized. Therefore, in Numerical Optimization, I tried to maximize the responses for the percentage TOC and COD removal by setting the criteria in Table 4.7.

4.5.1. Numerical Optimization

Table 4. 7. Optimization Criteria table

Name	Goal	Lower Limit	Upper Limit
[H ₂ O ₂]	In the range	30	200
[Fe ²⁺]	In the range	5	30
[2,4-D]	In the range	30	200
%TOC removal	Maximize	55	83
%COD removal	Maximize	72	95

i. Numerical optimization solution

The report of table 4.8 below summarizes the optimal solutions for the process.

Table 4. 8. Solution for the numerical optimization

2 Solutions found

Number	[H ₂ O ₂]	[Fe ²⁺]	2,4-D	%TOC removal	%COD removal	Desirability	Desirability (w/o Intervals)	
1	156.384	22.790	94.711	85.049	96.312	0.899	1.000	Selected
2	156.304	22.753	94.147	85.054	96.307	0.899	1.000	

- Intervals adjusted for variation in the factors (POE).

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

ii. Numerical Optimization Ramps

Ramps are a graphical view of each optimal solution.

- Optimal factor settings are shown with red points.
- Optimal response prediction values are displayed in blue.

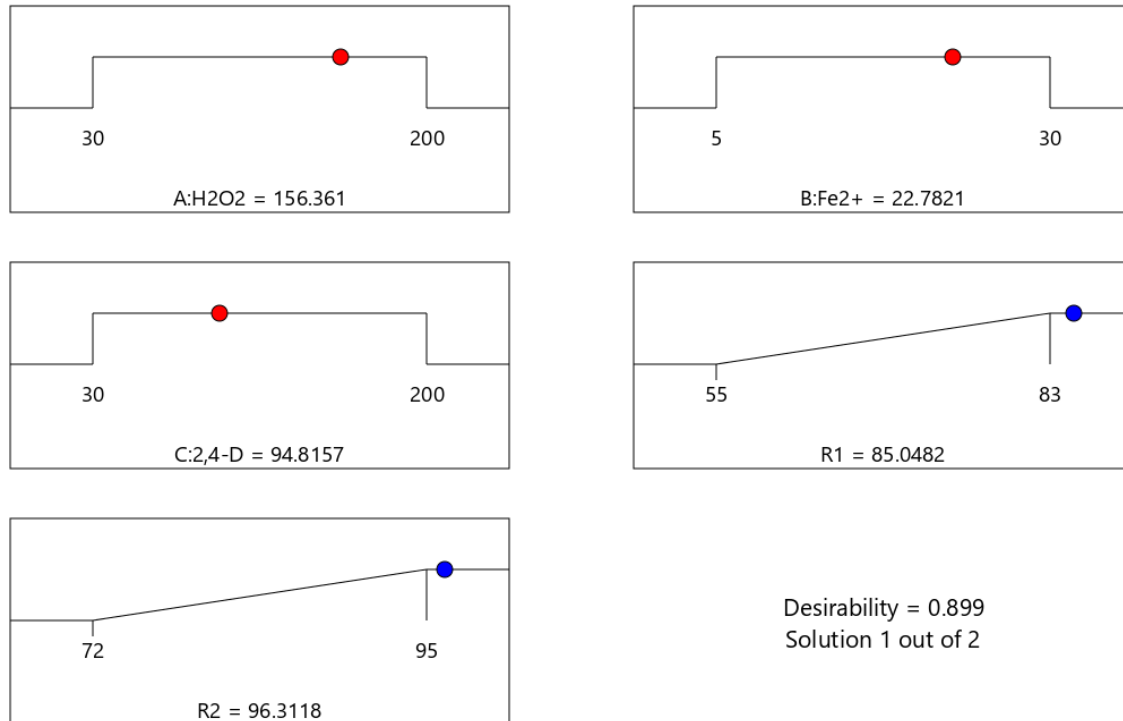


Figure 4.15. Numerical Optimization Ramps

iii. Numerical Optimization Bar Graph

The bar graph is a graphical view for each optimal solution.

- Optimal factor settings are shown with red bars.
- Optimal response prediction values are displayed in blue

