ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIOENGINEERING

REMOVAL OF PHENOLIC COMPOUND FROM SYNTHETIC PHENOL SOLUTION BY USING BENTONITE SUPPORTIVE IRON CATALYST

By: Dawit Alemu

A thesis submitted to the Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in partial fulfillment of the requirements for the Degree of Masters of Science in Chemical Engineering (Process Engineering)

Addis Ababa, Ethiopia

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June 2019

DECLARATION

This is to certify that the thesis prepared by Dawit Alemu, entitled: "Removal of Phenolic compounds from synthetic phenol solution using bentonite supportive iron catalyst" and submitted to School of Chemical and Bioengineering as Partial Fulfillment of the Requirements for the Degree of Masters of Science in Chemical Engineering (Chemical and Bio Engineering, Process stream) is my original work and it has not been presented elsewhere or by any other person for the award of degree in this or any other university. And it complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Acknowledgment

First of all, I would like to thank God who has given me the strength, wisdom and health to complete this thesis.

Next, I would like to express my deepest gratitude and sincere appreciation to my advisor Dr. Eng. Anuradha Jabasingh S, Associate Professor for her excellent scientific guidance, fruitful advice, patience, support and encouragement in this work and also, I would also like to acknowledge Dr. Beteley Tekola (Assist. Prof.), who has given me the title and supported me throughout my path, furthermore, I would like to acknowledge AAiT, School of Chemical and Bio-engineering lab assistants for their technical support and also my deepest gratefulness also goes to my family and friends for their continuous encouragement, love, endless moral support and cheerful working atmosphere during my research period.

I also greatly appreciate Ato Hinsta and all laboratory staffs of the chemical and bioengineering department for their unreserved assistance, sharing of knowledge and for extensive scientific discussions during the laboratory works.

Abstract

Due to their industrial relevance, phenolic compounds (PC) are amongst the most common organic pollutants found in many industrial wastewater effluents. The potential detrimental health and environmental impacts of PC necessitate their removal from wastewater to meet regulatory discharge standards in order to ensure meeting sustainable development goals. Searching for low cost, accessible, simple implementation and environmentally friendly catalyst has been one of the concerns of researchers in recent years. Therefore, the aim of this study was to investigate the efficient phenol removal from a synthetic aqueous solution using bentonite supported iron catalyst. Heterogeneous Fenton process was performed to evaluate the performance of the prepared catalyst and the effect of hydrogen peroxide concentration, reaction time, catalyst dosage and pH of solution on the removal process are investigated. The synthesized catalyst has then characterized the pH of zero points of the charge and bulk density was determined, FT-IR spectroscopy, X-ray diffraction (XRD), Atomic absorption spectroscopy (AAS) analysis was performed. Catalyst selection was optimized using the D-optimal experimental design by varying the ratio of bentonite to iron and the temperature of calcination. The result revealed that the iron to bentonite ratio of 1:5 and calcination temperature of 493°C has a high ability to remove the phenolic compound from the aqueous solution. The efficiency of phenol removal by bentonite support iron catalyst was evaluated in a batch system. Different parameters such as hydrogen peroxide concentration (2000, 4000, and 6000 mg/L), contact time (60, 90 and 120 min), catalyst dosage (1000, 1500 and 2000 mg/L) and pH (3, 3.5 and 4) were studied. The experimental results were analyzed. The optimal mineralization reaction process conditions for phenol removal were maximized at hydrogen peroxide concentration 4137 mg/L, reaction time 85.5 min, catalyst dosage 1445 mg/L and pH. 3.45 with 98.64% removal efficiency of phenol was obtained. The results of this study revealed that bentonite support iron catalyst has the suitable potential for removing phenol from aqueous solutions and hence a reduction of TOC by the application of heterogeneous Fenton process.

Keywords: Phenol removal, Bentonite clay, Batch experiments, Heterogeneous Fenton process, Catalyst reusability.

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Acronyms

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of variance
AOP	Advanced oxidation process
ASTM	American Section of the International Testing Materials
BD	Bulk Density
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
EPA	Environmental protection agency
FKM	First Order Kinetic Model
Fe/Bent	Bentonite support iron catalyst
FTIR	Fourier transform infrared spectroscopy
GLKM	Generalized Lumped Kinetic Model
LOI	Loss on ignition
MSH-D	Digital Magnetic Stirrer with Hotplate
MTBE	Methyl Tertiary Butyl Ether
NOM	Natural Organic Material
pH_{ZPC}	pH of Zero Point of Charge
PC	Phenolic Compound
RSM	Response Surface Method
TOC	Total Organic Compound
TPh	Total Phenol
USAEPA	United State Environmental Protection Agency
VOC	Volatile Organic Carbon
XRD	X-Ray Diffraction

1. Introduction

1.1. Background

Water is one of the vital necessities for the survival of human being. Earth is a planet with 71% of its surface covered by water. Of the total available water on earth, 97% is seawater and unavailable for human consumption, only 3% is available as fresh water. Out of this 3%, only a meager 0.06% can be easily accessed as the rest comprises of the frozen polar ice cap, groundwater, and swamp (Toor, 2010). Nevertheless, water is the biggest crisis faced by the world today. Toxic compounds are released to the surface water from different sources including the industries. When these compounds enter the stream, they show an adverse effect on the water cycle and hence towards living organisms. Due to their industrial relevance, phenolic compounds (PC) are amongst the most common organic pollutants found in many industrial wastewater effluents. The potential detrimental health and environmental impacts of PC necessitate and their removal from wastewater to meet regulatory discharge standards to ensure meeting sustainable development goals(Jarrah et al., 2017).

Phenol and its derivatives, collectively known as phenolic compounds are compounds with an aromatic ring(s) attached to one or more hydroxyl group (OH). During the manufacturing and production process of dyes, pesticides, oil refiners, plastics, petrochemical plants, coal conversion activities, and pharmaceuticals, explosives, herbicides, and phenolic resin production, there is a huge of phenolic compounds are released with the wastewater and enters to the water stream. This compound is toxic for human beings and aquatic living species. The presence of these compounds in water and wastewater can lead to further formation of more harmful byproducts during chemical treatment processes, thereby exacerbating their environmental and health impacts. They are very hazardous due to their poor biodegradability, high toxicity, and ecological aspect. The presence of phenols in drinking and irrigation water causes a health hazard and hence it is known as a human carcinogen. phenolic compounds are a considerable health concern, even at low concentration. It also has the potential to hamper the growth and the reproductive capacity of the aquatic organism.

There are various methods used for wastewater treatment. They are the physical, biological and chemical processes but some contaminants found in wastewater are to some degree recalcitrant to these commonly applied processes. Oxidation processes are addressed as viable alternatives when the most common biological treatments fail to achieve the necessary parameter(Rossi, 2014). Oxidation processes may remove certain compounds and constituents through oxidation and reduction reactions. The employment “advanced oxidation processes" leads to the decomposition and mineralization of many hazardous compounds from wastewater(Mehrjouei, 2012).

Advanced Oxidative Processes comprises of techniques which, under certain conditions, transform the organic contaminants into carbon dioxide, water, and inorganic ions with the aid of oxidation reaction(Pawar & Gawande, 2015). The relevance of AOP is destroying in high concentrated including biologically non-degradable chemical structures including pesticides and herbicides(Zeni & Leiliane, 2012).

The Fenton's process is one advanced oxidation processes based on the generation of highly reactive hydroxyl radicals, which attack the complex molecules. AOP with Fenton reagent ($Fe^{2+}/\ H_2O_2$) helps to degrade organic compounds presented in polluted water. In the specific case of Fenton's reagent, the radicals are produced by the reaction between Fe (II) ions and hydrogen peroxide. In fact, this technique allows mineralization of organic compounds, as it overcomes the high toxicity and/or refractory nature of the pollutants.

Hydrogen peroxide (H_2O_2) is a strong oxidant which could be used alone or with a catalyst. The catalyst usually used with hydrogen peroxide is ferrous sulfate and this combination is called Fenton’s reagent. It is a multipurpose oxidant for many systems, it can be applied with or without a catalyst. Another metal catalyst such as Fe^{3+}, $Cu^{2+,}$ and Al^{3+} could also be used. Its reactivity is enhanced by the use of a metal catalyst which generates hydroxyl radicals. Hydrogen peroxide has numerous advantages such as a low cost, high oxidizing power, and ease of handling compared to other oxidizing agents. the oxidant is an environmentally friendly compound which self-

decomposition leads to non-toxic products (H_2O and O_2). But hydrogen peroxide when used alone has very low reactivity and causes incomplete oxidation of many organic contaminants(Faisal, I, & Btihage, 2009)

In this research, synthetic phenol waste is prepared with the phenolic compound and it was treated by using heterogeneous Fenton process using bentonite as a supported iron catalyst which regenerates and iron [II] ion instead of enhancing the formation of iron precipitation. This bentonite was modified by the iron species to increase the catalytic performance for the removal of phenolic from the synthetic wastewater. This process is aimed to optimizing, hydrogen peroxide concentration, catalyst dosage, reaction time and pH. Heterogeneous Fenton process has no iron precipitation since a solid catalyst was used as a support. The catalyst employed in this study, Bentonite as support iron catalyst (Fe/bentonite), was characterized using the pH of zero points of charge, bulk density, FT-IR spectroscopy, X-ray diffraction (XRD) and Atomic absorption spectroscopy (AAS). The prepared catalyst was used in the phenol mineralization heterogeneous Fenton oxidation process and the process condition was optimized.

1.2 Statement of the problem

Removal of an organic pollutant from water has become a serious global issue because of the increasing demand for public health awareness and environmental quality. This pollutant in the wastewater effluents and drinking water influents have become a cause for concern in terms of the potential impact on human health. The considerable contamination of the aqueous environment by organic pollutants still requires the development of quick and simple methods for their removal. A common problem in many industries is the disposal of large volumes of wastewater containing major classes of organic compounds, which are carcinogenic and mutagenic, with high toxicological potentials. Phenol is one of the contaminating compounds that are extent in the wastewaters from many industrial sectors such as oil refineries, petrochemical, ceramic, coal, pharmaceuticals, pesticides, dyes, plastics, explosives, herbicides, and phenolic resin production industries. Phenol enters the water during the

manufacturing and processing steps from these industries. These compounds are very hazardous due to their poor biodegradability, high toxicity, and ecological aspects.

The discharge of these phenolic compounds in the watercourse and their exposure over a long period can cause severe impact to the environment, causes liver and kidney damage to human and animals, central nervous system impairment, diarrhea and excretion of dark urine. Phenolic compounds have negative impacts on the landscape as well as a major environmental problem. Phenolic compounds are a potential human carcinogen, which raises considerable health concerns, even at low concentrations. It is therefore essential to develop effective treatment techniques for the removal of these toxic compounds. There are several technologies for treating wastewaters containing phenol. like chemical coagulation, biological treatment (including wetland disposal), packed bed adsorption, evaporation, membrane separation and reverse osmosis. But the success of these techniques has never been completed for reasons that range from economic considerations to poor removal yields.

Hence advanced oxidation processes are gaining increasing interest as potential solutions in the field of wastewaters treatment. The use of suitable catalysts can substantially decrease the energy consumption of various well-known oxidation processes. Thus, in this research, bentonite has been selected as the catalytic support. In relation to the iron precursor, different factors were addressed to develop good and stable bentonite support iron catalyst in the catalytic peroxidation of phenolic compounds. The best technique is the heterogeneous Fenton process using bentonite as a supportive iron catalyst. It is the best suitable alternatives for the treatment of the wastewater containing toxic or non-degradable pollutant, like phenolic compounds.

1.3. Objectives

1.3.1. General objective

The main objective of this work is to remove the phenol from synthetic phenol solution by using bentonite supportive iron catalyst.

1.3.2. Specific objectives

To achieve the goal of the general objective, the author used the following specific objectives;

- ✓ To prepare, characterize and determine the physiochemical properties of the raw bentonite and bentonite support iron catalysts (Fe/bent).
- ✓ To study the performance of bentonite support iron catalyst employed in the heterogeneous Fenton process to oxidize phenols.
- ✓ To determine the degradation percentage of phenol from prepared synthetic phenol solution by heterogeneous Fenton using the prepared catalyst.
- ✓ To investigate the main and interaction effects of bentonite support iron catalyst dosage, reaction time, pH and peroxide concentration on the performance of phenol oxidation during the heterogeneous Fenton reaction.
- ✓ To determine the effect of mineralization reaction time and reusability of the catalyst
- ✓ To analyze the kinetics models during the oxidation of phenol by the heterogeneous Fenton mechanism.

1.4. The scope of the study

The research work generally covers bentonite clay support iron catalyst, also synthesis, characterization (X-ray diffraction, Fourier transformed infrared spectroscopy, Atomic absorption spectroscopy, and bulk density), iron stability and reusability. Phenol containing synthetic solution was prepared and heterogeneous Fenton oxidation using the synthesized Fe-bentonite catalysts was performed. Treated synthetic phenol solution analysis, total phenol removal, mineralization (TOC) and adsorption capacity were determined. Synthesis and characterization of catalyst, iron loading analysis, preparation of synthetic phenol solution, and analysis of phenol solution was carried out using standard procedures and test methods.

1.5. Significance of the study

The study is aimed to remove the phenolic compound from synthetic phenol solution by Fenton process using bentonite as a supportive iron catalyst. One of the most important tasks to sustain our quality of life and guarantee the development of many notable areas is to preserve the quality of the water resources. The development of techniques that permit the reuse of water and prevent the pollution of waters bodies are becoming progressively more and more important. Therefore, this study have:

- Greater contribution to effectively eliminate organic compounds in the aqueous phase, rather than collecting or transferring pollutants to another phase.
- Aid in investigating sustainable and renewable technologies, with the possibility of integrating the industry's leftovers with wastewater treatment.
- Provide information on promising systems based on the oxidative power of the Fenton’s reagent.
- Methods to produce a treated water (value added product) from wastewater.
- Provide useful knowledge on factors that have an impact on the removal efficiency of phenols.

2. Literature review

Wastewater treatment due to organic pollutants remains a serious environmental and public problem. Moreover, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Aromatic compounds (including phenolic derivatives and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses(Yang et al., 2010). Then it is necessary to develop various efficient technologies for the removal of pollutants from wastewater. Conventional methods for the removal of phenolic pollutants in aqueous solutions can be divided into three main categories: physical, chemical, and biological treatment. Among them, physical adsorption method is generally considered to be the best, effective, low cost, and most frequently used method for the removal of phenolic pollutants. It is now recognized as an effective, efficient, and economic method for water decontamination applications and for separation analytical purposes. The adsorbents may be of mineral, organic, or biological origin: such as activated carbons, zeolites, clay, silica beads, etc. However, the high initial cost and the need for a costly regeneration system make the clay less economically viable as excellent adsorbent. Therefore, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents. Natural zeolites, clays, and tree minerals, gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange capability. Clay is one of the potential alternatives as well. Similar to zeolites, clay minerals are also important inorganic components in soil. In recent years and because of its better mechanical strength and feasible regeneration under mild conditions, clays as support catalyst have increasingly been used for efficient removal of specific organic compounds from contaminated water(Auwal & Hossen, 2018).

Due to these aspects, their detection and removal pose a challenge to the scientific community. To develop efficient techniques to remove them, it is fundamental to understand their physicochemical properties and the available treatment types and

conditions. Developing these advanced technologies and improved operation of wastewater treatment plants results in higher quality effluents. At the same time, in the downstream analysis, improved techniques to detecting pollutants at lower concentrations and tools to evaluate the toxicity of the contaminated stream, feedback to the upstream process in order to optimize plant operation. The continual water scarcity in many parts of the world, providing clean drinking water and sustainable development necessitated the use of advanced technologies (Falconer et al., 2006). Consequently, extensive research and development in both upstream processing and downstream monitoring are needed.

Advanced oxidation processes are the focus of this literature review, as a potential treatment method to remove toxic pollutant micropollutants. This method has a high rejection rate (above 90%) for various micropollutants and removes micropollutants without generating secondary wastes, and further, it can also be applied and combined with other treatment methods(Silva et al., 2017). We discussed researches which is carried out by using different methods of phenol removal as following:

(Kulkarni, 2017) carried out an investigation on use of advanced oxidation for phenol removal. They used red mud and black nickel mud for increasing the rate. By ozonization without catalyst, they were able to remove 95 percent of the phenol. (Molva, 2004) reviewed various removal methods for phenol. According to their studies and their subsequent conclusion, adsorption is effective method. The reason for this lies in its simplicity, economic and easy design

According to (Paridah et al., 2016) phenolic effluent causes various long term and short-term health problems. Various biological and non-biological methods can be used for phenol removal. He reviewed various biological methods for phenol removal. Various suspended and attached growth processes can be used for phenol removal. The percentage removal by using various bio sorbents ranges from 75 to 90 percent for various bio sorbents. However, it has disadvantages that cannot treat high concentration of contaminants. (Abdel et al., 2013) carried out an investigation on phenol removal from wastewater using peroxidases. According to them, highly selective nature of enzymatic reactions, coupled with mild conditions and shorter reaction times are advantages of this method. Their investigation indicated that the

method has significant potential and capacity for treating phenol containing aqueous solutions.

A though review of the existing literature indicated that several natural and synthetic material has been studied for the removal of phenol and phenolic compound from their aqueous solution. It appears that the problems caused by phenolic-containing wastewater will become worse in the coming decades, therefore, an efficient and environmental- friendly technology must be found to treat wastewater. However, bentonite support iron catalyst has not been studied for the removal of phenols. Since raw bentonite as support iron catalyst is easily available and very low-cost has been applied to remove phenol from aqueous solution, there is a substantial scope for utilizing this industrial waste as a potential of adsorbent for the removal of phenol and its derivatives. Therefore, exploring the adsorbent potential of bentonite as support iron catalyst for the removal of phenol has been considered in this work. Aim of the present work is to investigate the capability of bentonite as support iron catalyst for removal of phenol from wastewater and to study the effects of hydrogen peroxide concentration, catalyst dosage, pH value and reaction time on the adsorption process, then, find then optimum conditions. In addition, the first order kinetic model and Generalized Lumped Kinetic Model were determined using the optimum conditions selected from the statistical design of experiments.

2.1. Phenols

Phenols are one of the most important raw and intermediate materials in various synthetic processes, including polycarbonates, epoxies, bake lite, nylon, detergents, herbicides, resin paint, dying, textile wood, pulp mill, pharmaceutical drugs and other chemicals (Saitoh et al., 2009). Similarly, they are synthesized industrially for a variety of domestic and industrial applications as components of other organic chemicals(Kurnik et al., 2015). Phenol and Phenolic compounds are ubiquitous organic pollutants which are released to natural water bodies and wastewater systems from the industrial processes (Ryan et al., 2007). The common name for a phenolic compound is hydroxyl benzene (C_6H_5OH) which belongs to the class of organic

compounds, commonly referred to as phenols, containing one or more hydroxyl group attached to an aromatic ring (Jarrah et al., 2017). It is also called carbolic acid, phenolic acid, phenyl hydroxide, or ox benzene. Phenol was first isolated from coal tar and named carbolic acid in 1834 by the German chemist Range. It is an aromatic compound (Busca et al., 2008). Until the advent of synthetic phenol production, just before World War I, coal tar remained the only source of phenol. The predominant uses of phenol are in bisphenol A, Phenolic resins, caprolactam, aniline, and alkylphenols. It is a white crystalline solid at room temperature and pressure. Phenol gradually turns pink if it contains impurities or is exposed to heat or light. It has a distinctive sweet, tarry odor, and burning taste. Phenol has limited solubility in water between 0 and 65°C. Above 65.3°C phenol and water are miscible in all proportions. They belong to a variety of groups of chemical substances naturally existing in many living tissues of plants and are also synthesized at lower concentrations by microorganisms(Martin et al., 2005).

Generally, Phenol was considered as the most hazardous organic pollutant. Due to its toxicity, they are harmful to living organism even at low concentrations (Pigatto et al., 2013). In addition to this, the presence of phenol in natural waters can lead to the formation of other toxic substituted compounds during disinfection and oxidation process (Saleh et al., 2019)**.** Phenol is a combustible compound that is also soluble in oils, carbon disulfide, and numerous organic solvents and is characterized by a typical pungent sweet, medicinal, or tar-like odor. Phenols have been considered as priority organic pollutants by the US environmental protection agency (EPA) and can cause considerable damage to the environment. It is one of the major organic compounds included in most substances and wastewaters, is degraded rapidly in the air (half-life of approximately 15 hours), but persistent in water for a longer period. It is associated with cardiovascular disease, serious gastrointestinal damage, severe skin damage, and muscle twitching (Green et al., 2017). Furthermore, phenol can also accumulate in the human breast milk, cause vomiting and lethargy of children. Some birth defects have been observed in animals due to female's exposure to phenol during pregnancy. Estimated lethal oral doses of phenol in adults vary widely, from 1 g (14 mg/kg, assuming an adult body weight of 70 kg) to as much as 65 g (930 mg/kg, assuming an

adult body weight of 70 kg(Pines, 2003). Therefore, The removal of the phenolic compound from waste and wastewater is important to protect public health and the environment (Pigatto et al., 2013). Even though the structure of phenol is similar to cyclohexanol, phenol is a much stronger weak acid. This characteristic allows aqueous hydroxides to convert phenol into their salts. The salts, especially those of sodium and potassium, are converted back into phenol by aqueous mineral acids or carboxylic acids. Besides being acidic, the significant industrial chemical property of phenol is the extremely high reactivity of its ring toward electrophilic substitution.

Pure phenols are generally colour less solids or liquids. The light colour usually associated with phenols is due to its oxidation by air in presence of light Phenols, in general, are insoluble in water; but phenol itself, and polyhydric phenols are fairly soluble in water which is believed to be due to the formation of hydrogen bonds with water. due to intermolecular hydrogen bonding, phenols usually have relatively high boiling points than the corresponding hydrocarbons, aryl halides and alcohols They possess characteristic colour. They are highly toxic in nature and possess antiseptic properties. They may produce wounds on skin. Molecular weight 94.11g/mol; Boiling point 182.0ºC; Melting point 43.0ºC; Vapour pressure 0.3513mm Hg at 25ºC; Solubility in water 8.3g/100ml; Viscosity 3.437mPa; pH 6; pKa 9.99.