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

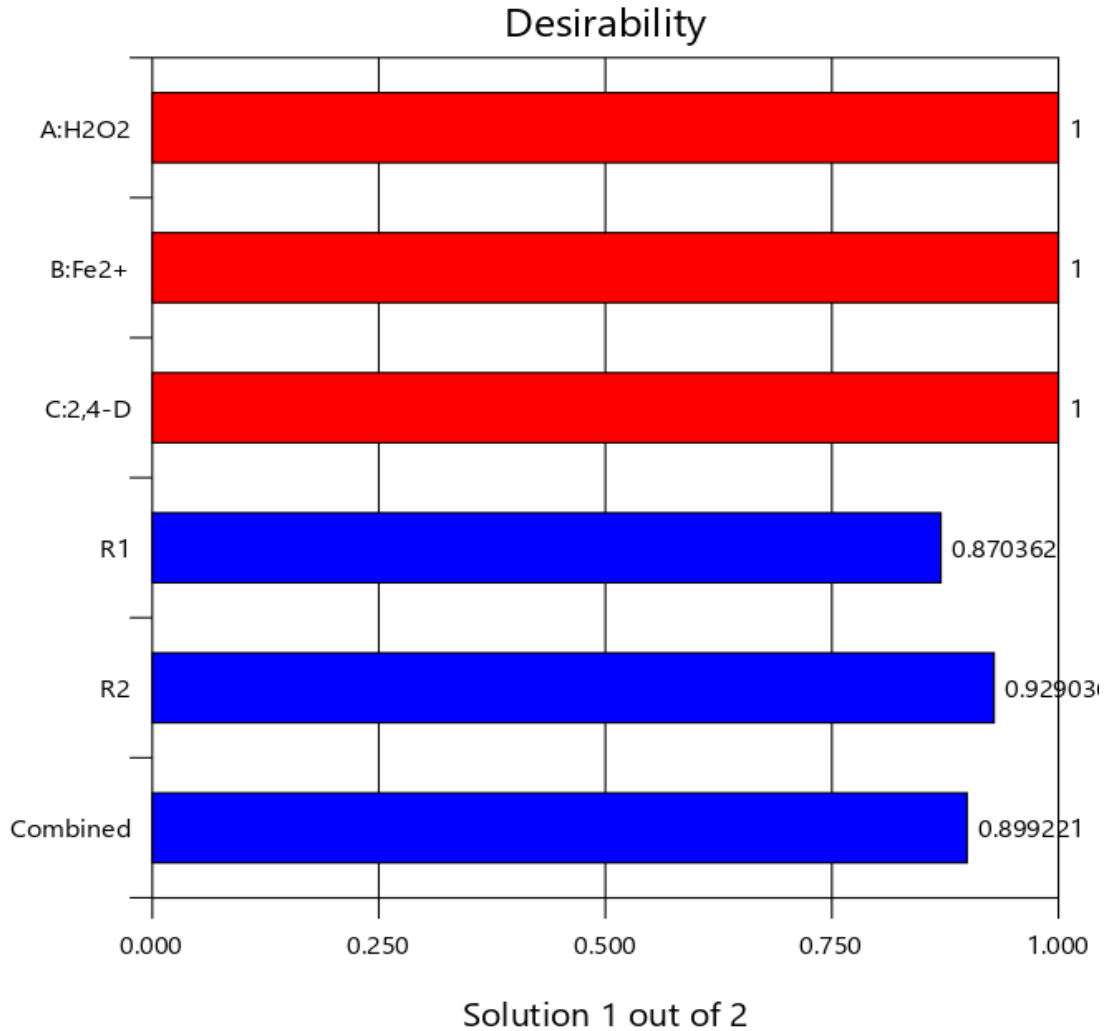


Figure 4. 16. Bar graphs which shows desirability

4.5.2. Graphical Optimization

Also known as an overlay graph. Produces a single plot highlighting the “sweet spot” for where response criteria can be met. It is also used to show the limits of failure in a process.

- The contours are plotted at the limits specified by the Criteria.
- One color (bright yellow by default) defines the acceptable factor settings.
- Another color (grey by default) defines the unacceptable factor settings.

If intervals are included on the criteria, then a blend of the acceptable and unacceptable colors is used to show where the interval limits are unacceptable.

The numerical optimization solutions (flags) are carried over and displayed if the graph is on the correct slice.

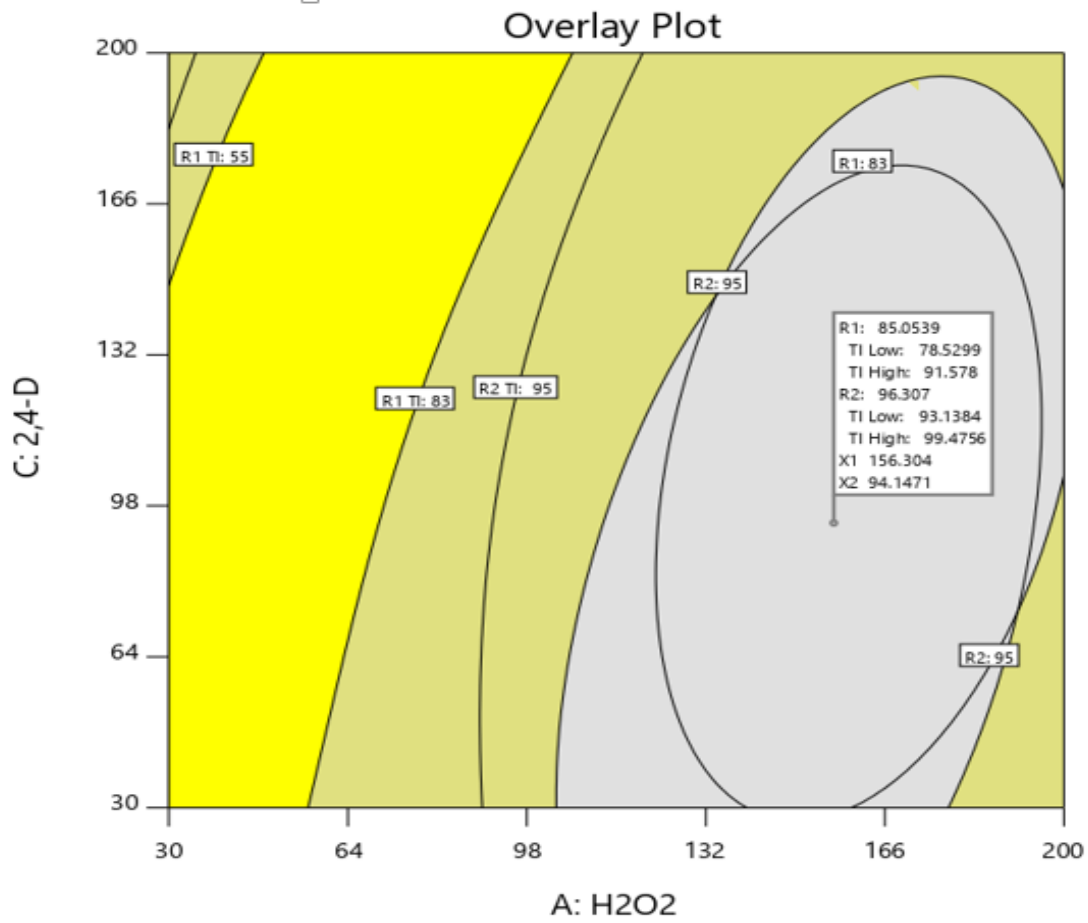


Figure 4. 17. Overlay plot showing graphical Optimization

The above Figure 4.17 tells us that for the 85% TOC and 96.3% COD removal. The optimum amount of [H₂O₂] is 156.3 mg/L and that of [2,4-D] is 94.15 mg/L.

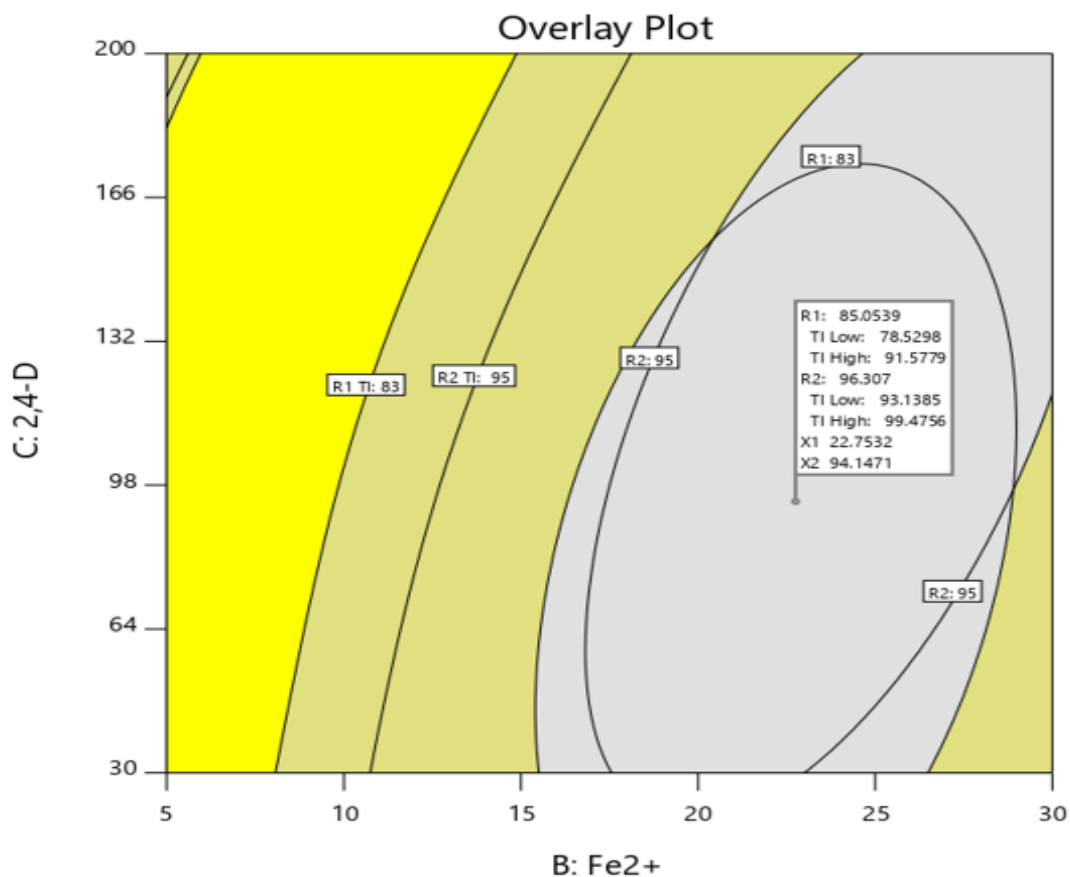


Figure 4. 18. Overlay plot showing graphical Optimization

The above Figure 4.18 tells us that for the 85% TOC and 96.3% COD removal. The optimum amount of [Fe²⁺] is 22.75 mg/L and that of [2,4-D] is 94.15 mg/L.

4.6. Comparison of the result with the research findings

The great interest of the academic community for the use of AOPs in wastewater treatment is reflected by the significant number of publications that have been produced during the last decade. Photo-Fenton processes have been used for the treatment of several types of wastewater including those produced in dye manufacture, pulp bleaching, agricultural processing and chemical manufacture (Stasinakis, 2008).

Photo-Fenton reaction was more efficient in degradation of pesticides than Photo-Catalysis processes (UV/TiO₂) and (UV/H₂O₂/TiO₂). This observation could be explained in terms of the sources of hydroxyl radicals in each process. In Photo-Catalysis, the hydroxyl radicals are formed only when positive holes react with water. On the other hand, in photo-Fenton reaction the

hydroxyl radicals are formed from several sources i.e. photolysis of $\text{Fe}(\text{OH})^{+2}$, reaction of Fe^{+2} with H_2O_2 , and photolysis of H_2O_2 . In addition, photo decomposition of Fe^{+3} with carboxylates in presences of visible light composes new Fe^{+2} which reproduce more radicals in presence of H_2O_2 (Mohamed Gar Alalm A. T., 2015).

The result of this study is compared with the performance of different oxidation processes and also with different types of pesticides and other industrial wastewaters in the [table 4.9](#) below. The degradation efficiency is evaluated in terms of chemical oxygen demand (COD), total organic carbon (TOC) and color removal.

Table 4. 9. Comparison of the results of the study with the research findings

Sr. NO.	Type of AOP	Type of wastewater	Efficiency	Reference
1	$\text{H}_2\text{O}_2/\text{UV}$	2,4-D	TOC = 70%	(El-Din, 2006)
2	Photo-Fenton	Remazol Red F3B	TOC = 81.5% COD = 94%	(Virkus, 2016)
3	Photo-Fenton	Carbofuran, $\text{C}_{12}\text{H}_{15}\text{NO}_3$ (pesticide)	TOC = 76.7%	(Hernández-Shek, 2012)
4	Solar photo-Fenton	Textile wastewater	Colour = 98-99% COD = 72%	(Virkus, 2016)
5	Fenton	Landfill leachate	COD = 50%	(Stasinakis, 2008)
6	Photo-Fenton	Chloropyrifos (pesticide)	COD = 91% Chloropyrifos = 78%	(Mohamed Gar Alalm A. T., 2013)
7	Solar photo-Fenton	Chlorpyrifos insecticide in wastewater	COD = 90%	(Youssef Samet, 2012)
8	Heterogeneous photo-Fenton	Winery wastewater	TOC = 50%	(Stasinakis, 2008)
9	$\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ (photo-Fenton like)	Acid Blue 193	Color = 98% COD = 78% TOC = 59%	(Virkus, 2016)
10	Photo-Fenton	Pesticides from real industrial wastewater	COD = 90.7%	(Mohamed Gar Alalm A. T., 2015)
11	Fenton	Oil recovery industry wastewater	COD = 86%	(Stasinakis, 2008)