Table2.1. Physical properties of phenol (Rizzo & Luigi, 2011)

Property	**Value**	**unit**
Molecular weight	94.11	g/mol
Boiling point at 101.3 kPa	182	℃
Melting point	43	℃
Vapor pressure at 25°C	46.84	MPa
Flashpoint (closed cup)	79	℃
Density at 20℃ (solid)	1.0722	g/cm^3
Critical temperature	421.1	℃
Critical pressure	6.13	MPa
Specific heat at 14-25 ℃	2.35	J/g.K

Heat of fusion			121.54	J/g
Heat of vaporization, at bp			528.7	J/g
Heat of combustion			-32.468	kJ/g
Viscosity,mPa (=cp)	At	50	3.49	°C
		70 °C	2.03	°C
		90 °C	1.26	°C
Specific heat	At	4.0°C(solid)	1.24	°C
		227°C(solid)	1.41	°C
		70-74°C(liqiud)	2.22	°C

The following table 2.2 shows phenol concentrations coming from different industries(Ltd, 2001).

Table 2.2 Phenols content in industrial waste

Industry	**Concentration of phenols (mg/L)**
Coal mining	1000-2000
Lignite transformation	10000-15000
Gas production	4000
Petrochemicals	50-700
Benzene factory	50
Pharmaceuticals	1000
Oil refining	2000-20000

Phenol in a concentration ranging from 50 to 2000 mg per liter has been reported by many researchers in industrial waste (Ywet et al., 2016). Proper treatment of wastewater containing phenol is required before it is discharged to the external environment. The permissible limit of phenol is 1 mg per L for industrial effluents to be discharged into inland surface waters (IS-2490,1974) and 5 mg/L for discharge into public sewers (IS-3306,1974).

2.2. Catalytic degradation of Environmental pollutants

Catalysis technology provides and acceptable solutions to many environmental issues and as well as an important marketing opportunity and enhances the quality of life.

Environmental catalysis has been recently defined as the development of catalysts to either decompose environmentally unacceptable compounds or provide alternative catalytic syntheses of important compounds without the environmentally unacceptable by-products. Emerging catalytic technologies, as well as problems related to the use of heterogeneous catalysts, are also mentioned. Despite its fundamental contribution to human development, the concept of catalysis reached the media and consequently the majority of the population only from late 1980s with the large-scale introduction of environmental catalysts and in particular of the car converters. Nowadays, it is well recognized that the use of heterogeneous catalysts significantly contributed to reducing the organic pollutant released from industries. Currently, environmental catalysis is widely used in many important commercial sectors, with enormous benefits for the protection of the environment and for the improvement of the quality of our life. Heterogeneous catalysts are efficiently used to reduce nitrogen oxides (NOx) emissions from stationary sources (power plants, boiler), to process oil in obtaining cleaner fuels having low sulfur and nitrogen content, to destroy waste, pesticides, dioxin and furnace, to control the Volatile Organic Compounds (VOCs) emissions and so on. More recently, environmental catalysts have been used to reduce water pollution, to oxidized organic particulate, to destroy ozone pollution in urban areas, to improve indoor air quality. In all these applications catalysis reveals as the essential tool to enable sustainable production and mobility(Ciambelli,,et.al 2002). Nevertheless, it must be stressed that environmental catalysis acts in a more general scenario with the aim of the protection of air, water, and soil also through prevention. It is, in fact, the base of the development of new and cleaner chemical processes, characterized by the use of safer reagents, by the production of a limited number, amount of by-products, by the elimination of production of dangerous intermediate and by the reduced mass and energy inputs requirements. Furthermore, heterogeneous catalysts are essentials to promote the conversion of renewables biomasses and in the production of cleaner fuels. Finally, heterogeneous catalysis is becoming more and more important for the mineralization of polluted organic contaminant. Other areas are the use of catalysts for user friendly technologies (e.g. to develop intelligent or self-cleaning materials) and the reduction of indoor pollution (conversion of ozone,

formaldehyde and other organic indoor pollutants, but also photocatalytic antibacterial air purification), and catalytic technologies for the decontamination of polluted sites (soil and water remediation, including areas contaminated by military actions). Finally, the reduction of the environmental impact in the use or disposal of catalysts must also be cited as part of the objectives of environmental catalysis. Historically, the interest of researchers working in the area of environmental catalysis was initially focused mainly on NOx control (mobile and stationary sources), and sulfur and VOC abatement. Scientific interest progressively then moved from the cleanup approach to the other cited subjects. However, recently new problems and questions have renewed research activity in the area of catalytic cleanup technologies. Catalytic technologies for the treatment of liquid waste, gaseous emissions, and solid waste is necessary for basic waste management applications(Centi et al., 2002).

2.2.1. Advanced water treatment technologies

Treatment of water bodies contaminated by agricultural practices (nitrate and pesticides, in particular), leakage of non-biodegradable compounds like phenol from a different industry and underground fuel tanks and pipelines, and accidental spills and leaking of cleaning solvents, degreasers is becoming a major problem worldwide. There are different aspects of water remediation technologies such as: elimination of nitrate and pesticides from water contaminated by agricultural practices, conversion of MTBE in contaminated underground water, advanced catalytic wet oxidation technologies (of both organics and inorganics, such as phenol), catalytic technologies of wastewater treatment by hydrotreating and photocatalytic wastewater purification (Perathoner & Russo, 2002). Hydrogen processes, commonly known as hydrotreating, are the most common processes for removing sulfur and nitrogen impurities. The oil is combined with high purity hydrogen, vaporized, and then passed over a catalyst such as tungsten, nickel, or a mixture of cobalt and molybdenum oxides supported on an alumina base. Operating temperatures are usually between 260 and 425 °C (500 and 800 °F) at pressures of 14 to 70 bars (1.4 to 7 MPa), or 200 to 1,000 psi. Operating conditions are set to facilitate the desired level without promoting any change to the other properties of the oil.

2.2.2. Advanced oxidation technologies

Advanced oxidation processes for wastewater treatment have received a great deal of attention in recent years. AOPs generate the highly reactive hydroxyl radical (·OH) to degrade the organic chemicals present in wastewater. These OH radicals attack the most organic molecules rapidly and no selectively. The versatility of AOPs is also enhanced by the fact that they offer various alternative methods of hydroxyl radical production, thus allowing better compliance with specific treatment requirements. The eco-friendly end product is the special feature of these AOPs, which are more efficient as they are capable of mineralizing a wide range of organic pollutants (Muruganandham et al., 2014).

The presence of many organic compounds in wastewater, surface water, and groundwater often results from different anthropogenic activities. In certain cases, conventional treatment methods such as biological processes are not effective for the removal of various pollutants due to their chemical structure of the pollutant nature. Therefore, the particular importance of these technologies appears to be in destroying biologically nondegradable chemical structures as well as ozone-resistant substances such as organic pesticides and herbicides(Pariente et al., 2015). These technologies are considered as non-waste generating technologies, they represent a robust alternative to traditional treatment processes as they are degrading the organic matter, not just transforming it into another phase and it can be successfully used in the field of wastewater treatment to reduce toxicity, to convert toxic and organic contaminants into biodegradable by-products, to remove color or to reach the complete mineralization of organic pollutants(Huang, 2013). Therefore, they can be successfully used for wastewater treatment, especially for the removal of phenol and other heavily polluted effluents(Rey, 2015).

AOPs refers specifically to processes in which oxidation of organic compound occurs primarily through reaction with ·OH radicals. This highly powerful and non-selective oxidant is essential for the achievement of a successful oxidation/degradation efficiency. The ultimate aim of oxidation of organic pollutants in an aqueous solution is to mineralize or to convert this organic pollutant into CO_2 and H_2O and inorganic

molecules(Rey & Rodríguez, 2015). Due to the generation of increased amounts of OH radicals, a combination of two or more AOPs usually leads to higher oxidation rates.With promising results observed on the laboratory scale, compared with conventional water and wastewater treatment methods, these technologies will likely be more essential for real applications in the near future. However, the reactivity of hydroxyl radicals with radical scavengers (carbonate, phosphate, etc.), which exist in real wastewaters, is the main disadvantage of all oxidative degradation processes based on hydroxyl radical reactions. Based on the oxidant power of hydrogen peroxide (H_2O_2) catalyzed by iron ions to endorse the formation of hydroxyl radicals (.OH), the Fenton's process (Fenton, 1894) is a very promising AOP due to the high mineralization promoted at about mild conditions of both temperature and pressure. This treatment technique is, generally, very effective in the depuration of toxic wastewater(Krishnan et al., 2017).

Photocatalytic oxidation: The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis”. Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. Generally speaking, photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself. And the photocatalyst is the substance which can modify the rate of a chemical reaction using light irradiation. Photocatalysis process has been known to provide substantial levels of degradation and mineralization of emerging pollutants under both artificial and solar irradiation conditions. Studies mainly focused on building or developing more cost and energy efficient systems that have enhanced ability to run under solar irradiation or simulated ultraviolet energy(Frontistis et al., 2017). This type of AOP occurs where a combination of TiO_2, UV light, and oxygen is employed for the oxidation and decomposition of an organic compound. Oxygen molecules are adsorbed on UV-illuminated TiO_2 and are involved in a number of reactions.

Ozonation: Catalytic ozonation has recently gained significant attention as an effective process used for the removal of phenols from water. Reactions of ozone with organic compound mainly lead to the formation of alcohols, aldehydes, and carboxylic acids. Due to the low reaction rate of these oxidation by-products with ozone, very slow further oxidation toward total mineralization by ozone is considered to be the most significant disadvantage of ozonation processes. An understanding of the mechanisms of catalytic ozonation is vital in order to introduce this technique in water treatment at an industrial scale(Xiong et al., 2018). The ozonation of phenolic pollutants involves two types of oxidation reactions, either molecular ozone reactions (ozonolysis) or hydroxyl radical reactions, depending on the reaction conditions such as pH and the type of pollutant.

At lower pH, molecular ozone reactions are predominant, where organic compounds are subjected to the electrophilic attack of ozone molecules and decomposed into carboxylic acids as final end products. On the other hand, in the presence of hydroxyl anion (HO-) at high pH (>8), ozone molecules are decomposed into free radicals ($^{\cdot}O_2$ and $HO_2^{\cdot}$), and subsequently produces hydroxyl radical ($OH^{\cdot}$), which will attack the organic compound. Generally, for organic compounds degradation, although its application to wastewater treatment is limited due to the high energy demand. However, the ozonation as a pre-treatment process to transform refractory compounds into substances to be removed by conventional methods appears more economically attractive(Chaplin, 2014).

Electrochemical oxidation: This technique can effectively oxidize many organic contaminants at high chloride concentration. Electrochemical oxidation is an alternative destructive of phenols which does not require addition of reagents. This technique is divided into direct and indirect oxidation. Direct or anodic treatment occurs through adsorption of the contaminants on the anode surface.

UV/H_2O_2 Process*:* The UV/H_2O_2 process is an AOP employing hydrogen peroxide with UV light. Hydrogen peroxide requires activation by an external source such as UV light and the photolysis of hydrogen peroxide generates the effective oxidizing species hydroxyl radical (. OH). Solar light could also be used as a radiation source

but the rate of photolysis may be low compared to UV light. In this process the dosage needs to be optimized, however, since excess H_2O_2 may scavenge hydroxyl radical.

Membrane processes: Membrane processes are applied in water and wastewater treatment to remove organic contaminants. At present, this technology has been investigated for the phenolic compounds removal. Low energy consumption, low operating cost and easy scale up by membrane modules are the main advantages of these technologies. Today, separation membranes have many uses with a growing potential for industrial applications in biotechnology, nanotechnology and purification processes

2.3. Fenton process

Fenton processes are classically reactive systems containing oxidation of tartaric acid into dihydroxy maleic acid by hydrogen peroxide in the presence of ferrous ions, which were discovered by Henery john Horst man in the last century (Fenton, 1894). Mechanisms for this reaction were suggested more than thirty years later, in 1932, in two lines: formation of hydroxyl radicals(·OH) followed by autocatalysis (Equations 2.1,2.2 and 2.3) by Haber and Weiss (1932), while Bray and Gorin (1932) proposed the formation of the ferry ion (FeO_2^{+}) combined with additional equilibrium to explain the presence of Fe^{3+} (Equations 2.4, 2.5 and 2.6). However, these two mechanisms are presented in the literature, the one involving hydroxyl radicals is much more accepted and preferred.

Haber and Weiss mechanism:

$$Fe3+ + O2. \longrightarrow Fe2+ + O2 \qquad (2.1)$$

$$Fe2+ + H2O2 \longrightarrow Fe3+ + OH- + OH* \qquad (2.2)$$

Overall: $$O2. + H2O2 \longrightarrow OH- + .OH + O2 \qquad (2.3)$$

$$OH*2 + H2 \longrightarrow O2 + OH* + H2O \qquad 2.4)$$

$$Fe3+ + H2O2 \longrightarrow Fe2+ + HO2● + H+ \qquad (2.5)$$

Bray and Gorin mechanism:

$$Fe2 + H2O2 \longrightarrow Fe2 + + H2O + O2 \quad (2.6)$$

$$FeO2 * + H2O2 \longrightarrow Fe2 + + H2O + O2 \quad (2.7)$$

$$Fe2 + + FeO2 + 2H + \longrightarrow 2Fe2 + + H2O \quad (2.8)$$

The Fenton-based processes (the Fenton process, in one or another of its modifications) are being increasingly used in the treatment of contaminated water. The reactions produce a range of free radicals, which can react with virtually all organic compounds. Reactions involving the highly reactive hydroxyl radicals are the most important and are characteristic of all advanced oxidation processes. Thus, due to generally accepted the free radicals pathway of reaction the Fenton chemistry belongs to AOP(Kulik et al. 2008). One of the most effective AOPs consists of the use of Fenton's reagent, a combination of H_2O_2 and Fe^{+2}. In this process, H_2O_2 decomposes catalytically by means of Fe^{+2} at acid pH, giving rise to hydroxyl radicals. In this way, producing hydroxyl radicals is simple and effective. It does require neither special apparatus nor reactants. The hydroxyl radical generated by Fenton's reagent is a powerful, non-selective oxidant. This oxidative system has been investigated by a large number of studies due to the fact that iron is a very abundant and non-toxic element and hydrogen peroxide is easy to handle and environmentally friendly. AOPs using the Fenton process have been suggested to be an effective strategy for wastewater treatment. Compared with conventional methods such as adsorption, filtration, and membrane separation, which mostly transfer the pollution from one phase (liquid) to another (solid), however, Fenton process manages to completely destroy organic molecules to CO_2 and water(Wang, 2008). That would become more promising when treating rapidly oxidize phenol over a wide range of concentration, which is comparatively more refractory to natural degradation. Among the advantages of Fenton's process relative to other oxidation, techniques are the simplicity of equipment and the mild operation conditions (atmospheric pressure and room temperature); mainly for these reasons, Fenton's process has been regarded as the most economical alternative(Faisal et al., 2009).

Among various forms of AOPs, there is a group of typical techniques based on the Fenton reaction, including Fenton, Fenton-like, electro-Fenton and photo-Fenton systems. Fenton mainly based on a series of chain reactions between Fe (II)/Fe (III) species and peroxide (H_2O_2) especially at acidic pH value, which is initiated by the reactions showed in Reaction (Eq.2.1) and (Eq.2 4) (Mora, 2010). According to De Laat & Gallard (1999) was investigated the mechanism of H_2O_2 catalytic by Fe (III) at acidic pH (pH<3). And at pH 3 to 7, the iron aqua-complex species changed significantly, which accounts for the coagulation capability of Fenton's reagent. Dissolved suspended solids are captured and precipitated (Neyens & Baeyens, 2003) hence the whole Fenton process is retarded to a large extent. In previous researches, UV-irradiation was introduced into the Fenton process, which is called a photo Fenton system. As shown in equation 2.8 and 2.9 the introduction of light, there is also some supplement to the Fenton mechanism(Wu et al., 1999)

$$Fe3 + (OH)2 + + h\nu \rightarrow .OH + Fe2 + \quad (2.1)$$

$$H2O2 + h\nu \rightarrow 2.OH \quad (2.2)$$

As far as we know homogeneous Fenton and Photo-Fenton systems have been widely examined and demonstrated to be effective in the removal of many kinds of organic chemical, especially many non-biodegradable chemicals in the aqueous phase, soil and sediment. In addition, Fenton process can be used to actual wastewater treatment such as dye wastewater and landfill leachate due to its non-selectivity to organic chemicals(Klauck et al., 2017). The effect of variables such as temperature, pH value, initial concentration, and inorganic ions was also determined in these related researches. The advantages and disadvantages of different homogenous Fenton system are shown in the table 2.3.

Table 2.3. Advantages and disadvantages in different Fenton systems

System	Advantage	Disadvantage
Fenton/Fenton-like	Simplicity: commonly available and inexpensive chemicals, no need for special equipment	Strict pH demand, easy production of iron-containing sludge
Photo-Fenton	Lower chemical dosage demand, faster degradation, inexpensive Equipment	Strict pH demand, the strict wavelength of light usable
Electro-Fenton	Lower chemical dosage demand, faster degradation	Special and quite expensive equipment's demand
Photo-electro-Fenton	Wide application pH value range, Lower chemical dosage demand, high degradation efficiency	Special and quite expensive equipment's demand

When the UV irradiation is introduced into Fenton system, some of the drawbacks could be overcome due to the lower concentration of iron salt needed (Plgnatello, 1992). Compared the degradation of Chlorophenoxy Herbicides in the presence of Fe_{III}/H_2O_2 with and without UV irradiation respectively, and it has been proved that the presence of UV irradiation could obviously enhance the efficiency of Fenton process in Chlorophenoxy herbicides degradation, and hence photo-Fenton is a promising way for wastewater treatment. Some researchers reported the kinetic studies of hydroxyl radical generation promoted by photo Fenton process ($UV/Fe\ (III)/H_2O_2$) at pH ranging from 3 to 8. And it is found that Fe^{2+}plus reacted with hydrogen peroxide under UV irradiation could produce •OH radicals at pH ranging from 3 to 8, and proved that such reactions provide a generally important pathway for oxidation in the environment and possibly for the treatment of contaminated waters (Zepp et al., 1992). Besides, many studies of organic pollutants treatment based on photo-Fenton the process were carried out, and it was practical to apply photo-Fenton system into actual wastewater treatment if the problems such as pH limitation and iron precipitation can be solved.

2.3.1. A general feature of an efficient Fenton catalyst

Considering the wide range of substrates that can be selected as model compounds and the range of reaction conditions it is convenient to describe in this section what would be the most important parameters that should be determined in order to rank different materials according to their activity to promote the Fenton reaction. The most important parameter is catalytic activity and stability of the material. Related to the stability of the solid catalysts and their use as heterogeneous catalysts, absence of leaching of metal species from the solid to the aqueous phase is one key issue since this process can afford a minimum concentration of the metal species in solution that can act as homogeneous catalyst. Therefore, in those cases in where leaching occurs, the overall catalytic activity could be a combination of the activity of the leached species plus the activity of the solid catalyst, and it is necessary to determine the contribution of both processes to the experimental activity. One of the disadvantages of leaching is that it produces depletion of the metal sites in the solid and, at long term, this will cause the loss of solid catalytic activity. Since Fenton requires the use of H_2O_2 for mineralization of the organic compounds, the perfect Fenton catalyst should also be selective in the use of H_2O_2. Therefore, it is always necessary to evaluate the material for the decomposition of H_2O_2. Moreover, generation of free hydroxyl radicals in the presence of the solid catalyst must always be addressed by determining the characteristic products formed by HO. In the ideal case, the consumption of H_2O_2 and phenol should be stoichiometrically related indicating that the consumption of H_2O_2 in spurious processes has been minimized. As commented in the above homogeneous Fenton process is very sensitive to the pH and cannot occur for pH values higher than 4. This is due to the formation of metal hydroxides that can be insoluble and undergo phase separation. In the case of solid catalyst for the Fenton process, tests have to be performed to assess the influence of the pH on the catalytic activity. As a general rule, the target is to develop efficient support solid catalysts for Fenton reaction at optimum pH and at room temperature. The support material that prepared for heterogeneous Fenton catalysts was very sensitive to pH due to iron specification(Navalon et al., 2010).

2.3.2. Homogeneous Fenton Process

In homogeneous Fenton process, Fenton reagents such as H_2O_2 and Fe^{2+} ions are used and only one phase is involved. The source of ·OH production is the externally added Fe^{2+} or Fe^{3+} ions. For instance, it uses iron salts as a catalyst. Moreover, it involves chemical change only and no mass transfer limitation because of its homogeneous catalytic nature. In other words, chemical change wholly relies on the nature of the interaction between Fenton's reagents with target compounds (Mora, 2016). The range of pH for the catalytic activity of homogeneous Fenton and Fenton-like processes is very narrow ranging from 2 to 4 thus strict control of pH is required. Its optimum pH is around 3 but the pH of wastewater in many cases is either neutral or alkali state that at lower pH (pH< 2.5), $[Fe^{2+}(H_2O)]^{2+}$ are formed and it reacts more slowly with H_2O_2. Consequently, less amount of· OH, is produced thus degradation efficiency of phenol reduced. Moreover, H^+ ions will scavenge the ·OH especially at very low pH and reaction between Fe^{3+} ions with H_2O_2 is prohibited. At higher pH (pH> 4), free iron species decrease in solution as the production of ferrous complexes with buffer restraining the production of free radicals and precipitation of ferric oxyhydroxide prohibits the reformation of Fe^{2+} ions. Thus, the decomposition rate decrease. In addition, the increment in pH will decrease the oxidation potential of ·OH. Thus, in order to have an effective Fenton reaction, a large amount of acid addition to the reaction medium is required to maintain pH of solution at 3(Mora, 2016).