12	TiO ₂ -based solar photocatalysis	Pesticides mixture wastewater	TOC = 80%	(José Colina-Márquez, 2013)
13	photo-Fenton	olive mill wastewater	Color = 90%	(Stasinakis, 2008)
14	TiO ₂ -assisted photo-catalysis (UV/TiO ₂)	pulp mill effluent	TOC = 79.6% toxicity = 94%	(Ebru Cokay Catalkaya, 2007)
15	Photo-Fenton	2,4-D	TOC = 85% COD = 96%	This study

By comparing the results of this study with previous studies, the results of this work are in strong agreement with the previous research works on the treatment of recalcitrant organic pollutants using advanced oxidation processes.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The results of this study indicate that photo-Fenton process is a powerful methods for the degradation of the 2,4-dichlorophenoxyacetic acid from wastewater. The photo-Fenton reaction was applied to the wastewater quality 595 mg/L and 185 mg/L of COD and TOC respectively, such that it showed that the pollutant was greatly decreased. The method led to efficient degradation of the pesticide (2,4-dichlorophenoxyacetic acid) up to 83% TOC and 95% COD removal from wastewater facilitating its application attractive. This study has demonstrated the potential of applying advanced oxidation process (photo-Fenton process) for the treatment of wastewater containing pesticides.

As Figure 4.15 shows the optimum conditions of the experimental factors were found to be 156.4 mg/L H₂O₂, 22.79 mg/L Fe²⁺ and 96.4 mg/L 2,4-D within the range studied. The achieved removal efficiency was obtained at 2.8 PH and 2 hours of degradation time using 254 nm UV light.

The removal of 2,4-Dichlorophenoxyacetic acid was greatly increased at high dosages of Fenton reagents (hydrogen peroxide and Ferrous iron). However, excessive dosages shown no improvement on the degradation of the pesticide and the negative effects were observed. On the other hand, the degradation process was preferred at low concentration of the 2,4-Dichlorophenoxyacetic acid due to high pollutant concentration imposes high organic load which requires large amount of Fenton reagents and also prolonged irradiation time.

The rate of organic pollutant degradation is increased by the enhancement of Fenton reaction with UV light irradiation (photo-Fenton process). UV light leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe³⁺. In this way, the concentration of Fe²⁺ is increased and the overall reaction is accelerated.

The Box-Benkhen experimental design allowed a constant 2,4-dichlorophenoxyacetic acid value to be eliminated to obtain optimal iron and hydrogen peroxide values to avoid unnecessary reagent use and avoid additional processes for removing residual reagents. The only disadvantage of the Box-Benkhen experimental design is that it doesn't show the results at the most extreme points, i.e., the results at the [-1 -1 -1] and [+1 +1 +1].

5.2. Recommendations

Based on these results, it is recommended to apply photo-Fenton process for treatment of wastewater rich pesticide. In considering the potential effect of pesticides to the environment (water, soil and atmosphere) attention has to be given to protecting the environment from being damaged by pesticides discharge with industrial wastewater. Hence, these photo-Fenton method has the potential to effectively remove these pollutants from wastewater and it should be incorporated with industrial facilities.

Industrial wastewater containing pesticides and other organic pollutants need to be treated using AOPs prior to making discharge to the environment. This is due to the fate of these pesticides are: leaching into soil and water, atmospheric deposition, runoff and uptake by plants. Dilution of the wastewater cannot be the proper solution to the effects of pesticides since the pollutants are capable of staying in the environment for long period of time and has a potential to affect the environment through a time.

Authors have also suggested that the combination of physical or chemical methods with biological treatment is likely a feasible option for the treatment of pesticide wastewater. In all their works they demonstrated the beneficial use of chemical oxidation process as a pretreatment or post-treatment of a biological process. Drinking water sources of industrial areas and agricultural areas where large amount of pesticides are employed as an agricultural inputs are susceptible to be contaminated with pesticides. The treatment of water containing these non-biodegradable toxic organic compounds should be facilitated with coupling AOPs and biological by considering the toxic nature of pesticides, it is clear that these kinds of xenobiotics are, in many cases, low biodegradable and, in most cases, highly refractory organic compounds. Due to this reasons, coupling AOPs and biological processes should be a good alternative to minimize the costs of treatment of water or wastewater containing this kind of pollutants.

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7. APPENDICES

Appendix A. Stock Solution Calculation

Stock solution of hydrogen peroxide (H₂O₂)

Volume in ml of H₂O₂ required for the desired concentration in mg/L is shown below.

Density of H₂O₂ is 1.11*10³ g/ml.

$$30\% * \text{density of } H_2O_2$$

$$\frac{30 \text{ g}}{100 \text{ g}} * \frac{1.11 * 10^3}{\text{mL}} = 333 \frac{\text{mg}}{\text{ml}}$$

$$H_2O_2 \text{ ml} = \frac{\text{ml}}{333 \text{ mg}} * H_2O_2 \frac{\text{mg}}{\text{l}} * \text{wastewater volume } l$$

Stock solution of Ferrous Iron (Fe(II))

Mass in mg of ferrous sulfate heptahydrate in solid form required for the desired concentration in mg/L is shown below.

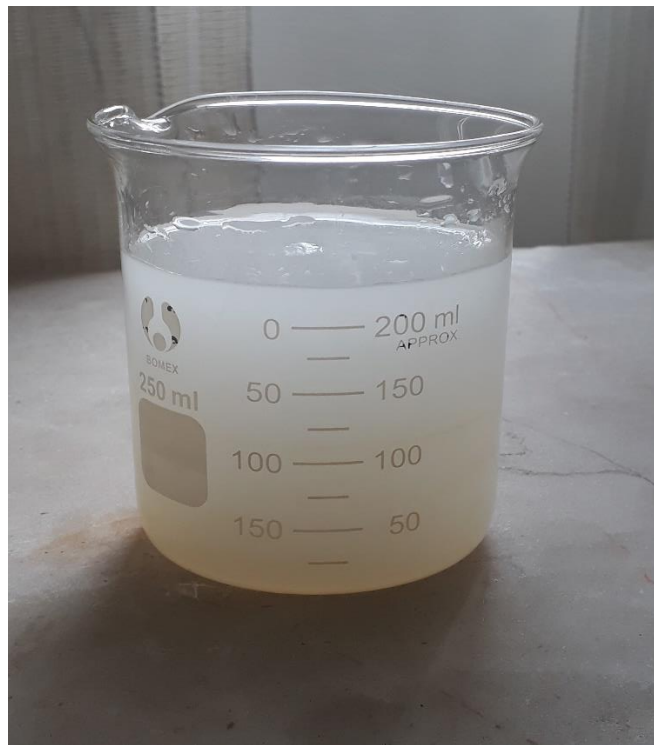
Molecular weight of ferrous iron is 56 g/mol and that of FeSO₄.7H₂O is 278.01 g/mol.

$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O mg} = \frac{1 \text{ m mol}}{56 \text{ mg of } Fe^{2+}} * H_2O_2 \frac{278.01 \text{ mg of } FeSO_4 \cdot 7H_2O}{\text{mmol}} * Fe^{2+} \frac{\text{mg}}{\text{l}} * \text{wastewater volume } l$$

Appendix B. Some Lists of laboratory works



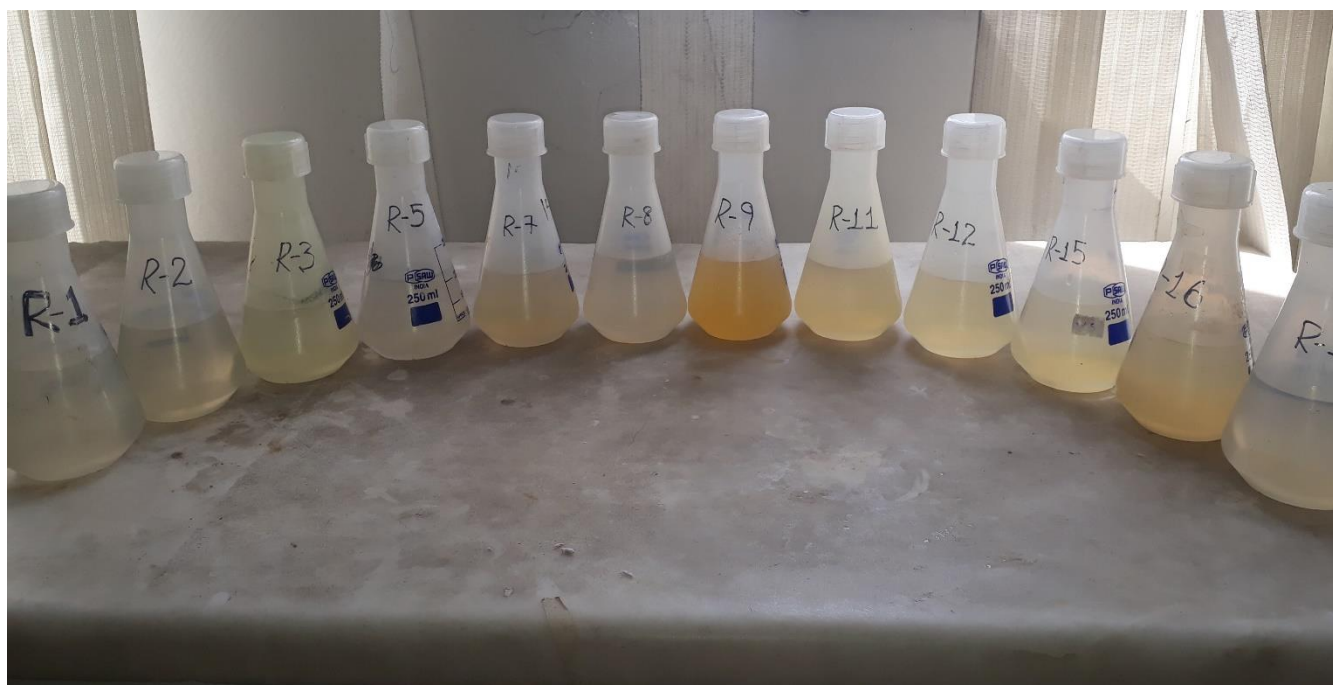
i. 2,4-Dichlorophenoxyacetic acid (2,4-D) herbicide



ii. Synthetic Wastewater prepared using 2,4-D



iii. Photo-Fenton experiment



iv. Sample prepared for analysis

C) Design Summary

Build Information

File Version	11.1.0.1		
Study Type	Response Surface	Subtype	Randomized
Design Type	Box-Behnken	Runs	17
Design Model	Quadratic	Blocks	No Blocks
Build Time (ms)	1.0000		

Factors

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	H2O2	mg/L	Numeric	30.00	200.00	-1 ↔ 30.00	+1 ↔ 200.00	115.00	60.10
B	Fe2+	mg/L	Numeric	5.00	30.00	-1 ↔ 5.00	+1 ↔ 30.00	17.50	8.84
C	2,4-D	mg/L	Numeric	30.00	200.00	-1 ↔ 30.00	+1 ↔ 200.00	115.00	60.10

Responses

Response	Name	Units	Observations	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio	Transform	Model
R1	TOC	mg/L	17	Polynomial	55	83	72.88	10.09	1.51	None	Quadratic
R2	COD	mg/L	17	Polynomial	72	95	86.24	8.39	1.32	None	Quadratic

D) Coefficient Table

p-value colors: $p < 0.05$ $0.05 \leq p < 0.1$ $p \geq 0.1$

	Intercept	A	B	C	AB	AC	BC	A ²	B ²	C ²
R1	81.8	7.125	5.25	-4.375	4.25	3.5	2.75	-8.9	-8.15	-1.9
p-values		< 0.0001	< 0.0001	< 0.0001	0.0007	0.0020	0.0072	< 0.0001	< 0.0001	0.0325
R2	93.2	6.375	4.875	-3	3.5	2.25	3.75	-6.85	-6.35	-1.6
p-values		< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.0004	< 0.0001	< 0.0001	< 0.0001	0.0025