In homogeneous process, an extensive amount of ferric hydroxide sludge will be produced (Garrido et al., 2010). During the process, there is an increment in the quantity of Fe^{3+} ions with the reaction time but the generation rate of Fe^{2+} ions is slow. Insoluble complexes are formed because of the increased concentration of Fe^{3+} ions. In addition, there is also an increment in the concentration of hydroxyl ions ($OH^{\cdot}$) with the reaction and lead to the further production of iron sludge as the pH of a solution is increased. The generation of sludge led to the disposal and other environmental problems (Garrido et al., 2010). The downstream treatment is required to increase the pH, thus precipitate and settle the ferric hydroxide. However, there is a difficulty to

separate it due to the colloidal features of the resulting dispersion (Araújo et al., 2011). Last but not least, the catalyst loss in homogeneous process is high as the amount of Fe^{2+} ions spent increases with the increment in the reaction time(Mora, 2016).

The discovery of sustain porous containing materials with degraded different particles create different research opportunities across many fields, such as adsorption, separation, and catalysis. Nevertheless, the homogeneous Fenton process can lead to high iron concentrations in solution (50–80 ppm), clearly above the legal limit imposed by the directives of the European Union (2 ppm). The presence of mesoporosity permits a high metal dispersion and consequently a high catalytic activity, however, these catalysts also present the higher leaching degree and thus the optimization of these parameters is a real challenge. In previous works, it was found that carbon aerogels are interesting materials for these applications, particularly when Fe is the transition metal used as a catalyst(Nawrocki & Kasprzyk-hordern, 2010) and are more promising than modified bentonite prepared from agricultural by-products. However, such pure supports are expensive materials and have to be synthesized under very specific conditions, making the process most likely unfeasible for large scale applications. Several experiments were carried out to differentiate the adsorptive and catalytic behavior, the homogeneous/heterogeneous character of the process and particularly the influence of textural parameters of the materials and their performances.

2.3.3. Heterogeneous Fenton Process

The heterogeneous Fenton's process requires a metal-impregnated solid and, finding new catalysts and evaluating their efficiency have been the objectives of many studies. Hereby, the state of the art of this technique will present information about the evolution of the search for heterogeneous catalysts used in these specific systems(Rossi, 2014). The heterogeneous process involves a solid and liquid phase where the reaction takes place at or near the interface between the phases. The application of heterogeneous catalyst can solve the limitation of the homogeneous process. The catalyst consists of surface $Fe^{2+}$and Fe^{3+}ions which are the source of $\cdot OH$ generation that is different from the homogeneous Fenton process. In this process in

addition to chemical changes, there is physical changes on the surface of the catalyst or at the active sites (mass transfer limited adsorption of reactant molecules occurs). Also play, a major significant role at the end of the reaction, the product molecules are desorbed and leave the active sites making space available for a new set of reactant molecules to attach to the surface and react. The heterogeneous solid catalysts are efficient in wide ranges of pH values as iron species were immobilized" within the structure and in the interlayer of the space. Therefore, OH can be generated from H_2O_2 continuously by the catalyst and the precipitation of iron hydroxide can be avoided (Mora, 2010). The process is able to reduce the formation rate of sludge. A rate of sludge production is affected by the catalyst's metal leaching properties. The production of sludge will increase when there is an increment in leaching rate. In general, there is slighta leaching of metal ions from catalyst which leads to insignificant sludge production(Nidheesh, 2015). No additional sludge treatment is needed for the heterogeneous process as leaching of metal ions from the catalyst is very limited. Furthermore, the amount of iron species is less consumed with compared to the homogeneous process. This is because of the very low leaching properties of the catalyst. After the process, the solid catalyst is easy to be recovered from liquid products.

Heterogeneous Fenton experiments started with a preliminary step without oxidant to separate as far as possible the contribution of adsorption and oxidation to the organic pollutant removal in solution. The oxidation step was then initiated by injection of hydrogen peroxide (H_2O_2). In the case of bentonite supported, iron catalyst the test were conducted without any pH adjustment reading to the conversion of the phenolic compound from aqueous solution as well as to some consumption of H_2O_2 confirming that Fe-bentonite was able to catalyze H_2O_2 decomposition and oxidize these organic compound to carbon dioxide and water (Toulouse, 2016). Heterogeneous Fenton system, can overcome the secondary pollution caused by the iron residue in the homogeneous Fenton system and has thus emerged as a promising technique of AOPs and attracted growing attention in wastewater treatment(Miao et al., 2018). It can be concluded that the heterogeneous Fenton reaction presents an acceptable removal rate of Phenolic pollutants without complicated procedures and several reactors. thus,

keeping it cost-effective and environmentally friendly. The combination of this process with a homogenous process could result in treated water to fit both environmental and economic requirements(Rey & Rodríguez, 2015)

Table 2.4.Comparison of homogenous and heterogeneous catalyzed Fenton under different phenomena (Moreau & Kathi, 2012)

Phenomena	Homogeneous Fenton	Heterogeneous Fenton
Phase	Same phase as the reagents	Involved solid-liquid phase
Mechanism	a chemical reaction is involved Solely in the degradation process	The dual process of physical absorption and desorption in addition to chemical reaction take place.
Catalytic activities	Fast	The reaction rate is enhanced by the application of ultra-violet irradiation source
Active site	Fe_2, Fe_3, Fe-OOH_2, iron complexes ion	dispersed on the surface in the form of iron oxide, iron complexes ion.
pH	Tight acidic pH range for the reaction and need pH adjustment before and after.	Broad pH range
Sludge treatment	The high amount of treated effluent is precipitated as ferric hydroxide sludge when the reaction solution was neutralized in the post-treatment	Minimal ferric hydroxide is formed due to leaching of active components into the bulk solution
Catalyst loss	High catalyst loss after reaction take place, additional recovery separation steps are required for the catalyst after treatment in order to comply with national environmental regulation. consuming and cost ineffective	iron loss is limited because the active phase occurred on the surface of pores solid material. Catalyst recovery Possible, but Easy of recovery and recycling is guaranteed.
Deactivation	Irreversible reaction with products refractory towards certain chemical pollutants slow down the reaction	The leaching of the active site from the support occurred at low pH and subsequently, catalytic activity is lost.

2.4. Factor affecting oxidation reaction in heterogeneous Fenton process

The development of phenol oxidation depends on the operation parameters and the catalyst nature as well. Extensive variations in the reaction conditions may lead to a change in the rate-limiting step due to the competition of the reactants for sites. As a result, heterogeneous catalyst and the reaction conditions along with the functional group in the aromatic ring determine the composition of the oxidation products(Charoenbut et al., 2018). Thus, it is important to evaluate the impact of the reaction conditions on the process and to discuss the actual influence of the reaction conditions to extend the Phenol Oxidation applications. It is generally known that the performance of bentonite supported iron catalyst for the heterogeneous Fenton process using hydrogen peroxide decomposition to generate hydroxyl radical for phenol mineralization mainly depends on the operating conditions. The basic control parameters of this reaction are pH, reaction time, the hydrogen peroxide and catalyst dosages.

2.4.1. The concentration of hydrogen peroxide

The concentration of hydrogen peroxide plays a crucial role in deciding the overall efficiency of the degradation process. Usually, it has been identified that the percent degradation of the organic pollutant increases with an increase in the dosage of hydrogen peroxide(Matavos,.et al, 2017)The phenol removal percentage was enhanced by an increase in the concentration of hydrogen peroxide. The removal of phenol was increased by an increase in the dosage due to more OH· production. However, the progress in the removal of phenol was not notable or even it was decreased with increases in the dosages of hydrogen peroxide. An extra increase in the concentration of hydrogen peroxide affected the reaction of the produced hydroxyl radicals with the additional H_2O_2 molecules to form hydroperoxyl radicals that have a less oxidizing ability. The hydrogen peroxide acts as a free-radical scavenger at high concentrations; so, the percentage removal of phenol decreased at high concentration of hydrogen peroxide. Also, the decomposition of H_2O_2 to water and oxygen and the

reaction of H_2O_2 with hydroxyl radicals instead of pollutant molecules were observed (Chedeville et al., 2005). The unused portion of hydrogen peroxide during the Fenton process contributes to organic pollutant like COD and hence excess amount is not recommended. Another negative effect of hydrogen peroxide is the scavenging of generated hydroxyl radicals, which occurs at large quantities of hydrogen peroxide(Chen et al., 2018). Consequently, the dosage of hydrogen peroxide should be adjusted in such a way that the entire amount was adopted and repeatability studies have to be conducted for finding the actual dosage.

2.4.2. Reaction time and pH

From the practical point of view, pH is one of the most important parameters influencing heterogeneous liquid phase catalytic oxidation of phenol. Phenol, itself is incapable to vary the pH due to relatively weak acidity that confers slight acidic properties to the aqueous solution. According to Guo eta.,2003 most appropriate pH for phenol degradation with hydrogen peroxide is in the acidic media. It can be explained, that at pH values above 4, the rapid H_2O_2 decomposition produces molecular oxygen without the actual formation of hydroxyl radicals. Consequently, the activity of Fenton reagent is reduced at higher pH due to the presence of relatively inactive iron-oxo hydroxides and formation of ferric hydroxide precipitate which decomposes hydrogen peroxide into O_2 and H_2O (Babuponnusami,, 2014). In addition to this high pH favors the formation of carbonate ions, which are effective scavengers of hydroxyl ions and therefore can reduce the efficiency of the overall degradation process. As a result of this, the percentages removal of phenol decreased (Kavitha & Palanivelu, 2005. Below pH 3, more charged ferric ions remained as hydrated ferric ions, which accelerate not only the decomposition of the peroxide but also the competitive reaction leading to hydroxyl radical's depletion and existence of iron complex species $[Fe\ (H2O)^6]^{2+}$. These complex species reacts more slowly with hydrogen peroxide than the other species (Ncibi & Matilainen, 2018)**.** Accordingly, for Fenton process, the most benign pH range is 3–3.5, although some authors have reported a wider 2–4 pH range. This range corresponds to the highest stability zone of $[Fe(OH)]^+$ (Rokhina, 2009). According to Guo and Al–Dahan (2003), it was

concluded that the optimum pH for the maximum reaction rate as well as for the highest degradation of the phenolic compound was at a pH range around 3-3.6, in most cases of the Fenton process. This phenomenon was also influenced by the concentration of ferrous ion present. In addition, the peroxide gets solvated in the presence of a high concentration of H^+ ions to form stable oxonium ion $[H_3O_2]^+$.ox onium ions make hydrogen peroxide more stable and reduce its existence with ferrous ions(Kuan et al., 2015). Therefore, the efficiency of the Fenton process to degrade organic compounds is reduced both at high and low pH. So, an adequate control of pH would increase the process efficiency.

Reaction time is an important factor for better understanding and improvement in the Fenton process. The Fenton reaction has a short reaction time. among all the AOP(Tengrui et al., 2007) The optimum contact time must also be set individually for each specific effluent. As a general rule, the period for the Fenton oxidation process stage is in most cases around 60-90 min(Ruiz, 2015). According to Long., et al., (2007), at some optimal reaction time COD decrease gradually and then increases this is interpreted as the reaction between ferrous ion and hydrogen peroxide with the production of hydroxyl radical was almost complete at an optimal reaction time.

2.4.3. Catalyst dosage

High Catalyst dosage increased the oxidation rate of phenol because catalyst activates the hydrogen peroxide to form hydroxyl radicals. The removal efficiency of phenol was reduced by an extra increase in the concentration of catalyst dosage. The reason is that at high dosage of catalyst, the production of hydroxyl radicals, generally originated from the breakdown of H_2O_2, was so high that many of the hydroxyl radicals were spent through the side reactions before being used for the removal of phenol (Shokri & Aref, 2018) The amount of the catalyst substantially affects the reaction rate. Increase in catalyst concentration accelerates the decomposition of hydrogen peroxide. However, too high amount of the catalyst catalyzes the surface chemical reaction so rapidly that reactants become depleted in the liquid phase and thus, the diffusion of reactants, controls the rate of the reaction (Bravo et al., 2013).

Moreover, an increased amount of active sites in concurrence with an increase in catalyst mass can also lead to the re-adsorption of products to active sites. Phenol oxidation with a bentonite support iron catalyst by H_2O_2 found an increase in the reaction rate when the catalyst concentration was increased, but only up to a certain load after which it becomes less efficient(Madeira, n.d.). This indicates that after a certain point the catalyst load has a detrimental effect on the performance (mineralization degree in this case), which can be explained by the formation of iron complexes (iron + organics) when excess amounts of catalyst are present. According to (Gil et al., 2010) the range of iron support catalyst concentrations was between 1 and 2 g/L for the heterogeneous Fenton process for the degradation of a phenolic pollutant that contained 1000mg/L concentration of phenol synthetic solution. In the most cases, the optimum concentration of iron support catalyst for the removal of TOC and for the highest percentage removal efficiency of phenol was around 1.5 g/L (Djeffal et al., 2014). Generally, the catalyst dosage should be optimized for more economic advantages.

2.4.4. Health effects and safety factors

The major hazard of phenol is its ability to penetrate the skin rapidly, causing severe burns. Toxic and even fatal amount of phenol can be absorbed through a relatively small area of skin. Due to its local anesthetizing properties, skin burns may be painless. Phenol may be fatal if swallowed, inhaled or absorbed through the skin. Care should be exercised not to walk in spills since phenol can penetrate the leather. According to the National Institute for Occupational Safety and Health (NIOSH), exposure to phenol should be controlled so that no employees are exposed to phenol concentrations > 20 mg/m^3, which is a time weighted average concentration for up to a 10-hr work day, 40-hr work week. Phenol is very toxic to fish and has a nearly unique property of tainting the taste of fish if present in marine environments at 0.1-1.0 ppm (Verschueren, 1977). Phenol presents no unusual fire hazard when handled at ambient temperatures but burns if ignited. The lower flammability limit for the vapor is 1.5 % in air. Phenol produces flammable, toxic vapors at elevated temperatures and has a flash point of 85℃ (open cup). Phenol is a general

protoplasmic poison that is corrosive to any living tissue it contacts. It is a local anesthetic, so that upon initial contact to the skin no pain is felt. By the time pain is felt, serious burns and absorption through skin may occur. Skin absorption occurs readily with a rapid onset of symptoms or death. Contact with eyes may cause severe damage and blindness. Upon contact with phenol, the skin should be washed with water, then washed with poly ethylene glycol of molecular weight 300 for at least 30 minutes. Eyes should be washed with flowing water for 10 minutes. Treatment for inhalation begins with the removal of the exposed person to fresh air and provision of breathing support if needed(Stern et al., 2014). Personnel who handle phenol should wear protective clothing, safety goggles, and rubber gloves, depending on the working conditions and amount of phenol handled. This toxic organic pollutant also affects the internal organ of human beings associated to cardiovascular disease, serious gastrointestinal damage, severe skin damage, and muscle twitching, due to these effects the US environmental protection agency (EPA) to be considered as priority organic pollutants.

2.5.Bentonite

Bentonite is an aluminum phyllosilicate clay minerals(Vessal, 2017) consisting mostly of smectite (montmorillonite) groups and has a wide range of industrial applications including clarification of edible and mineral oils, paints, cosmetics and pharmaceuticals(Vimonses et al., 2009). The abundance of bentonite in most continents of the world and its low cost make it a strong candidate as an adsorbent for the removal of many organic pollutants from wastewater (Kuma, 2010). In recent years, there has been increasing interest in utilizing natural clay minerals. Depending on the nature of the formation, bentonite can have a variety of accessory minerals in addition to its constituent mineral montmorillonite. These minerals may include attapulgite, kaolinite, mica, and illite as well as minerals like quartz, feldspar, and calcite for the removal of toxic metals and some organic pollutants from aqueous solutions(Banat et al., 2000). These are removal technologies available for the treatment of phenol-containing wastewater, adsorption is widely explored by researchers.

Activated carbons are among the most effective adsorbents, having high surface area per unit mass. It shows high adsorption capacity for phenolic compounds and is also preferential adsorbent for the removal of other types of organic compound (Gao et al., 2016). According to Banat et al.;2000 the adsorption of phenolic compounds on to activated carbon is abundant and due to the relatively high cost of activated carbons, there have been attempts to utilize low cost, naturally occurring adsorbents to remove trace organic and inorganic contaminants from wastewaters. Therefore, the economic and cost-effective catalyst needs to be developed for the elimination of organic pollutant like phenols. Among various adsorbents bentonite possess excellent adsorption capacities and sorption/exchange sites available within its interlayer space as well as on the outside surfaces, for these reasons, bentonite is the most effective support catalyst used in the removal of phenols from a solution. Furthermore, all synthetic composites of bentonite improved catalytic property, which resulted in a higher bentonite support iron catalytic performance compared to pure catalysts as single phases (Liu et al., 2015). Among the intercalated clay precursors indicated above, Fe^{3+} is an ongoing one for research in heterogeneous catalysis and adsorption, being of particular relevance in Fenton-based processes which make use of Fe species as a catalyst(Vedrenne et al., 2012). Bentonite support iron catalysts have been suggested as an effective and affordable, due to the low initial cost, flexibility, simplicity, and ease of operation. In this research, bentonite was modified by iron species (denoted as Fe/bent) to increase the catalytic performance for removal of phenols from a synthetic solution(Gao et al., 2016).

2.5.1. Preparation of support catalysts

The bentonite support iron catalysts(Fe/bent) was synthesized through impregnation constant weight of iron and different weight of bentonite means iron to bentonite ratio (1:5, 1:10, 1:20 and 1:30) to 500mL of H_2O under stirring for 1.5h at 400rpm at room temperature(Tomul & Fatma, 2016). A 500mL 0.2M solution of ferrous sulfate heptahydrate($FeSO_4.7H_2O$, analytical grade) was added into the dispersion of clay under vigorous stirring on a magnetic stirrer up to 6 hr at the same speed (Xu et al., 2009). The suspension was filtered, washed with 1% $NaHCO_3$ and soaked in 1%

$NaHCO_3$ solution overnight. Later, the suspension was decanted, washed with distilled water again and again and filtered until the filtrate was free from the ion. Finally, the solid residue was air dried for 2 h and then kept in an oven at 105°C up to 12h for complete drying (Shah *et al.*, 2015) Finally, the iron-loaded clay based catalyst was obtained. The solid was ground with pestle and mortar to afford the iron support bentonite clay catalyst as a fine powder.

According to (Kavitha,.etal, 2005), the solid obtained from the filtration and neutralization was dried before calcination at a temperature between 350 to 600°C for 2h under air flow(Petr et al., 2013). Dehydration and dehydroxylation occur upon calcination to give metal oxide clusters which act as bentonite support iron catalysts (Fe/bentonite) was obtained (Khelifi, 2016). The materials produced by these steps are referred to as iron support bentonite catalyst (Fe/Bentonite) (Tabet et al. 2006). The Fe-Bentonite catalyst was normally characterized by X-ray diffraction (XRD), Atomic absorption spectroscopy (AAS), and Fourier transforms infrared spectroscopy (FTIR). The effects of Fe-B catalyst dosage, hydrogen peroxide, and reaction time and pH on the decomposition and mineralization of phenols needs to be investigated in detail. The kinetics and reaction activation energy of phenol removal are critical to studied (Feng et al., 2005).

2.6.Assay for phenol mineralization

The development of heterogeneous Fenton process is mineralization reaction, the quality of treated wastewater could be measured by total phenol concentration using UV-Vis spectrophotometry and TOC reduction employed to know the percentage of mineralized phenol.

2.7.Determination total phenol content

The concentration of the phenolic compound in synthetic wastewater was analyzed by spectrophotometric method, this instrument used extensively for qualitative and quantitative analysis in different fields including environmental control and water management. Spectrophotometric manual 4-AAP is applicable to the analysis of water

characteristics, which is a photometric test method, based on the reaction of steam-distillable phenolic compounds with 4-amino antipyrine at a pH of 10.0 ± 0.2 in the presence of $K_3Fe\ (CN)_{6?}$ The antipyrine color formed in an aqueous solution was measured at 510 nm. By using the wavelength obtained, the final concentration of phenols could be determined. The concentration of phenolic compounds in the sample was expressed in terms of milligrams per liter of phenol (C_6H_5OH). Method 420 (Appendix B) is used to determine the amount of total phenol in synthetic water after treatment.

2.7.1. Determination of total organic carbon (TOC)

Measurement of TOC is the best method to determine the organic matter content in water and wastewater, which directly measures the total organic compound in the wastewater. The sum parameter TOC is one of the most important parameters used in any environmental applications. TOC analysis is therefore carried out in a wide variety of environment matrices from groundwater to seawater, from drinking water to wastewater, from soils to sewage sludge. One of the most important factors for a TOC analyzer is the ability to oxidize organic carbon (METH011.00, 2013). The Shimadzu total organic carbon analyzer in combination with the ASIV automated sampler was used to measure TOC in water samples.

3. Materials and Methods

The major raw bentonite used in this study was collected from the ministry of mines and biofuels organization which was delivered from Afar Region (Gawain area) in the northeastern part of Ethiopia whose basic clay mineral is calcium bentonite was used as iron support catalyst for the heterogeneous Fenton experiments**.** Preparation of bentonite support iron catalyst, size reduction, washing, calcination, and characterization of the catalyst such as zero-point charge, bulk density, the activity of the catalyst heterogeneous Fenton oxidation reaction were carried out at the School of Chemical and Bio Engineering Laboratory, AAU. Other characterizations were carried out Leather industry development institute (FTIR), Faculty of Natural Science Chemistry department at kilo (XRD), Geological Survey of Ethiopia (AAS), Addis Ababa Environmental Protection Authority (TOC analysis). All chemicals used for this study were bought from different chemical companies in Addis Ababa, Ethiopia.