E) Model Evaluation

Model Terms

Term	Standard Error*	VIF	R _i ²	Power
A	0.3536	1	0.0000	68.1 %
B	0.3536	1	0.0000	68.1 %
C	0.3536	1	0.0000	68.1 %
AB	0.5000	1	0.0000	40.8 %
AC	0.5000	1	0.0000	40.8 %
BC	0.5000	1	0.0000	40.8 %
A ²	0.4873	1.00588	0.0058	93.8 %
B ²	0.4873	1.00588	0.0058	93.8 %
C ²	0.4873	1.00588	0.0058	93.8 %

- For a standard deviation of 1.

Power calculations are performed using response type "Continuous" and parameters:

Delta=2, Sigma=1

Power is evaluated over the -1 to +1 coded factor space.

Standard errors should be similar to each other in a balanced design. Lower standard errors are better.

The ideal VIF value is 1.0. VIFs above 10 are cause for concern. VIFs above 100 are cause for alarm, indicating coefficients are poorly estimated due to multicollinearity.

Ideal R_i^2 is 0.0. High R_i^2 means terms are correlated with each other, possibly leading to poor models.

If the design has multilinear constraints, then multicollinearity will exist to a greater degree. This inflates the VIFs and the R_i^2 , rendering these statistics useless. Use FDS instead.

Power is an inappropriate tool to evaluate response surface designs.

Use prediction-based metrics provided in this program via Fraction of Design Space (FDS) statistics.

Click on the Graphs tab to find the FDS graph. More information about FDS is available in the Help.

Be sure that the model you selected contains only terms you expect to be significant.

Alias Matrix

No aliases found for Quadratic model

Degrees of Freedom

Model	9
Residuals	7
<i>Lack of Fit</i>	3
<i>Pure Error</i>	4
Corr Total	16

We recommend at least 3 lack of fit DF and 4 pure error DF to ensure a valid lack of fit test.

F) Fit Summary for TOC Removal

Response 1: R1

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0324	0.0001	0.3588	0.1467	
2FI	0.5598	< 0.0001	0.3154	-0.2123	
Quadratic	< 0.0001	0.0607	0.9789	0.8769	Suggested
Cubic	0.0607		0.9931		Aliased

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	90301.24	1	90301.24			
Linear vs Mean	779.75	3	259.92	3.98	0.0324	
2FI vs Linear	151.50	3	50.50	0.7250	0.5598	
Quadratic vs 2FI	681.46	3	227.15	105.65	< 0.0001	Suggested
Cubic vs Quadratic	12.25	3	4.08	5.83	0.0607	Aliased
Residual	2.80	4	0.7000			
Total	91929.00	17	5407.59			

Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Model Summary Statistics

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	8.08	0.4790	0.3588	0.1467	1388.96	
2FI	8.35	0.5721	0.3154	-0.2123	1973.30	
Quadratic	1.47	0.9908	0.9789	0.8769	200.37	Suggested
Cubic	0.8367	0.9983	0.9931		*	Aliased

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

Focus on the model maximizing the **Adjusted R²** and the **Predicted R²**.

Lack of Fit Tests

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Linear	845.21	9	93.91	134.16	0.0001	
2FI	693.71	6	115.62	165.17	< 0.0001	
Quadratic	12.25	3	4.08	5.83	0.0607	Suggested
Cubic	0.0000	0				Aliased
Pure Error	2.80	4	0.7000			

The selected model should have insignificant lack-of-fit.

G) Fit Summary for COD removal

Response 2: R2

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0194	0.0003	0.4105	0.2073	
2FI	0.4284	0.0003	0.4118	-0.0160	
Quadratic	< 0.0001	0.7880	0.9928	0.9855	Suggested
Cubic	0.7880		0.9901		Aliased

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	1.264E+05	1	1.264E+05			
Linear vs Mean	587.25	3	195.75	4.71	0.0194	
2FI vs Linear	125.50	3	41.83	1.01	0.4284	
Quadratic vs 2FI	410.76	3	136.92	269.98	< 0.0001	Suggested
Cubic vs Quadratic	0.7500	3	0.2500	0.3571	0.7880	Aliased
Residual	2.80	4	0.7000			
Total	1.275E+05	17	7502.82			

Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Model Summary Statistics

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	6.44	0.5210	0.4105	0.2073	893.37	
2FI	6.44	0.6324	0.4118	-0.0160	1145.11	
Quadratic	0.7121	0.9969	0.9928	0.9855	16.38	Suggested
Cubic	0.8367	0.9975	0.9901		*	Aliased

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

Focus on the model maximizing the **Adjusted R²** and the **Predicted R²**.

Lack of Fit Tests

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Linear	537.01	9	59.67	85.24	0.0003	
2FI	411.51	6	68.58	97.98	0.0003	
Quadratic	0.7500	3	0.2500	0.3571	0.7880	Suggested
Cubic	0.0000	0				Aliased
Pure Error	2.80	4	0.7000			

The selected model should have insignificant lack-of-fit.

H) Solution for numerical Optimization

Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:H ₂ O ₂	is in range	30	200	1	1	3
B:Fe ²⁺	is in range	5	30	1	1	3
C:2,4-D	is in range	30	200	1	1	3
R1	Maximize	55	83	1	1	3
R2	Maximize	72	95	1	1	3

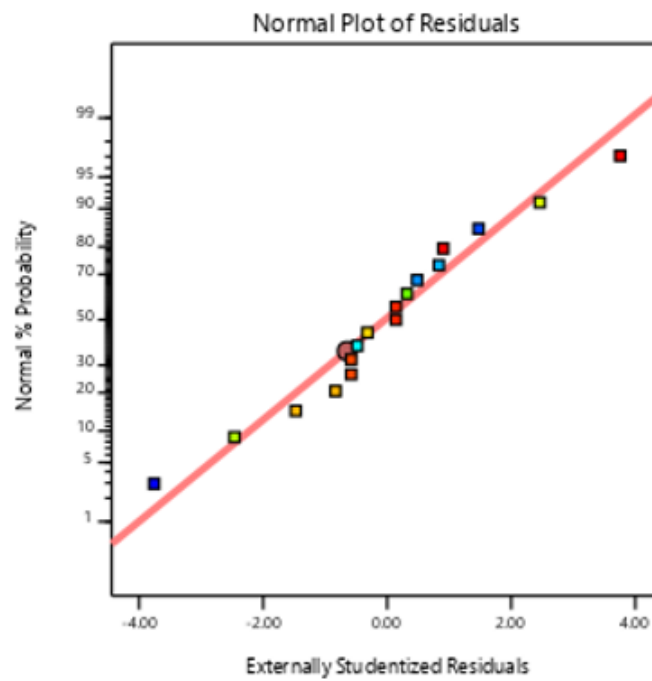
Solutions

2 Solutions found

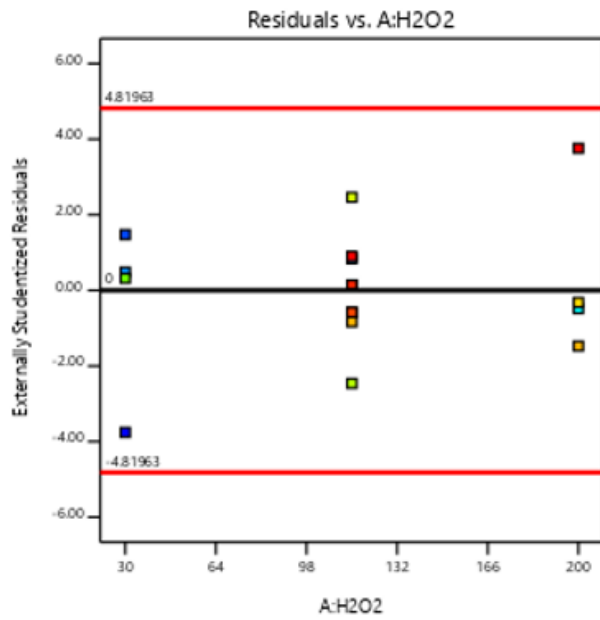
Number	H2O2	Fe2+	2,4-D	R1*	R2*	Desirability	Desirability (w/o Intervals)	
1	156.317	22.780	94.668	85.050	96.311	0.899	1.000	Selected
2	156.532	22.826	95.357	85.042	96.317	0.899	1.000	

- Intervals adjusted for variation in the factors (POE).