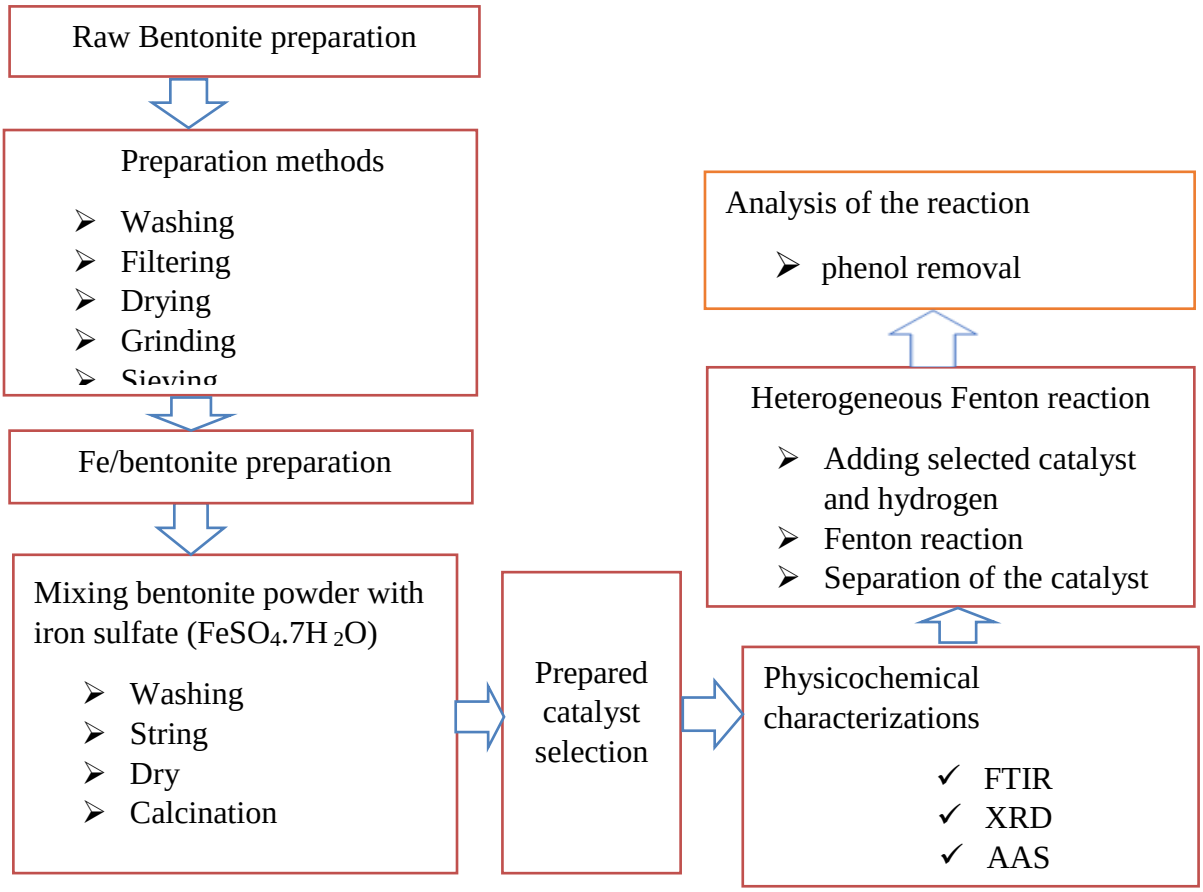


Figure 3.1. The overall structure of the experimental framework

3.1. Sample Collection and pretreatment of raw Bentonite

3.1.1. Materials and equipment

In this study raw bentonite was used as raw material and the main equipment used for sample preparation were jaw crusher, attrition mill, mortar and pestle, rotary sieve machine analytical balance, sieve shaker, drying oven, plastic bags and distilled water.

3.1.2. Methods

Raw Bentonite has been used as support iron catalysts for this study. Raw Bentonite has collected from Ethiopian Mineral, Petroleum and Biofuel Corporation. This bentonite originally comes from Afar region Gawain. The sample was crushed, milled, screened, and wash with distilled water and dried at 105℃ for 12hr to remove moisture and volatile organics from the clay. Then the dried raw bentonite was milled again using attrition mill and further size reduced using mortar and pestle. The powdered raw bentonite was sieved and the particle size between 74μm (200 mesh) to 150μm (100 mesh) was retained, Previous studies by (Miao et al., 2018) concluded that smaller particles of medium were more effective than larger ones because of greater available surface area and consequently high adsorption capacity. After that, the powdered bentonite was weighed and preserved in an airtight plastic bag for the next step and stored at room temperature.

3.1.3. Synthesis and characterization of support catalyst

3.1.3.1. Materials and equipment

The material and equipment used for synthesis of support catalyst were analytical balance, spatulas, stirring rods, mechanical and magnetic stirrer, different size sieve, desiccator used to store samples in a moisture-free environment, oven, Jenway model 3505 digital pH meter, thermometer, Aluminum foil, hotplate magnetic stirrer, glass test tubes, plastic bags, vacuum pump, filter paper, funnel, Goggles for eyes protection, protective gloves for hand, , Iron (II) sulfate

3.1.3.2. Methods

Bentonite was prepared for the purpose of heterogeneous Fenton process. Even though the final objectives were to optimize the phenol mineralization using the different configurations of bentonite support iron catalysts, the performance of the material was determined and the reaction was carried out in a batch reactor.

The bentonite support iron catalysts(Fe/bent) was synthesized through an impregnation at constant iron and a different ratio of bentonite(1:5,1:10,1:20 and 1:30)wt% to 500mL of distilled water under stirring for 4h at 400rpm at room temperature. A 500mL equal solution of ferrous sulfate heptahydrate($FeSO_4.7H_2O$, analytical grade) was added into the dispersion of clay under vigorous stirring on a magnetic stirrer up to 4h at the same speed(Xu et al., 2009). The suspension was filtered, washed with 1% $NaHCO_3$ and soaked in 1% $NaHCO_3$ solution overnight. Later, the suspension was decanted, washed with distilled water again and again and filtered, the mixture was filtered until the filtrate was free from ion and the pH was adjusted by 0.1 M of NaOH and HCl. Finally, the solid residue was air dried for 2 h and then kept in an oven at 105°C up to 12h for complete drying(Shah et al., 2015). Finally, the iron-loaded clay based catalyst was obtained and denoted as Fe/1:5 wt%, Fe/1:10 wt% Fe/1:20 wt% and Fe/1:30 wt%). The solid was ground to attain the iron support bentonite catalyst at particle size between 75-100 μm (fine powder). Then the sample was stored at room temperature for further use.

3.1.4. Calcination of support catalyst

3.1.4.1 Material and equipment

Equipment used for calcination of support catalyst were furnace, desiccator crucibles, plastic bags.

3.1.4.2. Methods

The bentonite support iron catalyst was thermally treated to enhance the specific surface area and increase its catalytic capacity. The preparation of thermal activated

bentonite support iron catalysts was calcinated in the furnace. The thermal activation of bentonite support iron catalysts was performed at a temperature of 400,500 and 600°C for 2 h. For the thermal activation 50g of 1:5wt% bentonite support iron catalysts were taken on a crucible and placed in the furnace. The temperature of the furnace was set at 400°C. The temperature was allowed to rise steadily to the desired temperature after 15 min. After the desired temperature was reached, the sample was maintained at the set temperature and was calcined for 2h. as calcination completed, the samples were taken out of the furnace and cooled in the desiccator for 30 min. Similar experiments were carried out at 500°C, 600°C for 50 g of bentonite support iron catalyst(1:10 wt%, 1:20 wt% and 1:30 wt%) of 2h. According to (Khelifi, 2016)dehydration and dehydroxylation occur during calcination to give metal oxide clusters which act as bentonite support iron catalysts (Fe/bent). The materials produced by these steps were referred to as bentonite support iron catalysts(Fe/Bent) (Tomul & Fatma, 2016).

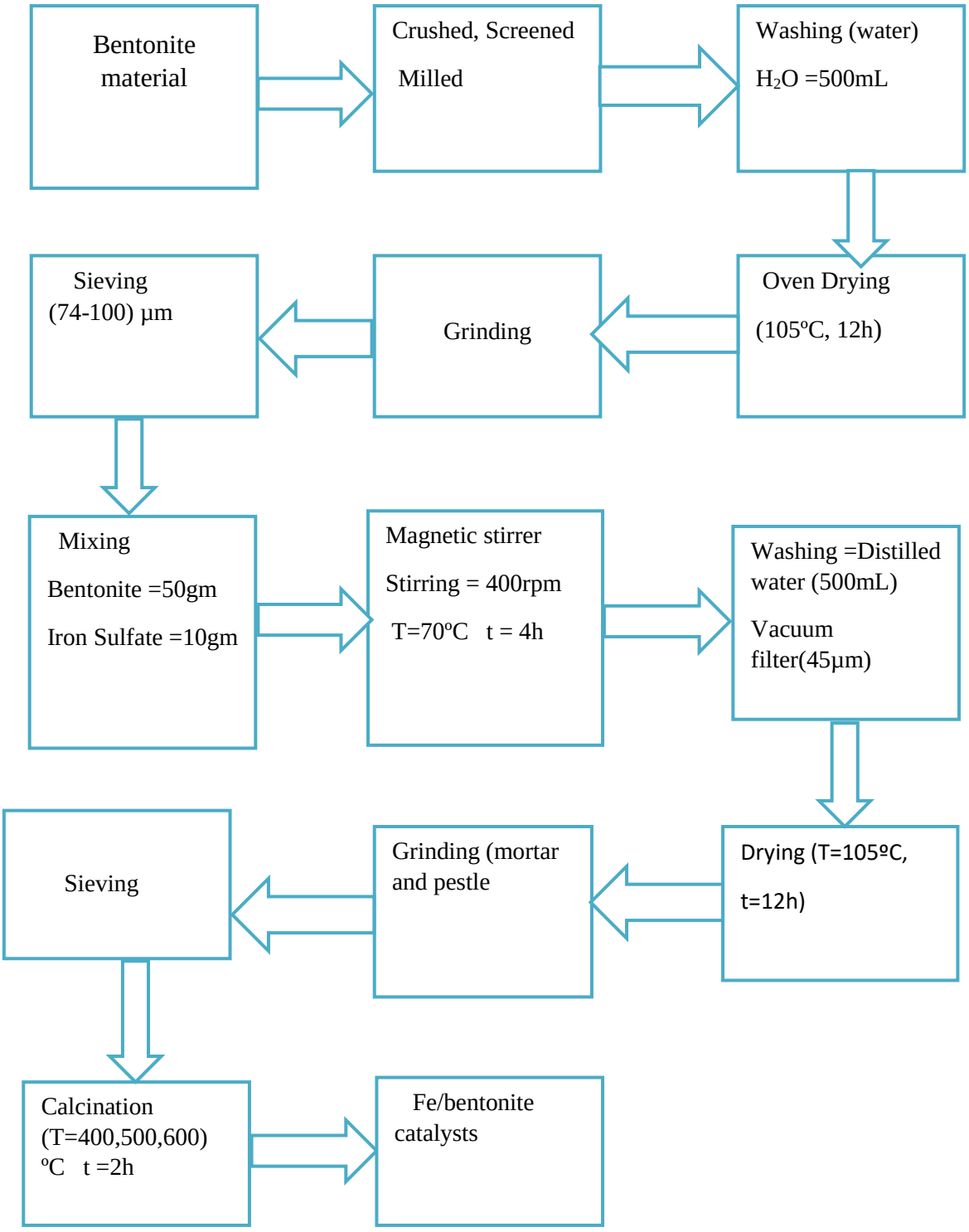


Figure 3.2. Schematic block flow diagram for the preparation of bentonite clay

3.1.5. Selection of optimum mixing ratio of iron to bentonite and calcination temperature

The optimum mixing ratio and optimum calcination temperature were determined based on the removal efficiency of phenol after heterogeneous Fenton process. The thermal activation of each catalyst composition was carried out at 400,500 and 600°C. The best optimum catalyst ratio and calcination temperature were chosen based on the D-optimal experimental design that was applied to obtain the regression model which were subsequently used for attaining the optimum process conditions.

Table 3. 1. D-Optimal design experimental for selection of mixing ratio and calcination temperature

Std	Run	Block	Factor 1 A-Temperature °C	Factor -2 B-catalyst Ratio(%wt.)
2	1	Block 1	500.00	0.20
10	2	Block 1	400.00	0.03
12	3	Block 1	600.00	0.03
4	4	Block 1	400.00	0.10
3	5	Block 1	600.00	0.20
6	6	Block 1	600.00	0.10
7	7	Block 1	400.00	0.05
11	8	Block 1	500.00	0.03
9	9	Block 1	600.00	0.05
5	10	Block 1	500.00	0.10
1	11	Block 1	400.00	0.20
8	12	Block 1	500.00	0.05

3.1.6. Determination of the Most Active Catalyst for Phenol Oxidation

3.1.6.1. Materials and equipment

Material used for determine most active catalyst were magnetic stirrer, different size volumetric glass flasks, Jenway model 3505 digital pH meter, stirring rods, UV-spectrophotometer(UVD-3000/3200), centrifuge, cuvettes for spectrophotometer, synthetic phenol solution, 4-amino antipyrine, ferric cyanide, sodium hydroxide, hydrochloric acid and distilled water

3.1.6.2 Methods

Four Bentonite support iron catalysts (Fe/bent) were prepared and were carried out at the same reaction condition out at the same reaction conditions, for each of the four experiments to determine the most active catalyst. This was based on the phenol oxidation capacity and total organic carbon reduction capacity from the solution. The reaction was carried out as follows.250mg/L of the synthetic water containing phenol solution and 1.5g/L from each ratio of bentonite support iron catalyst powder were loaded in the 500 mL flask. They were subjected to vigorous stirring on a magnetic stirrer at 300 rpm and the temperature was set at 25°C. The operating parameters for all the experiments were pH (3.2) synthetic phenol solution of (250mg/L) and reaction time of (1.5h). The mixture was stirred vigorously, slurrying the catalyst uniformly throughout the solution. After the completion of the reaction, the samples were drawn periodically from each run and the catalysts were separated from the aqueous phase by centrifugal forcing at 3000 rpm(Katzer, 2005). Finally, the treated sample was analyzed by UV-spectrophotometer for the conversion of phenol (proportion of phenol eliminated) and the reduction of total organic carbon was analyzed by the TOC analyzer with an infrared detector.

3.1.7. Characterization of bentonite support iron catalyst

3.1.7.1. Determination of pH at the point of zero charges (pHpzc)

Material and equipment

Material and equipment used for determination of pH at the point of zero charge were 0.5 g of the prepared catalyst, NaCl solution, conical flasks, mechanical shaker, 0.1 NaOH or 0.1 HCl using Jenway 350 pH meter.

Methods

The point of zero charges (pHzpc) of the catalyst is an important parameter to determine the pH at which the surface has net electrical neutrality and surface charge plays a main role in the adsorption of ionizable pollutants into catalyst from aqueous solutions. The point of zero surface charge characteristics of the raw and prepared catalyst was determined using the pH solid method (Ajemba, 2016). 40 mL of 0.1 M NaCl solution was transferred to a series of 250mL stoppered conical flasks. The pH_i values of the solutions were then adjusted to between 2 and 10 by adding 0.1 NaOH or 0.1 HCl using Jenway 350 pH meter. The total volume of the solution in each flask was adjusted to exactly 50mL by adding NaCl solution of the same strength. The pH_i of the solution was accurately measured then 0.5 g of the prepared catalyst was added in turn to each flask and the flask was securely capped immediately. The suspensions were then kept in a mechanical shaker for 24 h at room temperature. The final pH values(pHf) of the supernatant liquids were noted. The difference between the initial and final pH (pHf) values (ΔpH) was plotted against the pH_i.The point of intersection of the resulting curve with the pH_i axis, i.e. at $\Delta pH = 0$, gave the pHpzc.

3.1.7.2. Determination of bulk density.

Material and equipment

Bentonite powder, prepared catalyst, measuring cylinder, measuring balance, plastic tapping stick, paper, pen.

Methods

The density of the prepared raw bentonite powder and Fe/bent was obtained by weight the prepared materials and transferring it to a 10 mL graduated cylinder. The sample was compacted by tapping on the bench top until the mass (g) occupied the volume (V). The cylinder was tapped on the bench until the volume of the sample stopped decreasing. The cylinder was tamped with a rubber pad while the bentonite powder and Fe/bent catalysts were being added until the entire original sample was transferred to the cylinder. Tamping was continued for 5 min until there was no further settling p. The volume was recorded and the bulk density was calculated on a dry basis. Bulk density is the mass per volume ratio that includes the cavities in a porous material. Density can indicate a change in the composition of a material, or a defect in a product, such as a crack or a bubble in the voids.

3.1.7.3. Characterization of bentonite support iron catalyst

The essential purpose of catalyst characterization is to comprehend the relationship among physical, chemical and catalytic properties. Several types of characterization techniques are employed to identify the physical and chemical properties of catalyst and relate these to its activity. The developed solid structures of Fe/bent were characterized by Atomic absorption spectroscopy (AAS), X-Ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.

3.1.7.4. Fourier transforms infrared (FTIR) spectroscopy.

Materials and equipment

Raw bentonite and bentonite support iron catalyst**,** 65 FT-IR (Perkin Elmer), sample holder. polyethylene bag, pen and paper.

Methods

FTIR spectroscopy is a powerful tool to identify characteristic functional groups as well as the coordination between active functional groups by producing an infrared absorption spectrum. In this study, the functional group of raw bentonite powder and prepared catalyst were characterized by using 65 FT-IR (Perkin Elmer) machine with samples prepared by the conventional KBr disc method. FTIR shows the presence of quartz, montmorillonite, alumina, hematite, and other mineral matters present in the sample. The spectral data were collected in the IR wavelength of 400 to 4000 cm^{-1}. Solid samples were milled together with potassium bromide to form a very fine powder which was then uniaxially compressed into a thin pellet which can be further analyzed.

3.1.7.5. X-Ray diffraction (XRD)

X-ray diffraction is most widely used for the identification of unknown crystal structure of the materials. In this study, the crystallography of both raw bentonite and prepared Fe/bent catalyst were characterized by using Miniflex 300/600 +, 150 (Rigaka) X-ray diffraction instrument. X-ray diffraction (XRD) patterns were recorded with D8 Avance XRD of Brucker powder diffractometer with Cu-Kα (λ=1.540593-1.544414 Å, 40 KV, and 15 mA) radiation having a continuous scanning mode with speed of 12deg/min. X-ray diffractograms of raw bentonite powder and prepared Fe/bent catalyst were obtained for the 2θ angles ranging from 10^0 to 70^0 with scan step 0.02^0. XRD was used to determine the mineralogical composition of the raw and Fe/bent. In addition to this, XRD provides details about the crystalline structure of matter on an atomic scale. Thus, the established relationships between the crystals structure, the physical and chemical properties of the material under investigation (bentonite clay).

3.1.7.6. Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy is the qualitative and quantitative determination of chemical elements that present in different samples using the absorption of optical radiation (light) by wet free atoms in the gaseous state. AAS is based on the absorption of light by free metallic ions. In this study, the chemical composition of raw and activated bentonite was analyzed using Atomic Absorption Spectrometer at the Geological Survey of Ethiopia. Nitric acid (HNO_3) was added to the samples for two purposes, during sample collection, the pH was reduced less than 2. Since precipitation, adsorption to container wall and microbial degradation are minimized at pH<2. Though any acid will serve this purpose, HNO_3 is preferred because of its oxidizing nature (is the most widely used primary oxidant for the decomposition of organic matter). Adding HNO3 converts metal ions into their nitrate salts, which are highly soluble. Secondly, sample digestion was required before AAS analysis in order to get accurate results. The purpose is to destroy the matrix, which otherwise interferes during atomization.

3.2. Initial Performance analysis of the catalysts.

3.2.1. Materials and equipment

Material used for determine most active catalyst were magnetic stirrer, different size volumetric glass flasks, Jenway model 3505 digital pH meter, stirring rods, UV-spectrophotometer(UVD-3000/3200), centrifuge, cuvettes for spectrophotometer, synthetic phenol solution, 4-amino antipyrine, ferric cyanide, sodium hydroxide, hydrochloric acid and distilled water

3.2.2. Methods

Before carrying out the phenol oxidation, phenol adsorption tests were carried out in order to differentiate adsorption from the Fenton oxidation reaction. The adsorption test was carried out by adding the bentonite powder and the Fe/bent catalysts (without hydrogen peroxide addition) in synthetic phenol solution and subjecting it to shaking for 3h. The adsorbed TOC (%) after 3 h was then measured using TOC analyzer.

3.2.3. Experimental setup for heterogenous experiments

Material and equipment

Phenol (purity over 99%), prepared support catalysts, 0.1MNaOH and 0.1MHCl (for pH adjustment), Hydrogen peroxide and distilled water.

Methods

An experimental study was developed to obtain the maximum TOC and phenol removal at optimum experimental parameters selected as shown on the following table (3.2) Phenol (purity over 99%), prepared support catalysts, 0.1MNaOH and 0.1MHCl (for pH adjustment) of analytical grade chemicals used via purchasing from different companies. Synthetic phenol solution was prepared with 800 mg/L phenol concentration in distilled water.

Table 3. 2.Selected experimental parameters

Parameter	Values
Time (min)	60, 90 and 120
Hydrogen peroxide concentrations (mg/L)	2000, 4000 and 6000
Catalyst dosage (mg/L)	1000, 1500 and 2000
pH	3, 3.5 and 4

3.3. Catalytic oxidation of phenol using a prepared catalyst

Material and equipment

Materials and equipment used for catalyst oxidation of phenol were MSH-D hotplate magnetic stirrer, magnetic road cuvettes for spectrophotometer, synthetic phenol solution, Hydrogen peroxide, bentonite supportive iron catalyst, NaOH, HCl, 4-amino antipyrine, ferric cyanide.

Methods

In the heterogeneous Fenton study, the effects of the peroxide (H_2O_2) concentration, reaction time, catalyst dosage and pH were analyzed. Heterogeneous Fenton experiments were carried out at the initial phenol concentration of 800 mg/L, Hydrogen peroxide (H_2O_2) concentration range between 2000,4000 and 6000 mg/L, the reaction time of 60, 90 and 120 min, catalyst dosage ranging between 1000, 1500 and 2000 mg/L and pH of 3,3.5 and 4. During the experiments, the volume of the synthetic phenol solution was to be taken as 250 mL. Figure 3.2 shows the schematic representation of the heterogeneous Fenton oxidation experimental procedure. The heterogeneous Fenton experiments were carried out by the addition of bentonite supportive iron catalyst (Fe/bent) and hydrogen peroxide to synthetic phenol solution after it adjusting the pH of the solution, using an MSH-D hotplate magnetic stirrer equipped with a magnetic road for determining the reaction time and the temperature was adjusted controlling manually at 25 ℃. At the end of the run, the solution was neutralized by addition of 0.1NaOH and HCl, the solution was then poured into the settling tank to separate the settled Fe/bent catalyst from the treated phenol solution. Unreacted phenol concentration was determined using spectrophotometer at 510nm by using (Method420 Phenolics, Manual 4-AAP With Distillation)

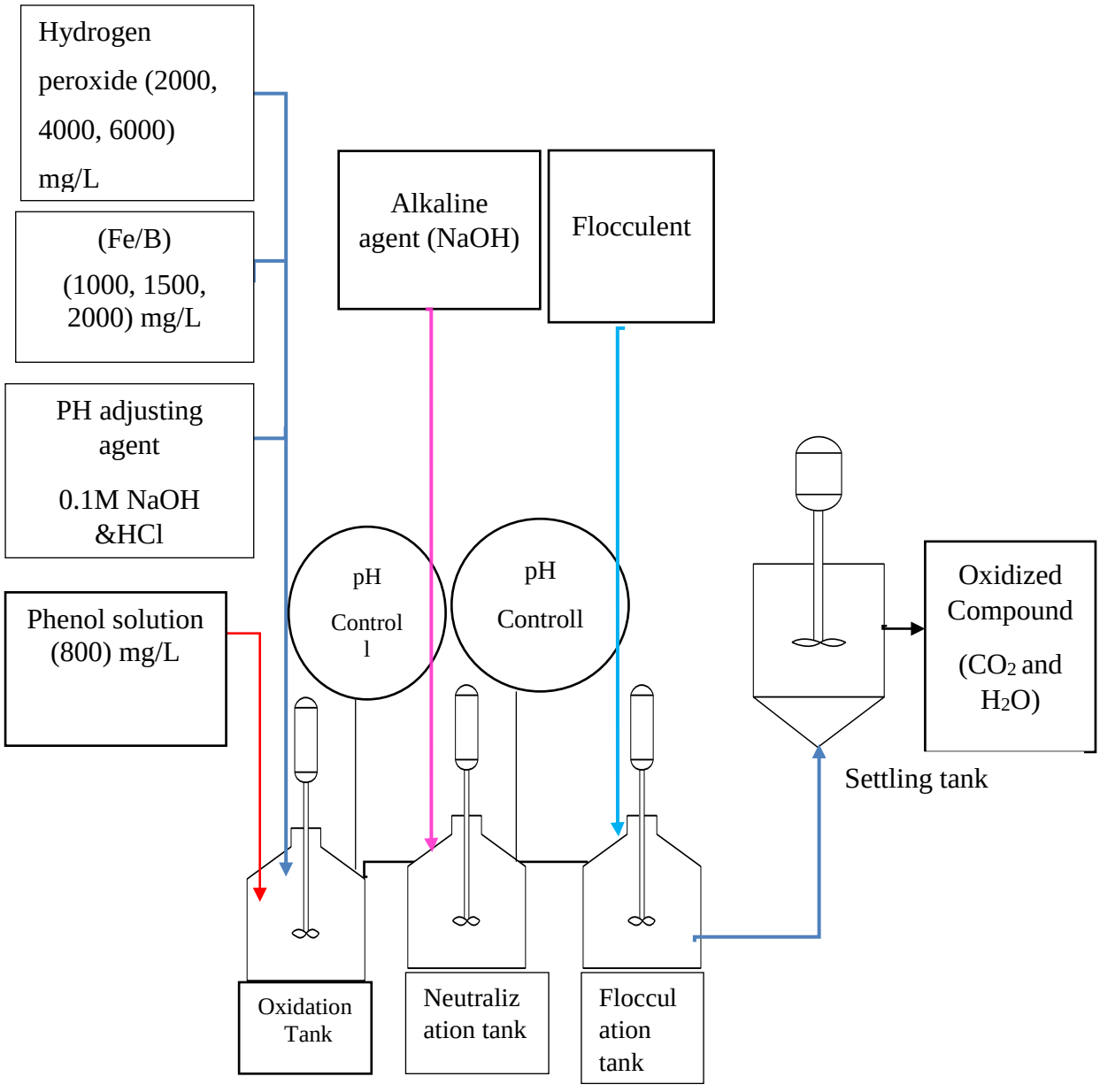


Figure 3.3. The Schematic diagram of heterogeneous Fenton oxidation experiment

3.3.1. Performance analysis of the Heterogeneous Fenton oxidation

The treated synthetic phenol solution was analyzed for the percentage removal of phenol and the mineralization capacity was determined using the total organic carbon (TOC) analyzer.

3.3.2. Total Phenol content determination and TOC analyzer

One of the best parameters to assess the catalysts performances in the Fenton's oxidation was the phenolic content removal and the reduction of total organic carbon. The concentration of phenolic compounds in synthetic phenol solution was determined by spectrophotometric method, with 4-amino antipyrine at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide ($K_3Fe(CN)_6$). By using methods 420, 2mL of 4-amino antipyrine and 2mL potassium ferricyanide were added in the phenol solution and mixed well. After the reaction, the antipyrine red color formed in an aqueous solution was measured at 510 nm. The concentration of phenolic compounds in the sample was expressed in terms of milligrams per liter of synthetic phenol solution (C_6H_5OH).

3.3.2.1. Preparation of Standard Calibration curve for phenols

A series of 100 mL phenol standards containing 0, 4, 8, 12, 16 and 20 mL of intermediate phenol solution (1 mL = 1 mg phenol) were prepared in distilled water. Then 4-amino antipyrine and potassium ferricyanide in a basic condition was added to each sample. After 15 min reaction time, the absorbance of each standard was measured at 510 nm against the reagent blank as zero absorbance. Finally, the phenol concentration was plotted against absorbance and the calibration was fitted in a linear correlation. Based calibration curves the unknown phenol concentration was determined. The full UV spectrum of standard phenol solution shown in fig 3.4.

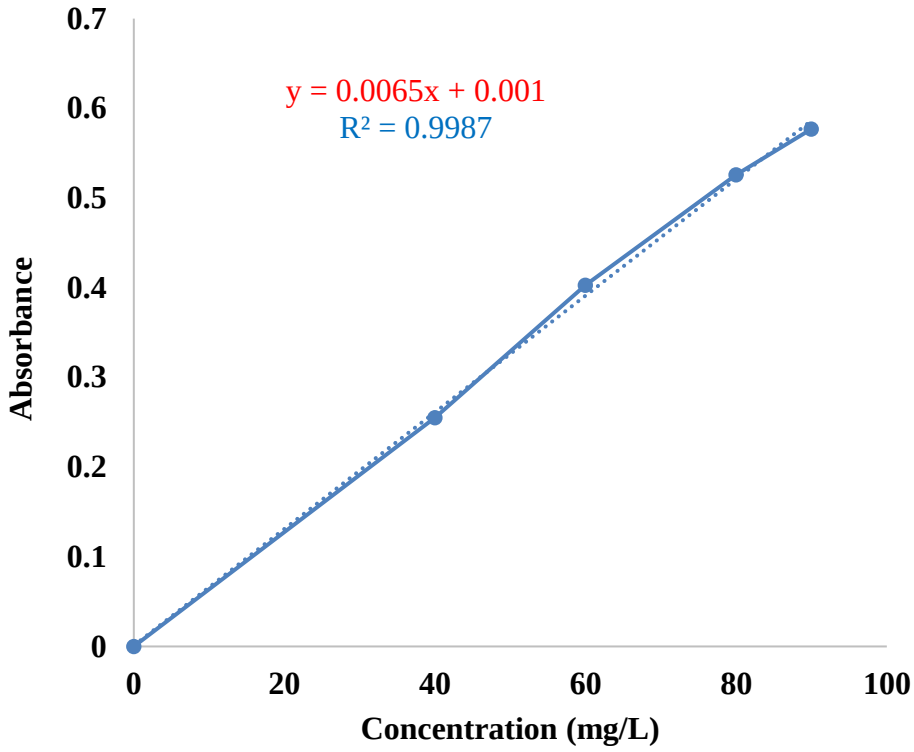


Figure 3.4. Calibration curve of phenol

3.4. Experimental design

The experiments were designed to determine the four most important factors that were considered during the experimental design. They are; time(min), peroxide concentration(mg/L), catalyst dosage(mg/L) and pH at 3 levels which were -1, 0, 1 are known as response function. So as to determine the effect of these all parameter on the removal of phenols and reduction of total organic carbon from synthetic phenol solution as well as to optimize all the affecting parameters collectively by statistical experimental design Thus, a suitable experimental design to analyze multiple factors is required. In an experimental design, once the region of optimal response is detected by preliminary studies, it is often required to characterize the response. Box Behnken design and central composite design (CCD) is mainly used in experiments for response

surface methodology to approximate a second order polynomial estimation to a response. Response surface methodology is one of the powerful statistical experimental design techniques that is applied to build models and investigate individual and interaction effects of the selected operating condition on the given response in a given experiment (Gunst et al., 2006).

The response surface method (RSM) was applied to evaluate the effects of reaction parameters and optimize conditions for various responses. Three level factorial design with four numeric factors with five center points was used the optimum reaction conditions were determined percentage removal of phenol. Treatment of responses and selection of optimal conditions were based on the desirability function. The experimental design and multiple linear regression analysis were performed using design expert 7.0. Box-Behnken design is a three-level fractional factorial design built by Box and Behnken (1960). Box-Behnken Design (BBD), which require fewer runs than the other RSM designs, was the selected experimental design used to determine the optimal response of phenol adsorption by this bio sorbent. The Box Behnken design is based on the construction of balanced incomplete block designs and requires at least three levels for each factor(Tekindal et al., 2012). BBD can provide a maximum amount of complex information with minimum experimental time. Moreover, Box–Behnken design allows calculations of the response function at intermediate levels and enables estimation of the system performance at any experimental point within the range studied through careful design and analysis of experiments(Rietjens et al., 2016). The response variable was fitted to the following second-order polynomial model (Equation (2)) which is generally able to describe the relationship between the responses and the independent variables.

$$Y = Bo + \sum_{i=1}^{k} Bii\,Xi + \sum_{i=1}^{k} Biixi2 + \sum_{i=j}^{k} BijXixj \qquad (2)$$

where Y is the predicted response, B_0 the offset term, Bi the linear effect, Bii the square effect, and Bij the interaction effect. This design consisted of fifteen randomized runs with three replicates at the central point to minimize the error. Each

variable was studied over three levels: low, middle and high. The level of each variable was selected based on the preliminary experiment-trials, and also on the available literature.

Table 3.3. The level variable selected for the trials

Variable	Range		
	low	Middle	High
Concentration of hydrogen	2000	4000	6000
Dosage of catalyst(mg/L)	1000	1500	2000
Reaction time(min)	60	90	120
pH	3	3.5	4

3.5.Reusability of the catalysts

The Reusability of bentonite support iron catalyst (Fe/bent) for the degradation of phenols by heterogeneous Fenton process with H_2O_2 was also determined. The residual or depleted catalyst resulting from the degradation of phenols was filtered, washed gently with deionized water and the catalyst was dried in air without any additional treatment. The dried catalyst samples were used for the oxidation of phenol, employing similar conditions as in the previous experiments.

3.6.Kinetics of phenol mineralization

The models first order kinetic(FKM) and generalized lumped kinetic model(GLKM) were investigated after the experiments the synthetic phenol solution was assumed to be mineralized by only one step in the FKM but includes intermediates formation in GLKM, where the OH radical generation results in the final products.

3.6.1. First order kinetic model

First order kinetic mode Is Phenol in the synthetic solution is assumed to be mineralized by only one step

$$C6H5OH \xrightarrow{K'3} CO2 + H2O \quad (3.3)$$

Where - K'$_3$ =is the apparent kinetic constant:

$$-r\ C6H5OH\ = \frac{-dCC6H5OH}{dt} = \quad K'1C\ C6H5OH \qquad (3.4)$$

3.6.2. Generalized Lumped Kinetic Model (GLKM)

Generalized Lumped Kinetic Model is the alternative approach for the oxidation of organic pollutant using solid catalyzed is useful to the design and scale-up of phenol oxidation treatment. Due to their simplicity, the overall kinetics using power law rates are often unable to capture the important feature in such oxidation systems. However, detailed mechanistic approaches aimed at establishing complex reaction networks where several species and intermediates need to be identified become quickly time-consuming and costly.

A lumped kinetic model which allows insight into the contribution of Phenols intermediates step, which FKM does not account for, is the simple Generalized Lumped Kinetic Model (GLKM). The simplicity of the model relates to its assumption of negligible influence of Phenol to CO_2 and H_2O. It involves the addition of the produced -OH to the aromatic, heterocyclic rings, and unsaturated bonds of alkenes or alkynes, thereby enhancing the degradability of aliphatic compounds. However, byproducts are generated along time through partial mineralization of the other aromatic substances (Figure). These intermediates are the results of the collapse of the aromatic ring during hydroxylation (mineralization), which yields low molecular-weight carboxylic acids(Basheer et al., 2014).

All of the intermediates that could possibly be produced are lumped into intermediate, the parent organic substance as phenol, while the final mineralization products are CO_2 and H_2O.

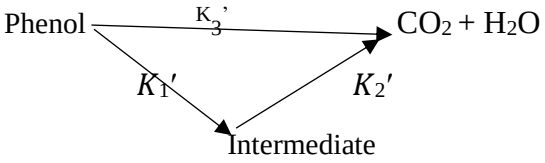


Figure 3.5. Schematic representation of phenol mineralization to final product

$$-rCC6H5OH = \frac{-dCC6H5OH}{dt} = CC6H5OH\ (K1' + k\ 3') \quad 3.5$$

$$-rC6H5OH\ int = \frac{-dCC6H5OHint}{dt} = (K2'CC6H5OHint - K1'CC6H5OH) \quad 3.6$$

4. Results and discussions

4.1 Characterization of raw bentonite and bentonite support iron catalyst

4.1.1 Bulky density of raw bentonite and bentonite support iron catalyst

The Bulk density of raw bentonite powder and Fe/bent catalysts are shown in the table (4.1 and 4.2). It was observed that the bulk density of raw bentonite as well as the bentonite support iron catalyst was 0.479 and 0.501 respectively. The bulk density of both samples was calculated based on the methods discussed in section 3.2 and the detail calculations are attached in the appendix-A2. As illustrated in table 4.1, and 4.2, the bulk density of raw bentonite is lower than bentonite support iron catalyst which indicates that the impregnation of Fe (from sulfite functional group) on the surface and in the pore of the raw bentonite.

Table 4.1. Bulk density of raw bentonite

Sample	Mass of sample(g)	Volume occupied(ml)	Bulk density(g/ml)	Average density(g/ml)
1	0.9030	2 .0	0.4515	0.479
2	1.15	2.4	0.482	
3	1.43	3.0	0.479	
4	1.70	3.4	0.503	

Table 4.2. Bulk density of bentonite support iron catalyst

Sample	Mass of sample(g)	Volume occupied(ml)	Bulk density (g/ml)	Average density(g/ml)
1	0.887	1.8	0.493	0.501
2	1.056	2.2	0.479	
3	1.634	3.2	0.510	
4	1.986	3.8	0.523	

4.1.2. pHpzc of raw bentonite and bentonite support iron catalyst

The point of zero charges (pH_{pzc}) is the pH at which the total number of positive and negative charges on its surface becomes zero(Ajemba, 2016). The influence of all the functional group present in each sample determines pHpzc, the pH at which the net surface charge on each sample is zero. At pH< pH_{pzc}, the sample surface has a net positive charge while at pH > $pH_{pzc}$the sample surface has net negative charges. Anion adsorption becomes to enhance at lower pH than the pH_{pzc} while adsorption of cations is also enhanced at pH higher than pH_{pzc}(Onyekwere et al., 2018). The pH of natural calcium bentonite is alkaline (8.9) because of the exchangeable cation and the presence of excess hydroxyl groups in the structure of montmorillonite. As it was observed in Figure 4.1 there is an increase in the pHpzc on the introduction of Fe^{3+} cations which results in a slight difference in pHpzc of bentonite support iron catalyst as compared to raw bentonite. Both raw bentonite and bentonite support iron catalyst have high pHpzc since it is a characteristic of clay minerals, dominated by montmorillonites. After calcination, the pH, as well as pHpzc decreases since more OH, were removed during the thermal treatment and the pH becomes acidic. From Figure 4.1, the point at which the total concentration of surface anionic sites is equal to the total concentration of surface cationic sites were determined before and after activation. The pH_{pzc} of raw bentonite is higher than the Fe/bent catalyst since it contains more hydroxyl groups. In the acidic environment (pH<4), the sorption of anionic ions was suppressed by the excessive presence of H^+ which compete for available reactive sites. It has been reported previously that the pHpzc of the catalyst decreases with an increase in acidic groups on the surface of the catalyst. From the results, it can be concluded that activation of bentonite gave a positive surface charge for the catalyst since the pH_{pzc} for iron support catalyst surface was found to be lower than that of the raw bentonite surface.

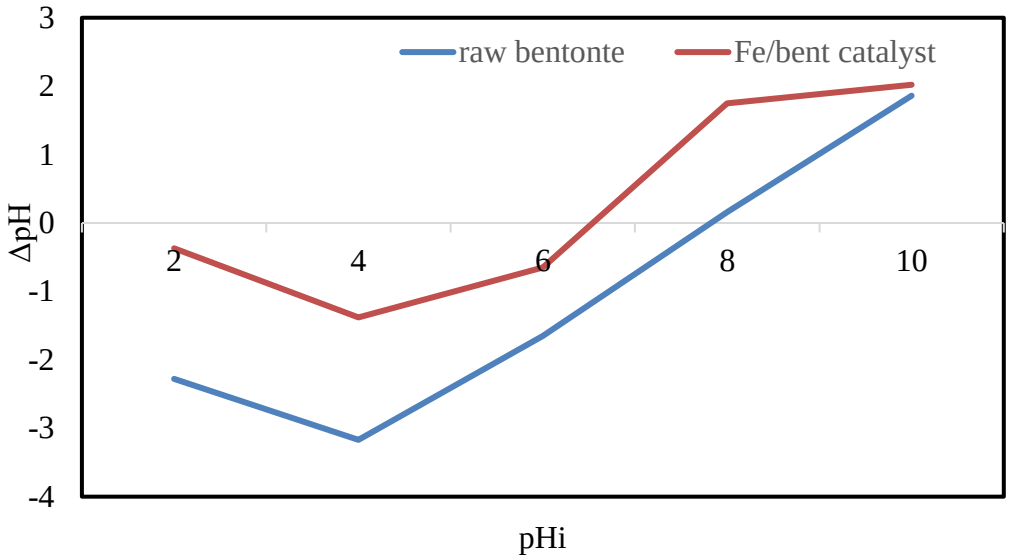


Figure 4.1. Variation of pHi and ΔpH at 0.1MNaCl concentrations

4.1.3. FTIR spectroscopy of raw bentonite and bentonite support iron catalyst

The FTIR spectra were performed in the range from 4000 to 400cm^{-1} for raw bentonite and bentonite support iron catalyst. These spectra revealed a reduction, broadening, disappearance or appearance of new peaks after the process of modification. The shifts in the spectra revealed the effect of the modification. Comparing the spectrum of bentonite with that of the iron supported catalyst, a new absorption peak emerged at 2337.72 cm^{-1}, which referred to as the bending vibration of O-H with Fe(III) species present on the surface of Fe/bentonite. It has been shown that Fe(III) species were intercalated into the interlayers of bentonite by the adopted process(Gao, Yaowen, et al., 2016). The absorption band at 3635.97 cm^{-1} was due to the stretching vibration of structural O-H groups of the montmorillonite clay, as well as the band between 522.73-468.72 cm^{-1} due to bending H-O-H vibration in the adsorbed water in the interlayer. The very strong characteristic peak observed at 1051.25 cm^{-1} was recognized to unequal stretching vibrations of Si-O-Si bonds. The bands at 522.73 and 468 .72 cm^{-1}were responsible for Al- O - Si and Si-O-Si bending vibrations respectively. The absorption band at 1641.49 cm^{-1}was recognized to the OH

deformation mode of water. The 794.71 cm^{-1}band corresponded to attached Al–O, and Si–O out-of-plane vibrations. FTIR is very sensitive to the structural changes which occur in the clay upon the impregnation of iron (III) and the IR data recorded herein suggest that both the octahedral and tetrahedral sheets were susceptible to iron (III) ion attachment. The intensity of stretching bands detected at 3622.7 cm^{-1} (Al–OH–Al along with the Mg–OH stretching vibrations) due to the effect of iron (III) after modification the intensity of stretching bands decreased. Modification with iron (III) ion has also resulted in a decrease in the peaks of the bands associated with the adsorbed water at 2325 (H–O–H stretching) and 1584.95cm^{-1} (H–O–H bending). It is due to the removal of octahedral cations, causing the loss of water and hydroxyl groups coordinated to them. The raw bentonite leads to the formation of amorphous silica, indicated by the increased intensity of the peak, which may provide more adsorption sites.