I) Diagnostics plots for TOC response

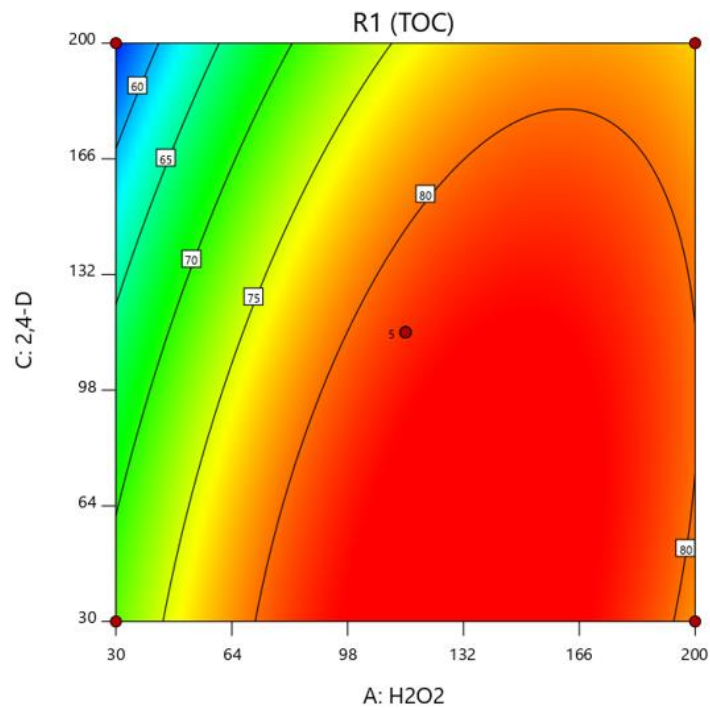


a) Normal Probability plot

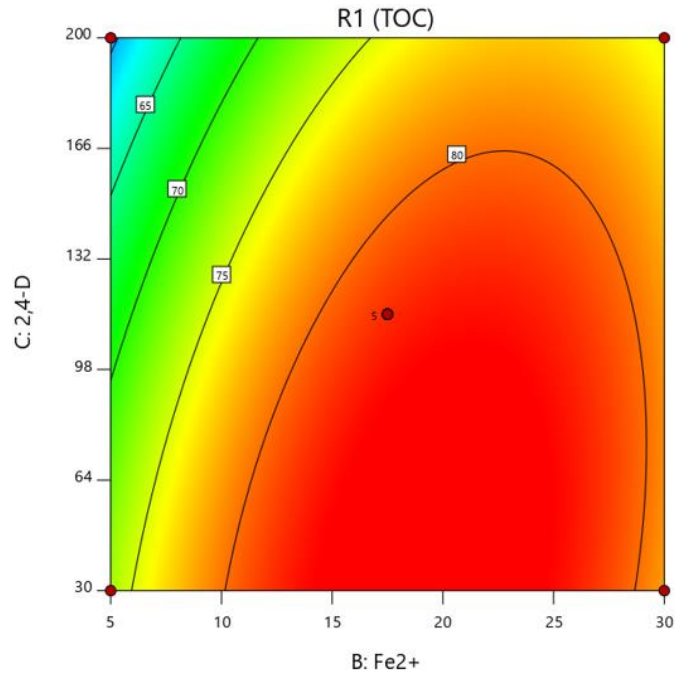


b) Residuals vs. Factor plot

J) Model Graphs for TOC response

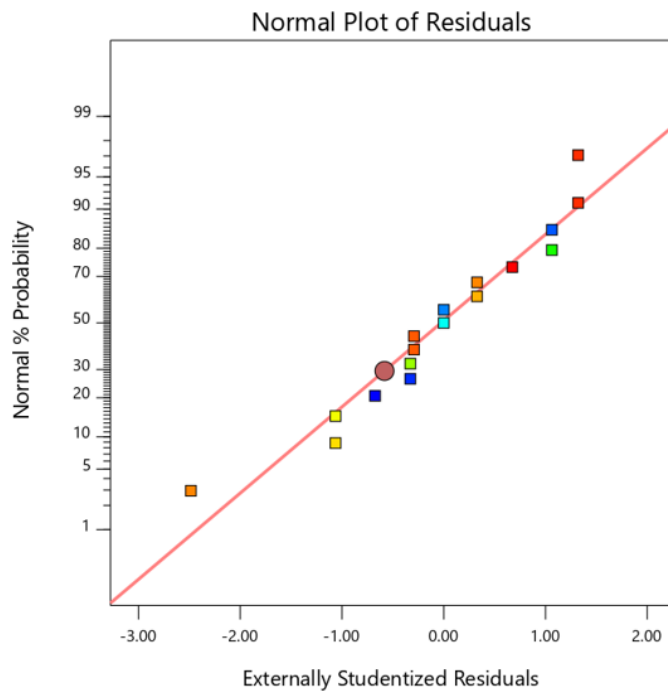


Contour Plot of H₂O₂ and 2,4-D

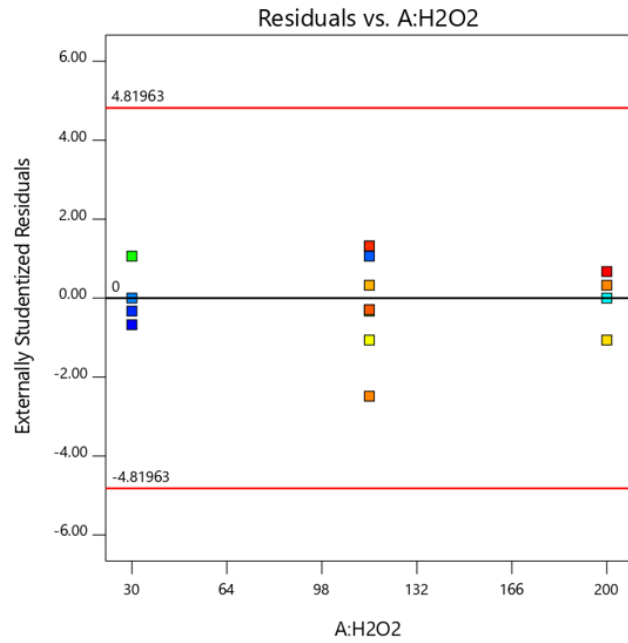


Contour Plot of Fe²⁺ and 2,4-D

K) Diagnostics plots for COD response

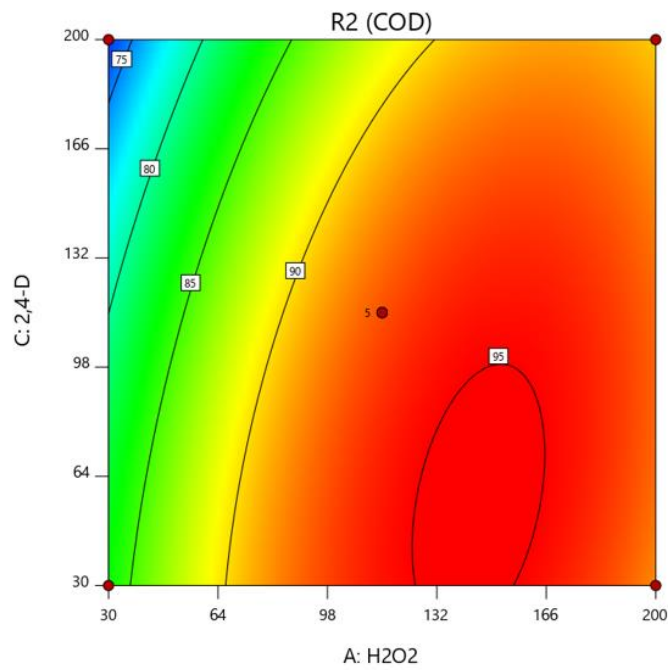


a) Normal Probability plot

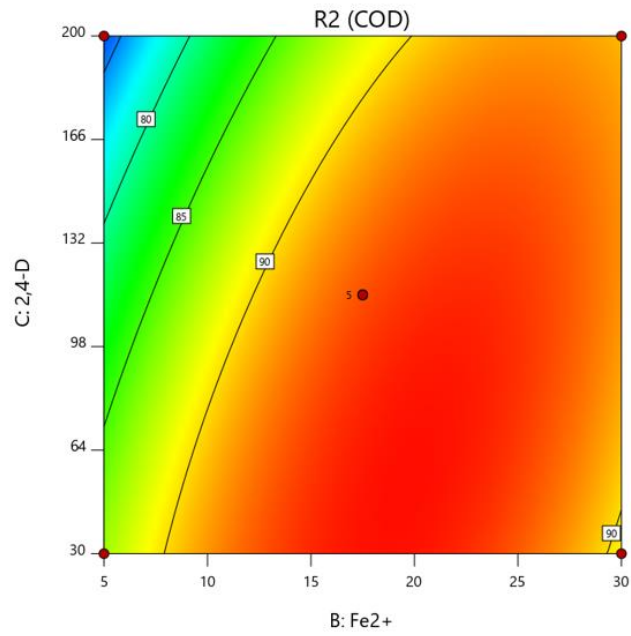


b) Residuals vs. Factor plot

L) Model Graphs for COD response



Contour Plot of H₂O₂ and 2,4-D



Contour Plot of Fe²⁺ and 2,4-D