Table 4.3.Studies of IR band assignment of bentonite clay by various author(Kaolinite, 2002)

Band	Ogubunka,.etal 2001)	(Ayaria et al., 2005)	(Baker et al., 2014)	Present work
Si-O-Fe	-	420	-	
Si-O(ben)	467	470	469	468.72
Si-O-Al	521	520	520	522.73
Al-Al-OH(ben)	915	915	916	923.73-
Si-O(str vib)	1036	1030	1040	1051.25
Si-O(str)	1100	1100	-	
OH-(ben)	1642	1635	1636	1641.49
OH-(str)		3430	3457	3635.97
Al-Al-OH(str)		3620	3618	3622.7

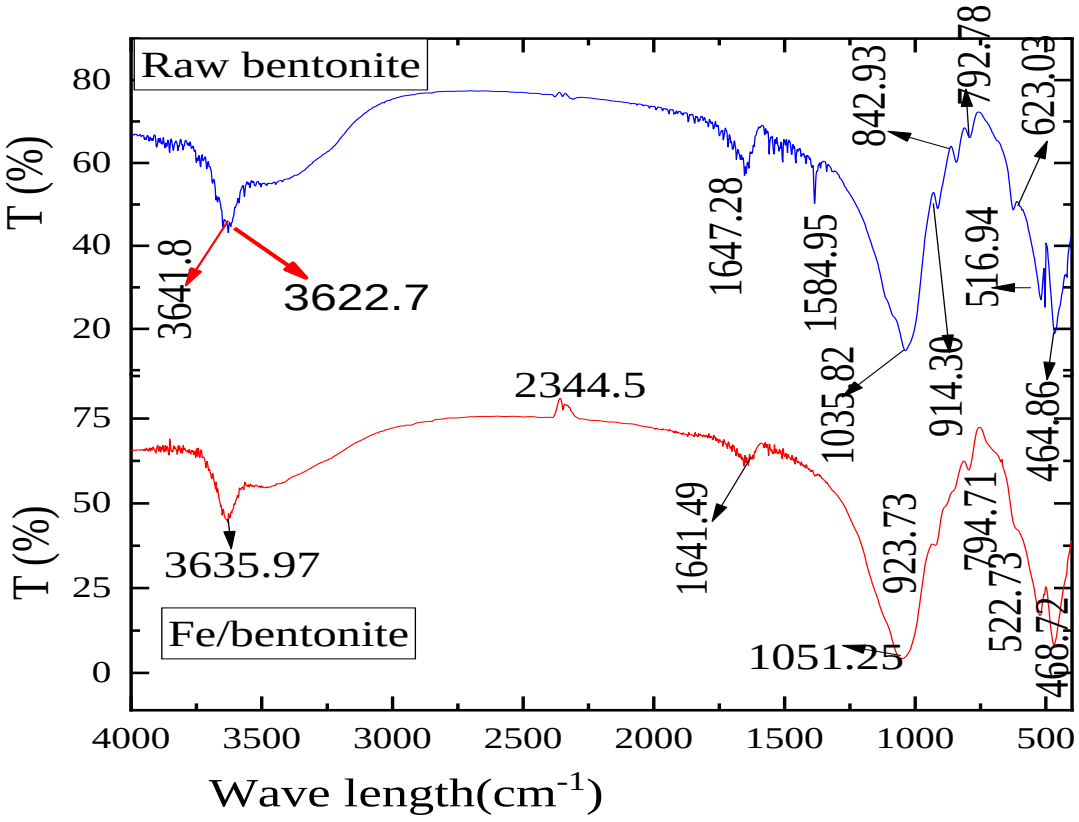


Figure 4.2. FTIR spectra of raw bentonite and bentonite support iron catalyst

4.1.4. XRD analysis of raw bentonite and bentonite support iron catalyst

The crystallography and mineral composition of both raw and bentonite support iron catalyst was determined by using MiniFlex 300/600 +,150 (Rigaka) x-ray diffraction instrument. X-ray diffraction (XRD) patterns were recorded with D8 Avance XRD of Brucker powder diffractometer with Cu-Kα (λ=1.540593-1.544414 Å, 40 KV,15 mA) radiation having a continuous scanning mode with speed of 10deg/min. X-ray diffractograms of raw bentonite powder and prepared catalyst were obtained for the 2θ angles ranging from 5^0 to 50^0 with scan step 0.02^0. Characterization of XRD patterns for raw bentonite and prepared catalyst indicates the presence of Montmorillonite (Mo), Cristobalite (Cr), Quartz (Q), Muscovite (Mu), Hematite (H) and Feldspar (F) as the major phases. Due to the effect of the iron (III) ion treatment, it can be seen that montmorillonite and quartz phases which gave an intensity

difference of 250 and 193 respectively. The results are shown below in Figure 4.2. The patterns showed the presence of diffraction peaks corresponding to angles (9.32,20.12, and 35.5º) confirming the presence of montmorillonite in the samples. The data also showed the presence of impurities such as Muscovite (18.5º), Cristobalite (18.32º), Hematite (28º), Feldspar (21.81º) and quartz and (19.73 and 31.91º) in both samples were obtained. What was observable from figure 4.3, the peak (crystalline structure) of the raw bentonite disappear around intensity 404 due to calcination of support catalyst, Also, it could be confirmed from following Figure 4., the sample did not undergo phase change and is thermally stable up to 483 º C. Therefore, the crystallinity of bentonite was preserved and no significant difference in its crystalline structure.

Table 4. 4. Descriptions of the indicated minerals

Mineral name	Formula	Crystal system
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	Monoclinic
Quartz	SiO_2	Trigonal (hexagonal axes)
Hematite	Fe_2O_3	Hexagonal
Cristobalite	SiO_2	Tetragonal
Muscovite	$KAl_2(Si_3Al)\ O_{10}(OH)_2$	Monoclinic
Feldspar	$KAlSi_3O_8 – NaAlSi_3O_8 – CaA_{l2}Si_2O_8$	Triclinic

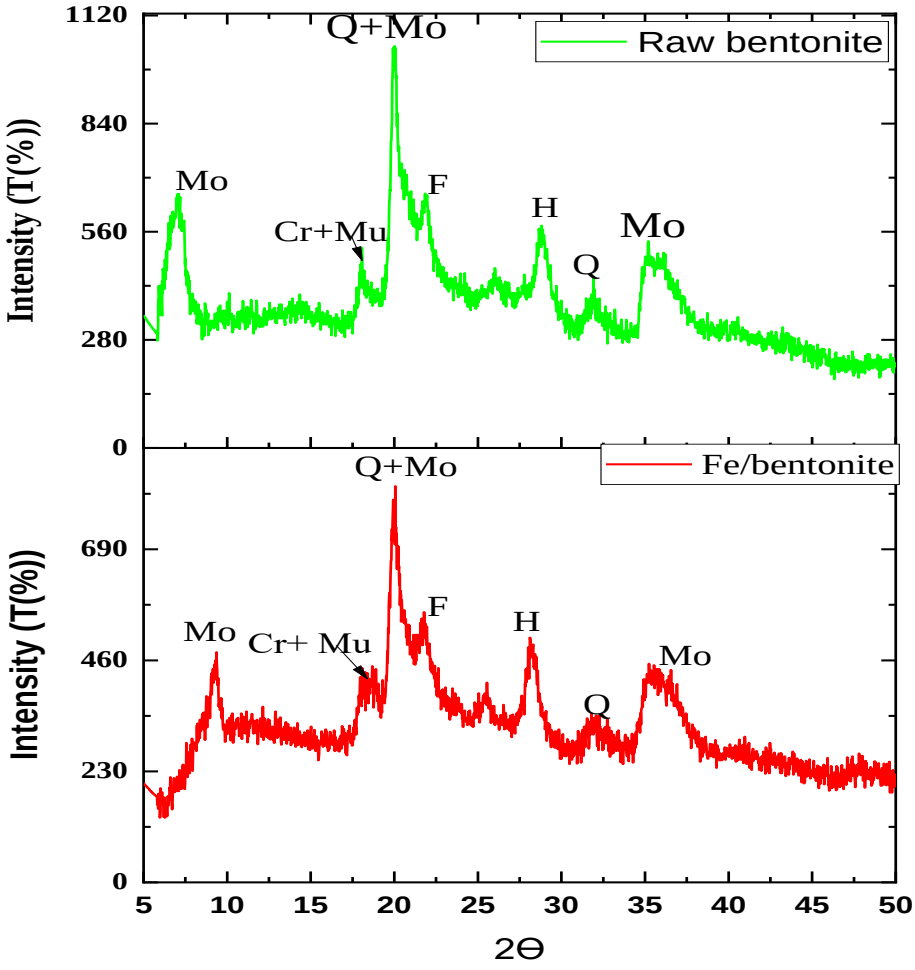


Figure 4.3.XRD of raw bentonite and bentonite support iron catalyst (Fe/bent)

4.1.5.AAS of raw bentonite and bentonite support iron catalyst

Atomic absorption spectroscopy is the qualitative and quantitative determination of chemical elements that present in different samples using the absorption of optical radiation (light) by free atoms in the gaseous state. In these studies, raw bentonite and bentonite support iron catalyst were analyzed by using atomic absorption spectroscopy. The analysis of these results showed that the predominant constituents of the raw and bentonite support iron catalysts were silica, alumina, iron, calcium and magnesium oxide. The results showed there were increased the chemical compositions from raw bentonite to bentonite support iron catalyst except for Titanium oxide, H_2O

and LOD there is no significant change in manganese oxide. It was clear that before analysis both samples could be digested by nitric acid and also the sample was treated by dissolved with calcite for good conformity. This additional process was significantly affecting the chemical composition of both samples, so this reason the analysis showed that the content of chemical composition in both samples increases or decrease.

Table 4 5. Analysis of raw bentonite and bentonite support iron catalyst by AAS

	Chemical composition (%)	
Chemical oxide	Raw bentonite	Bentonite support iron catalyst (Fe/bent)
SiO_2	58.06	63.64
Al_2O_3	13.48	18.29
Fe_2O_3	1.40	2.54
CaO	0.70	2.84
MgO	3.42	3.76
Na_2O	1.76	2.02
K_2O	<0.01	0.10
MnO	<0.01	<0.01
P_2O_5	0.02	0.06
TiO_2	0.08	0.11
H_2O	13.30	<0.01
LOI	6.54	5.99

The above table 4.5 Showed as the elemental composition of raw bentonite and bentonite support iron catalyst. Silica was the major constituent followed by aluminum

oxide. This was expected, as bentonite is aluminum phyllosilicate clay, with sheets of silicates forming parallel sheets of silica tetrahedral with Si_2O_5(Vessal, 2017).

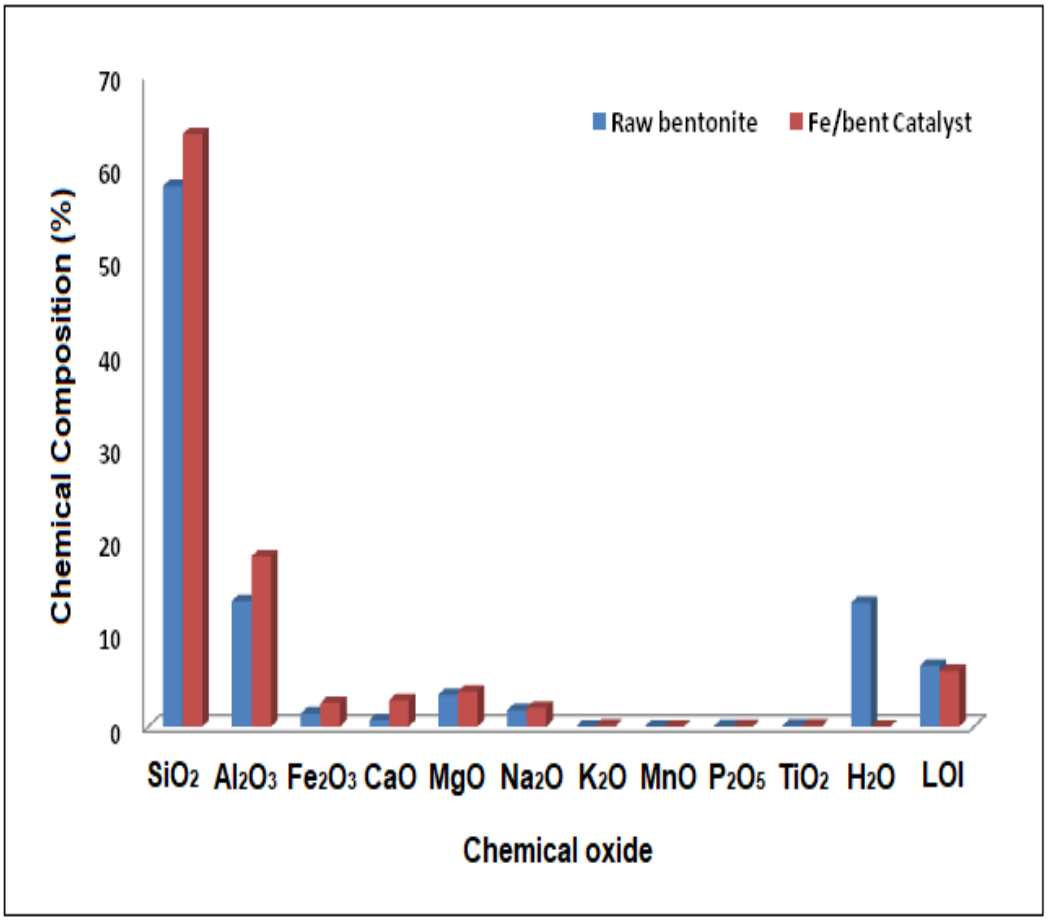


Figure 4.4.AAS of analysis raw bentonite and bentonite support iron catalyst.

4.2. Catalyst selection

The ratio of the supported catalyst as well as the calcination temperature was selected based on the percentage removal efficiency of phenol measured by 4-AAP method and TOC reduction measured by TOC analyzer as discussed in above section 3. The preliminary experiments showed that the adequate mixing ratio was obtained at 1:5. So based on the following results of two combinations of categorical factor level the maximum percentage removal of phenol and reduction of total organic carbon

occurred at the ratio of iron to bentonite 1:5 and calcination temperature at 493°C and TOC reduction which is measured by TOC analyzer with infrared detector TOC-Vsch. Shimadzu.

Table 4. 6. Solutions for 2 combinations of categorical factor levels and temperature

Number	Temperatur °C	Ratio (Fe:bent)	Phenol removal (wt%)	TOC reduction (%)	Desirability	
1	492.9	0.20	96.35	99.25	0.992	Selected
2	485.34	0.15	93.58	96.235	0.982	
3	476.16	0.13	89.57	84.731	0.983	
4	453.03	0.12	82.99	78.722	0.922	

From the solution given with desirability ramp on design expert, the catalyst was selected by the desirability of 0.992 at a ratio of Fe: bent, 1:5 and calcination temperature at 493°C were selected. Accordingly, to select the optimum heterogeneous catalyst for phenol degradation through heterogeneous Fenton process. From the following figure (a) The result was observed that the degradation of phenols was decreased at a minimum and maximum calcination temperature. As calcination temperature increases the particle size of the prepared catalyst increase subsequently the surface area of catalyst was decreased so the removal efficiency of phenol could be limited(Pozan & Kambur, 2014). And also, it can be seen that the percentage removal of phenol increases until it reached the optimum calcination temperature and due to the effect of calcination on the active site of catalyst the efficiency of mineralization of phenol would be decreased the graph also declined. From the figure (b) showed that the best mixing ratio was obtained at the maximum mixing point of the iron to bentonite due to the effect of iron on the surface of bentonite. So, the maximum percentage removal efficiency of phenol and reduction of TOC were observed at the ratio of iron to bentonite (1:5) or 0.2wt%.

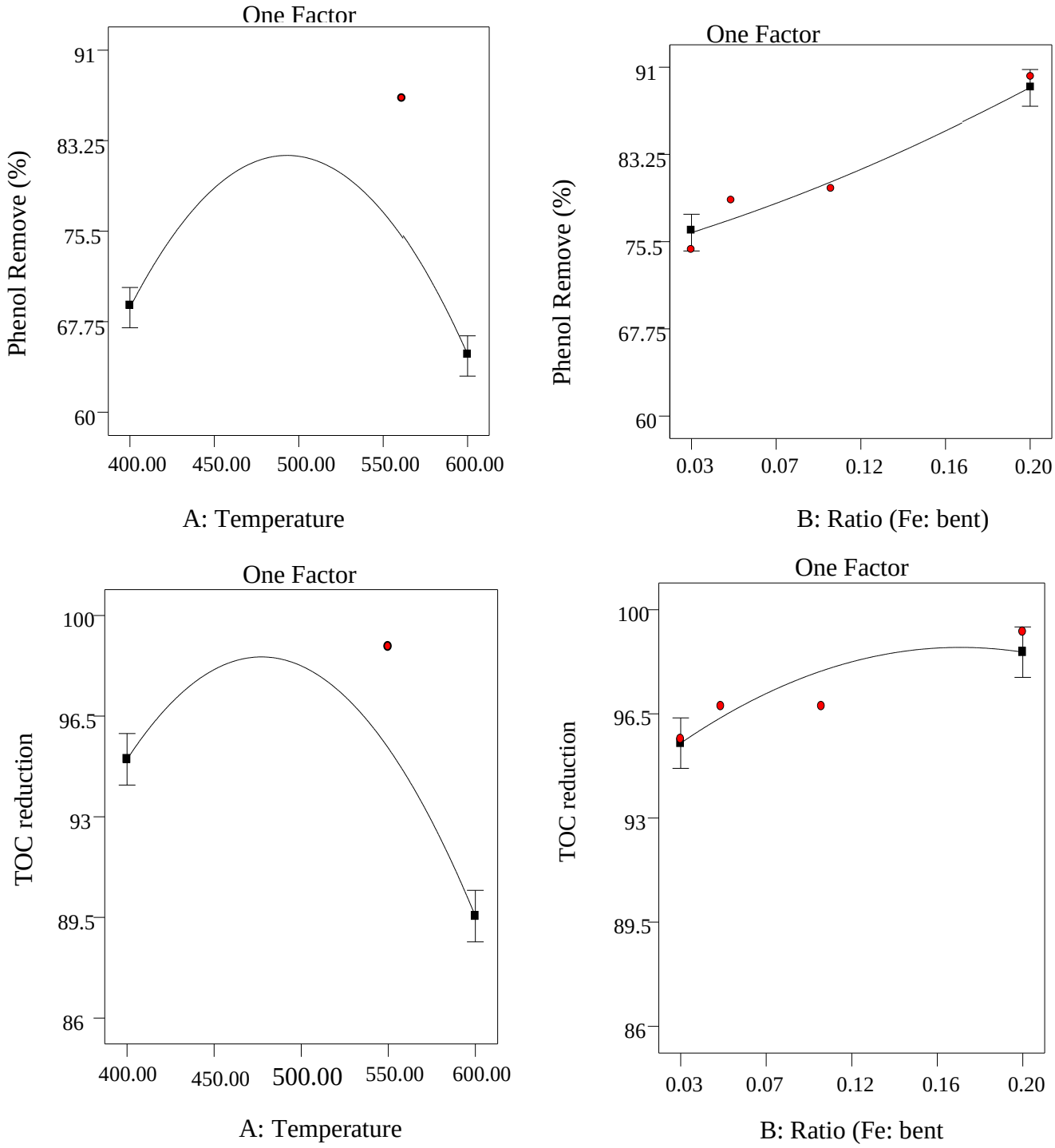


Figure4.5. Effect of process variable on selection of the catalyst

4.2.1. Performance analysis results for Phenol adsorption

Phenol adsorption experiment for raw bentonite and Fe/bent were carried out for 4h contact time, with synthetic phenol solution. The degree of phenol removal by raw bentonite and bentonite support iron catalyst was determined as relative to the standard curve as shown in figure 3.4. The concentration of the unknown samples was calculated based on standard curve equation. The percentage removal of phenol was then determined. The phenol adsorption is diminished due to the presence of acid type surface oxygen groups on the surface of bentonite clay (Srinivasan & Rajani, 2011. In addition to this, the adsorption capacity of bentonite is higher than that of the catalysts. This is expected since the pore volume of the catalysts is lower due to the deposition of Fe^{3+} on the surface.

The percentage removal of phenol was then determined using equation 4.1

$$\%Removal\ of\ Phenol = \frac{(Ci-C)}{Ci} * 100\% \qquad 4.1$$

Where: C_i = Initial phenol concentration (mg/L)

C= Phenol concentration after treatment(mg/L)

Table 4.7. Concentration of phenol adsorbed and percentage removal

Raw bentonite				Bentonite support iron catalyst (Fe/bent)		
No	Initial phenol concentration(mg/L)	Final phenol concentration(mg/L)	%Phenol removal	Initial phenol concentration(mg/L)	Final phenol concentration (mg/L)	%Phenol removal
1	800	117.30	78.63	800	170.24	69.25
2	800	173.58		800	343.07	
3	800	222		800	224.61	

4.3. Response surface methodology for the removal of phenol.

Additional investigation on the activity of the catalyst was conducted in the heterogeneous Fenton process for the mineralization of phenol. The heterogeneous Fenton reaction was carried out in a batch-wise reactor using 750 mL Erlenmeyer flask supported on a magnetic stirrer (MSH-20D) at the following operating conditions: 300 rpm, atmospheric pressure, and 250 mL of reaction volume and the temperature was adjusted at room temperature (25℃), the pH was adjusted using a 0.1N HCl and 0.1N NaOH The performance analysis of phenol mineralization was carried using RSM (three level factorial) with five center point and 4 factors, such as hydrogen peroxide concentration (2000,4000 and 6000)mg/L, Reaction time (60, 90 and 120)min ,Catalyst dosage(1000,1500 and 2000)mg/L and pH(3,3.5 and 4).

4.3.1. Model adequacy and RSM for the removal of phenol

According to the experimental design and response value, the mathematical model was generated, the adequacy of the model was examined. An ANOVA was generated for this response. The analysis showed that the model is significant as the model F-value was 425.72 as shown on the table 14. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, D, AB, AC, AD, A^2, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant(BC, BD, and CD are non significant term). If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The "Lack of Fit F-value" of 1.05 implies the Lack of Fit is not significant relative to the pure error. There is a 52.54% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good so that the model could fit If there are many insignificant model terms (not counting those required to support hierarchy). The model was used for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, Adjusted R-Squared and Predicted R-Squared having values of 0.9977, 0.9953 and 0.9892 respectively. The quality of the model developed could be evaluated from their coefficients of

correlation. The value of R-Squared for the developed correlation was 0.9977. It implies that 99.77% of the total variation in the percentage removal of phenol was attributed to the experimental variables studied. The "Pred R-Squared" of 0.9892 is in reasonable agreement with the "Adj R-Squared" of 0.9953. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 63.511 indicates an adequate signal. This model can be used to navigate the design space. The statistical software program is used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variable constants. The three-level full factorial combinations with their respective responses and the ANOVA are attached in the appendix -F

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

Table 4. 8. Analysis of variance for phenol removal of the surface Quadratic Models

Source	Sum of Squares	Df	Mean Square	F- Value	p-value Prob > F	
Model	160.93	1	154.35	425.72	< 0.0001	significant
A-hydrogen Peroxide	42.53	1	42.53	117.29	< 0.0001	
B-catalyst dosage	4.86	1	4.86	13.42	0.0026	
C-Time	7.65	1	7.65	21.09	0.0004	
D-pH	33.30	1	33.30	91.85	< 0.0001	
AB	28.09	1	28.09	77.48	< 0.0001	
AC	18.15	1	18.15	50.05	< 0.0001	
AD	1.92	1	1.92	5.29	0.0373	
BC	0.032	1	0.032	0.089	0.7694	
BD	0.084	1	0.084	0.23	0.6375	
CD	0.49	1	0.49	1.35	0.2645	
A^2	1981.12	1	1981.12	5464.15	< 0.0001	
B^2	91.46	1	91.46	252.27	< 0.0001	
C^2	69.58	1	69.58	191.90	< 0.0001	
D^2	217.18	1	217.18	599.00	< 0.0001	
Residual	5.08	14	0.36			
Lack of Fit	3.68	10	0.37	1.05	0.5254	not significant
Pure Error	1.40	4	0.35			
Cor Total	2166.01	28				

A, B, C and **D** representing experimental variables: hydrogen peroxide concentration, reaction time, catalyst dosage and pH respectively.

Table 4.9 Correlation coefficients

Standard Deviation	0.60	R^2	0.9977
Mean	85.82	Adj R^2	0.9953
Coefficient of variation(%)	0.70	Pred R^2	0.9892
Precision	23.37	Adequacy Precision	63.511

The graph of the predicted values obtained using the developed correlation predicted versus actual values is shown in Figure (4.6). The results in Figure illustrated that the regression model equation provided an acceptable description of the experimental data, in which most of the points are close to the line of the perfect fit. This result showed that it was successful in capturing the correlation between the input process variables data for the percentage removal of phenols from synthetic phenol solution. Therefore, these results showed a good agreement between experimental and predicted values for degradation efficiencies of phenol.

In addition to this, as shown in figures on (Appendix H, I) diagnostics data plots (normal plot of residuals, residuals vs predicted and residuals vs run) and influence plots (cook's distance, DFFITS, and DFBETAS) ensured there is no any out layer and the model fits to the experimental data.

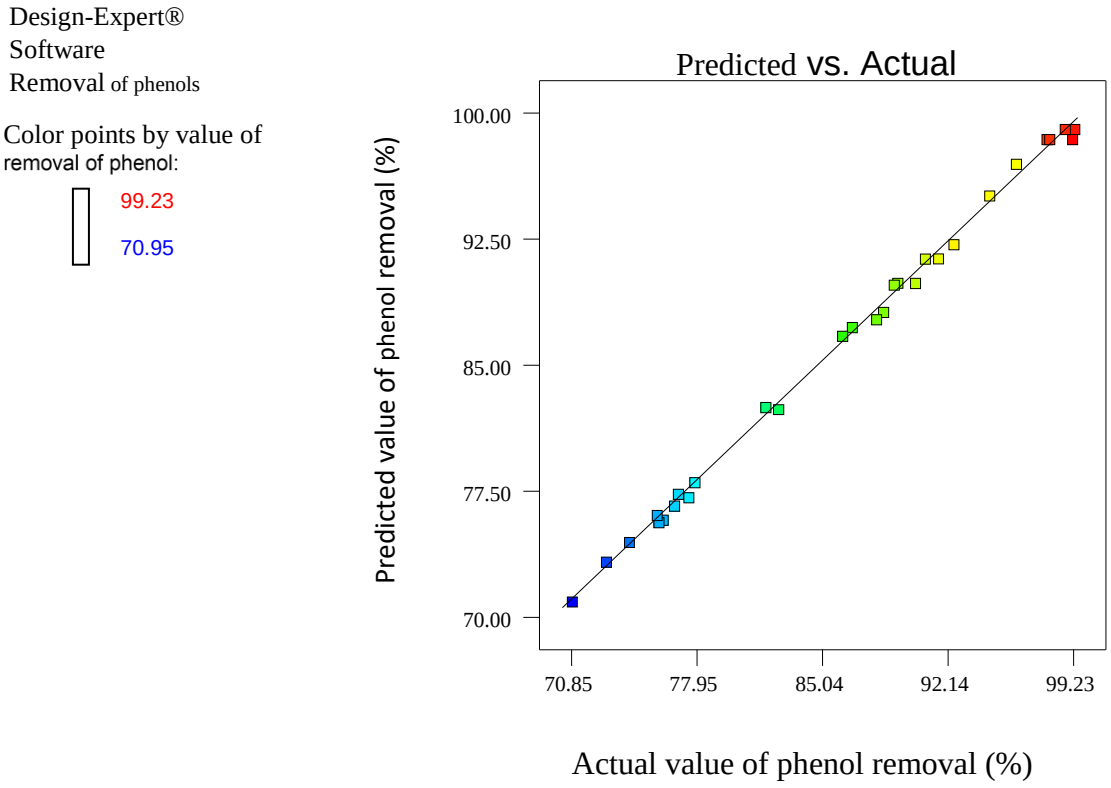


Figure 4.6. Predicted vs actual percentage removal of phenol solution

4.3.2. Effect of process variables on the percentage removal of phenols

According to the results of variance, The experimental design showed that heterogeneous Fenton oxidation reaction was significantly affected by various interactions between the process variables. The effects of each process variables which include hydrogen peroxide concentration, time, catalyst dosage and the pH were studied.In addition to individual effects, significant interaction effects were considered for the analysis of the target response of phenol degradation. From experimental data and developed the three-dimensional response surface and single factor plots, the main and interactive effect of independent variables on the response are illustrated in Figure(3.6 to 3.13).

4.3.3. The main effect of process variables

The mineralization of phenol was catalyzed by the prepared bentonite support iron catalyst (Figure 4.6) the percentage removal of phenol was significantly affected by all selected process variables. The phenol removal percentage was enhanced by an increase in the concentration of hydrogen peroxide. The removal of phenol increased by an increase in the dosage of hydrogen peroxide from 2200mg/L to 4000mg/L since more OH· radicals were produced. From figure 4.6, as it can be seen the concentration of hydrogen peroxide increased until it reached 4136.99mg/L, consequently the result of percentage removal of phenol increase. However, the progress in the removal of phenol was not notable or even it was decreasing with increases in the dosages of hydrogen peroxide from 4000mg/L to 5500mg/L. Increase in the concentration of hydrogen peroxide affected the reaction of the produced hydroxyl radicals with the additional H_2O_2 molecules to form hydroperoxyl radicals that have a less oxidizing ability. After that, the percentage removal of phenol would started to drop as the concentration of hydrogen peroxide increase such behavior could be justified by the following reasons.

According to Kausley et al., 2017 the medium concentration of hydrogen peroxide increases the percentage removal of phenols this can be attributed as the effect of excess hydrogen peroxide was the scavenging of generated hydroxyl radicals. Which

implies that the produced hydroxyl radical is converted to other chemical composition without further mineralizing phenol. Moreover, self-scavenging characteristics of hydroxyl radical. The unused portion of hydrogen peroxide during the Fenton process contributes to decrease the removal efficiency of phenolic compound and also Increasing the dosage of H_2O_2 would affect the overall degradation efficiency significantly (Matavos et al., 2017) hence excess amount did not recommended.

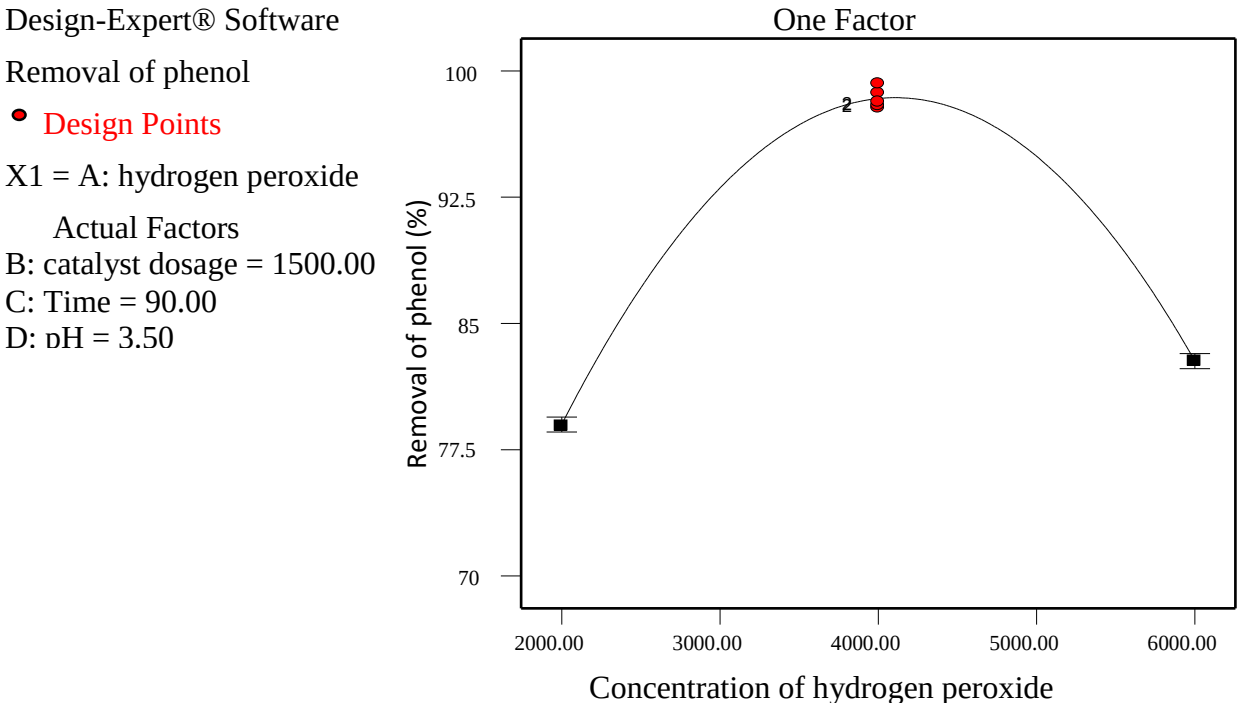


Figure 4.7. Effect of hydrogen per oxide concentration on removal of phenols

From a practical point of view, pH significantly affected the Fenton reaction. Figure 4.8, It can be seen that the mineralization efficiency of phenol increased to a certain level then started to drop the removal efficiency of phenol as the pH of the Fenton reaction increased from 3.5 to 3.8. This due to the presence of relatively inactive iron-oxo hydroxides and formation of ferric hydroxide precipitate. According to Guo and Al–Dahan 2003, the optimum pH for the maximum reaction rate as well as for the highest degradation of phenolic compound was at a pH range 3 to 3.6 in most cases of Fenton process, This suggests that when the pH was less than or below 2.8 and

greater than 4 the oxidation potential of hydroxyl radicals for phenol removal was decreased due to the presence of iron complex species $[Fe(H_2O)^6]^{2+}$ This phenomenon was influenced the mineralization efficiency of phenols. According to the ANOVA, the optimal mineralization level was obtained in pH range 3 to 3.6 at which the mineralization rate of phenol was high.

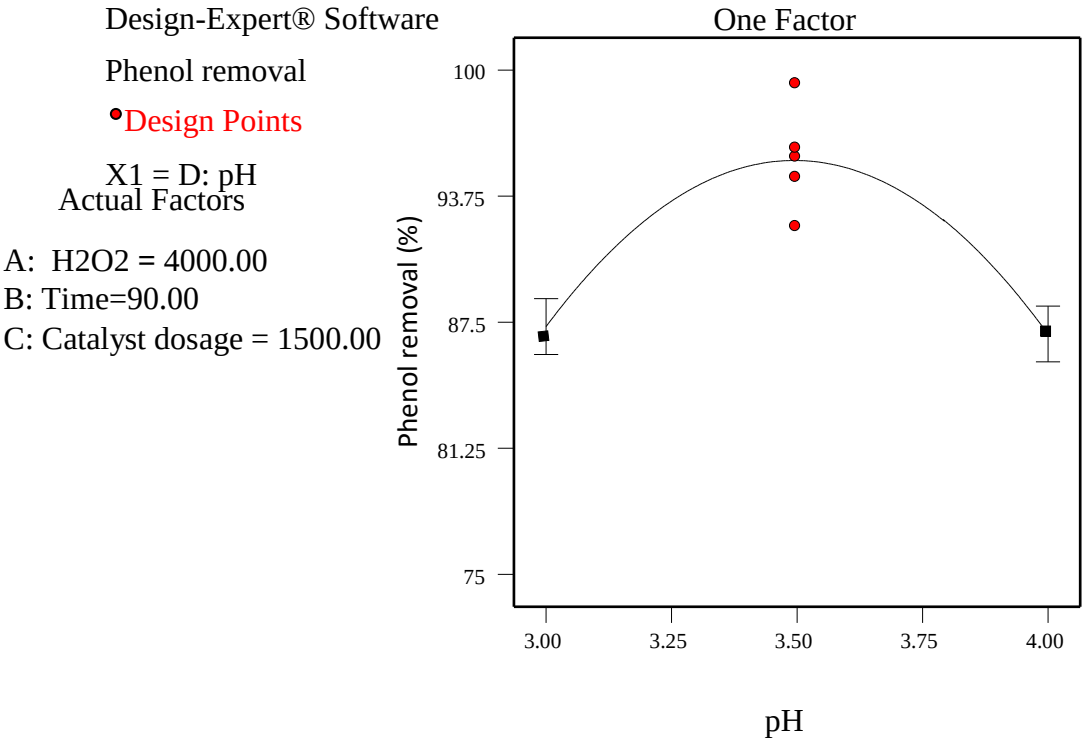


Figure 4.8. Effect of pH on percentage removal efficiency of phenols

The influence of different reaction time on the removal efficiency of phenol shown in the Figure **(**4.9**)**, Accordingly, the percentage removal of phenol was high at the reaction time interval of 60 to 90 min. As described by Long T., et al.,2007 longer degradation times are required after the removal of the parent compound to achieve complete mineralization in the Fenton process. In another approach Percentage removal of phenol decreased as the oxidation reaction time increases.

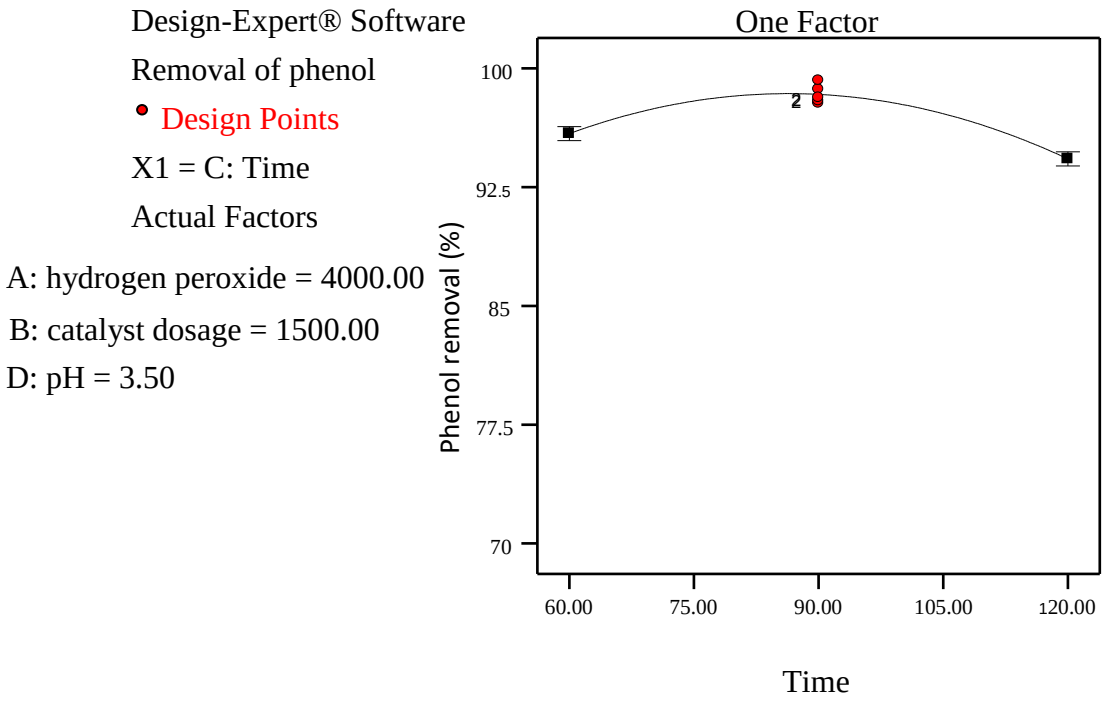


Figure 4.9. Effect of reaction time on the removal efficiency of phenol

As shown in Figure 4.10 ,the percentage removal of phenol significantly affected by a dosage of catalyst. The removal efficiency of phenol reduced by an increase in the concentration of catalyst dosage. The reason is that at a high dosage of catalyst, the production of hydroxyl radicals, Which, generally originated from the breakdown of H_2O_2, was very high that many of the hydroxyl radicals were spent through the side reactions before being used for the removal of phenol. From the Fig (4.10), it can be observed that the dosage of catalyst increase with increase the percentage removal of phenol until it reaches the maximum point then it becomes dropped when there increased in the catalyst dosage. This indicates that after a certain point the catalyst load has a detrimental effect on the performance (mineralization degree in this case), which can be explained by the formation of iron complexes (iron + organics) when excess amounts of catalyst are present. According to the data obtained from the literature the optimum catalyst dosage for highest mineralization of phenol was around

1 and 2 g/L, for 1000mg /L of phenol concentration beyond this range the percentage removal efficiency of phenol was decreased.

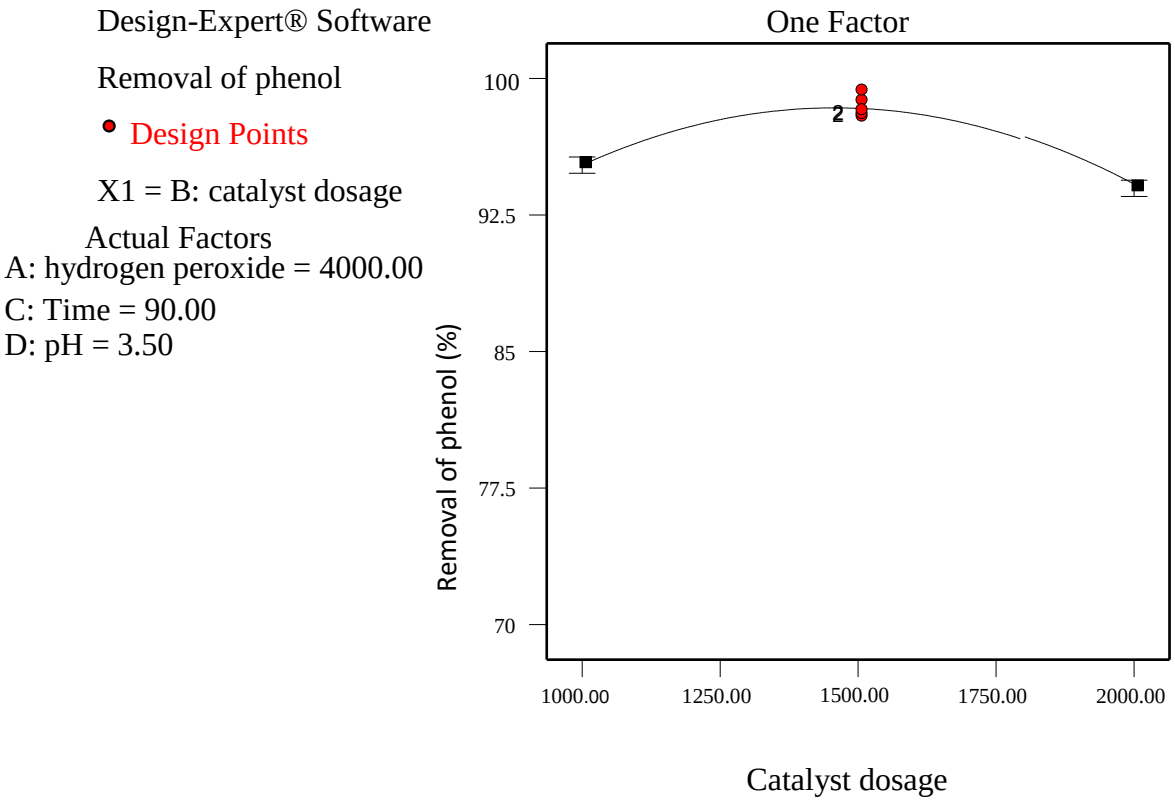


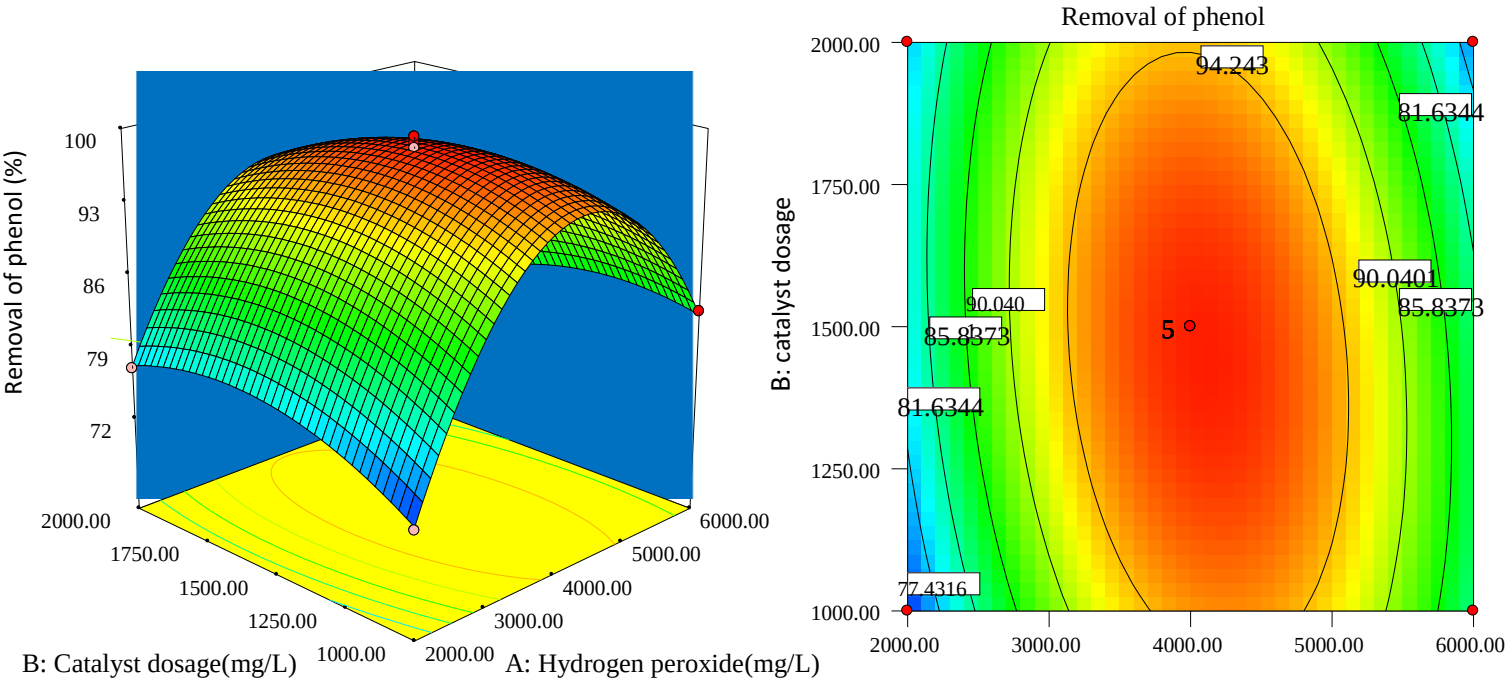
Figure 4.10.Effect of catalyst dosage on the percentage removal efficiency of phenol

4.3.4. The Interaction effect of process variables on removal of phenol

The study of the interactions between variables showed the impact of one variable on another affecting the percentage removal efficiency of phenols. According to the second-order coefficients, three interactions seemed to be significant. The most common way to summarize the results of an RSM (three-level full factorial) experiment is in the form of three-dimensional response surface or contour plot. The process variables were found to have significant interaction effects and the interaction effect of hydrogen peroxide concentration with catalyst dosage, the interaction effect of hydrogen peroxide concentration with reaction time and the interaction effect of

hydrogen peroxide with pH are shown in Figure (4.11,4.12 and 4.13) The highest interaction effect was the effect of hydrogen peroxide concentration with catalyst dosage and the interaction effect of hydrogen peroxide concentration with pH. As can be seen from Figure 4.11 (a) and Figue (4.11b) The maximum percentage removal efficiency of phenol of 94.24% was achieved at medium catalyst dosage of approximately 1300mg/L, and medium hydrogen peroxide concentration of approximately 4000mg/L. The combined effect of hydrogen peroxide and reaction time Fig 4.12a and 4.12b shows as the interaction between hydrogen peroxide with reaction time as the hydrogen peroxide increase. As it can be observed from the Fig 4.12 the intermediate reaction time of approximately 90 min and the medium concentration of hydrogen peroxide 4000mg/L results in the maximum percentage of 94.45 removal efficiency of phenol and the similar result were obtained for the interaction of hydrogen peroxide with pH. From the Fig 4.13 (a) the highest interaction effect was observed the highest mineralization of 93.91% phenol was obtained at the medium concentration of hydrogen peroxide of 4000mg/L and the middle point pH of 3.5. From the three interaction effect at medium of catalyst dosage, at medium range of hydrogen peroxide concentration, reaction time at intermediate and at middle pH allways resulted in higher mineralization of phenol.

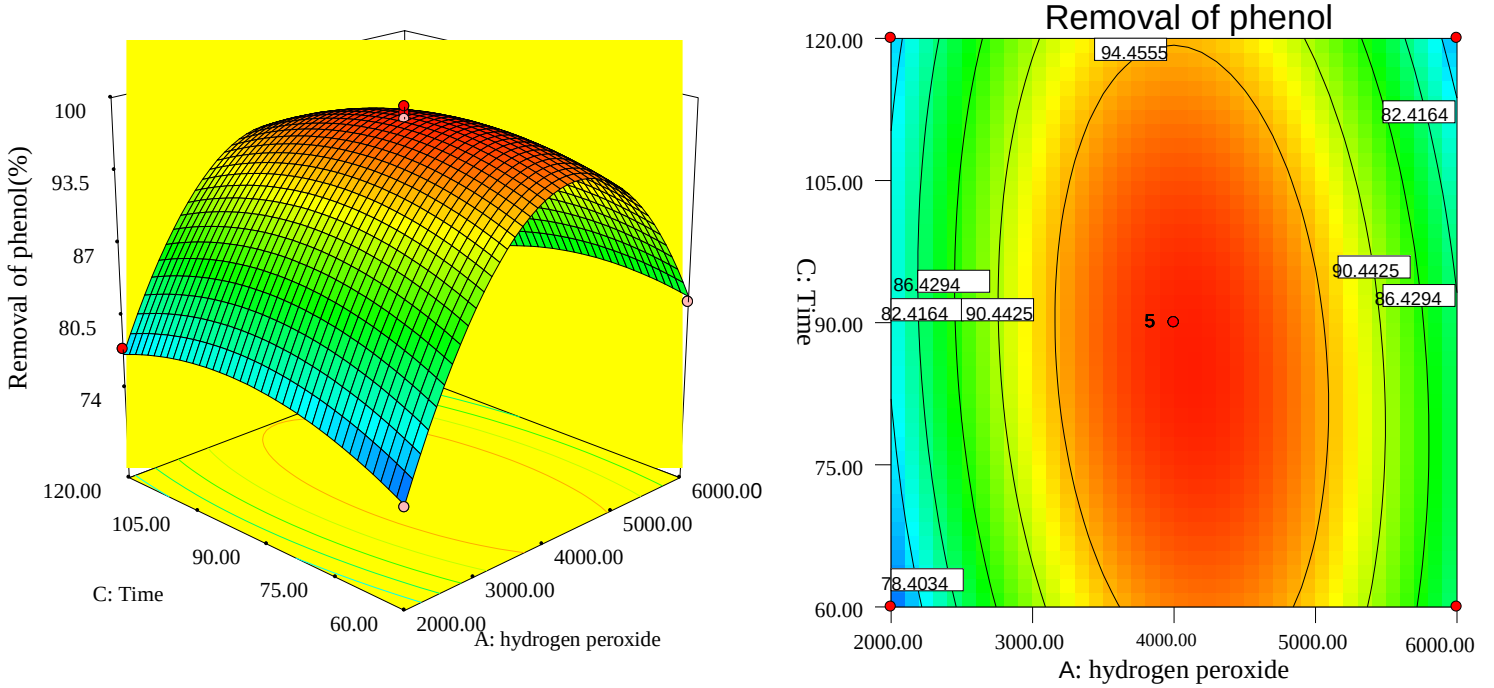
The above observations can easily be explained as medium hydrogen peroxide concentration, medium range of catalyst dosage, medium reaction time and medium pH solution will drive reaction forward and ensure the mineralization reaction goes to a maximum value which resulting in higher removal efficiency of phenol when the values of each variable were arranged as a medium range. Another notable observation is that at higher reaction time, a higher amount of hydrogen peroxide concentration and higher catalyst dosage and higher pH is not beneficial in increasing the percentage of mineralization (Shokri & Aref, 2018).



a):3D- surface plot

b): contour plot

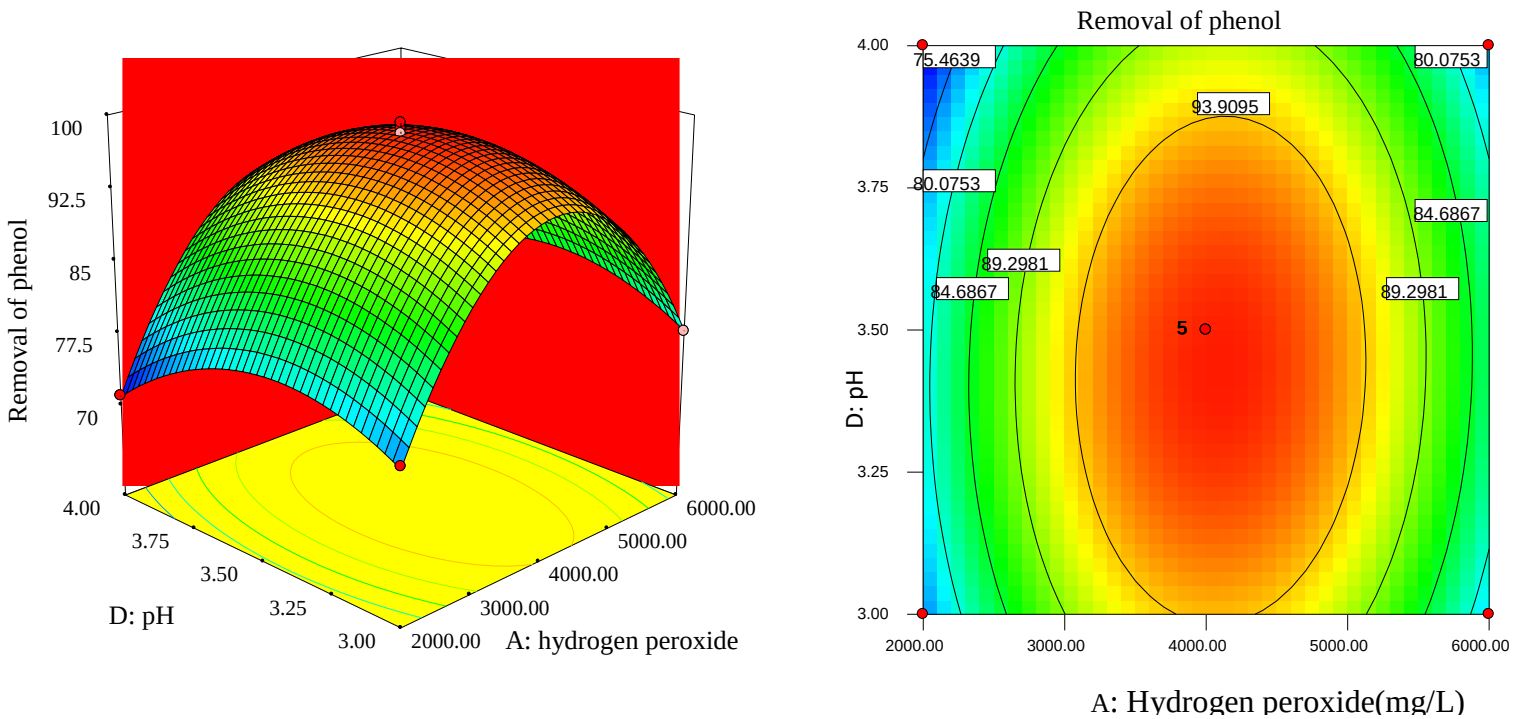
Figure 4.11. The interaction effect of hydrogen peroxide concentration with catalyst vs the percentage of removal of phenol.



a): 3D-surface plot

b): Contour plot

Figure 4.12 The interaction effect of hydrogen peroxide concentration with reaction time vs the percentage of removal of phenol.



a) 3D – surface plot b) Contour plot

Figure 4.13. The interaction effect of hydrogen peroxide concentration with pH vs the percentage of removal of phenol.

4.3.5. Regression Model Analysis

All the Experimental results were fitted to a second-order polynomial model Equation (4.2). The model equation that correlates the response (%Removal of phenol) to the heterogeneous Fenton reaction process variables in terms of actual value after excluding the insignificant terms is shown in equation 4.2. The model equation was used to determine the influence of the process variables on the removal of phenols in synthetic phenol from synthetic phenol solution by bentonite support iron catalyst (Fe/bent). The predicted model for a percentage of removal of phenol in terms of the coded factors is provided.

$$Phenol\ removal\ (\%) = +98.36 + 1.88\ A - 0.64B - 0.80C - 1.67\ D - 2.65\ AB - 2.13A\ C + 0.69AD - 0.090BC + 0.14BD + 0.35CD - 17.48A^2 - 3.76B^2 - 3.28C^2 - 5.79D^2 \quad (4.1)$$

Where A= Hydrogen peroxide concentration(mg/L) C= Reaction time(min)

B=Catalyst dosage(mg/L) D=pH

4.3.6. Process Variables optimization and validation

The main purpose of the optimization was to obtain the optimum conditions and variables for the removal of phenol in heterogeneous Fenton process. The requested goal was introduced as "phenol (%) maximum" to obtain high removal. The results above have shown that the mineralization process variables and the interaction among the variables affect the percentage removal of phenols. Therefore, the next step is to optimize the process variables in order to obtain the highest percentage removal of phenol. The removal efficiency at optimum values of the process variables is presented in Table 4.11. Under these conditions, the model predicted the percentage removal of phenol as 98.63% with a desirability value of 0.979. The results showed that the maximum degradation percent was achieved when the values of each variable were at their optimum values. To evaluate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized mineralization process conditions and the mean percentage conversion value of 98.93% was obtained. The results are closely related to the data obtained from optimization analysis using desirability functions. Therefore, this work showed that bentonite support iron catalyst(Fe/bent) can be used. In the heterogeneous Fenton process for the mineralization of phenol.

Table 4. 10.working conditions of response and factors for optimization

Constraint	Ultimate goal	Experimental region	
		lower limit	upper limit
Hydrogen peroxide concentration(mg/L)	is in range	2000	6000
Catalyst dosage(mg/L)	is in range	1000	2000
Time(min)	is in range	60	120
pH	is in range	3	4
%Removal of phenol	Maximize	70.95	99.23

Table 4. 11. Removal efficiency of phenol at optimum values of the process variables

Variable	Optimum values for the removal of phenols (%)
Dosage of hydrogen peroxide (mg/L)	4136.99
Dosage of catalyst (mg/L)	1445.18
Reaction time(min)	85.45
pH	3.43
Removal of phenol(%)	Pred.(98.64),Exp.(99.23)

4.4. The reusability of bentonite support iron catalyst (Fe/bent)

The reusability of bentonite support iron catalyst (Fe/bent) was done by selecting the run which gave maximum percentage removal of phenols (99.23%) from the ANOVA results. The variables that resulted in maximum percentage removal were hydrogen peroxide concentration of 4000mg/l, catalyst dosage of 1500m mg/l, reaction time 90 minutes and pH of 3.50. As it can be seen from the following figure, the catalyst has shown a consistently high removal efficiency of phenol (up to 95.192%) when used

repeatedly even after 5 cycles and this reflects on its high reusability of catalyst. Therefore, the removal efficiency of phenol was high enough up to five runs.

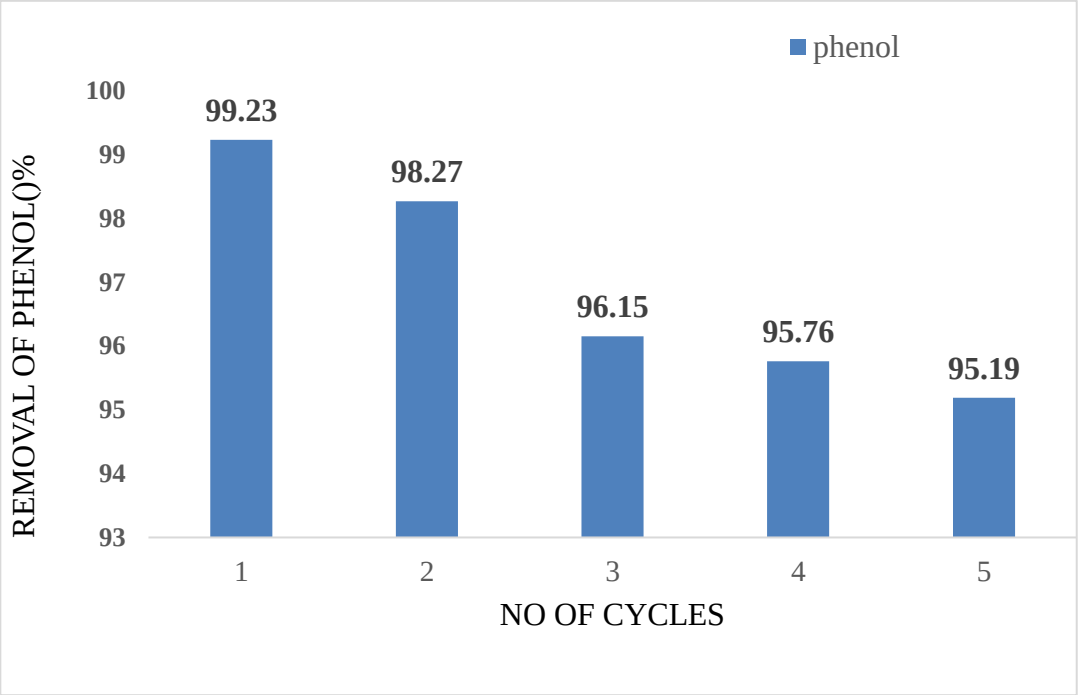


Figure 4.14*.Reusability of catalyst on the removal efficiency of phenol versus the number of cycles*

4.5. Kinetic mineralization of phenol

4.5.1. First order kinetic model

Based on the plot of $-ln\,(\frac{CC6H5O}{CC6H5OHo})$ against time at isothermal temperature, the apparent first-order kinetic rate constant (K'$_1$) and the corresponding correlation coefficients (R^2) of 0.96547 between the experimental and predicted data (Table 4.12), it was observed that the model could well be used to confirm the mineralization process.

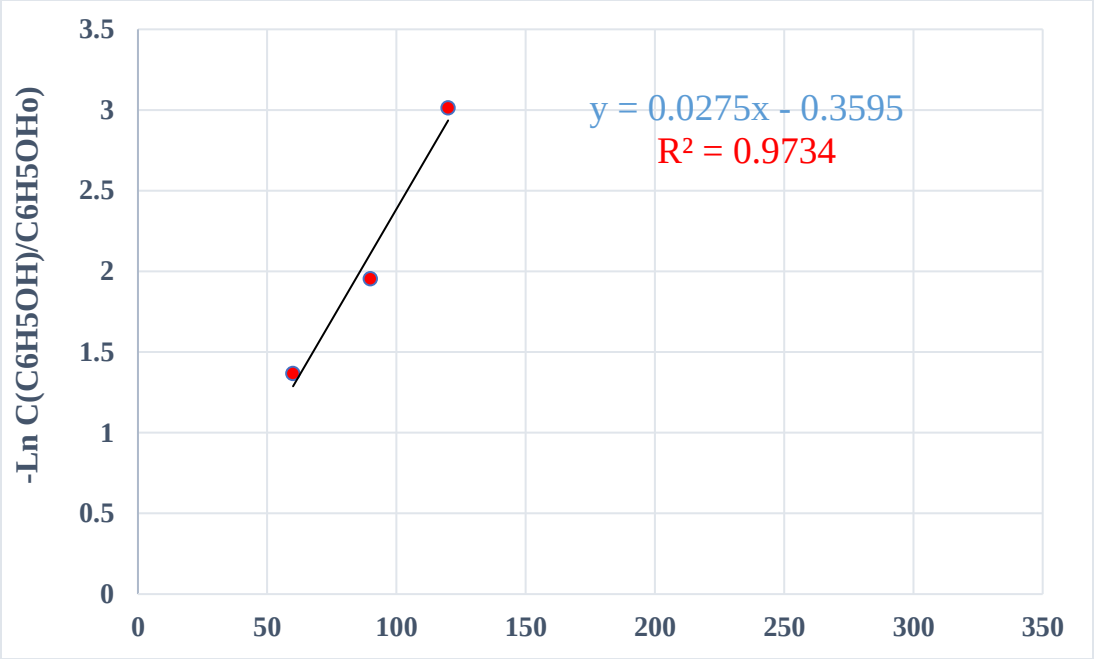


Figure 4.15. Plots for FKM and GLKM kinetic model

Data were fitted to the different models, minimizing the sum of squares error (SSE) between empirical and modeled data. Even though the R-squared and the good agreement the sum of squares error (SSE) suggest explaining the mineralization process by the FKM, the limitation imposed calls for further exploring other robust models in addressing kinetic mineralization of such an intricate compound, with a vast diversity of possible reaction pathways. Moreover, as the mineralization of phenol is attained in multiple stages involving an initial oxidation step leading to the transitional conversion of the contaminants to intermediates and followed by subsequent mineralization of the intermediates to the products, a simple one-step model may not be sufficient hence one or more model was plotted.

4.5.2. Generalized Lumped Kinetic Model (GLKM)

The generalized degradation schemes and kinetic rate constant are shown in Figure 3.5, with K_1', K_2' *and* K_3', and as the apparent first-order kinetic rate constants for the initial oxidation step, the final oxidation step, and the direct conversion to end products

step, respectively. These two equations (3.5 and 3.6) describe the degradation of phenol and intermediates into carbon dioxide and water respectively:

As the mineralization occurs through the transitional conversion to intermediates followed by subsequent mineralization of the intermediates to the products, K_3' is then supposedly to be much smaller than K_1'or $K_2'$and thus neglected. Hence, by rearranging (3.5) and (3.6), the GLKM becomes.

$$\frac{CC6H5OH}{CC6H5OHo} = \frac{K1'}{k2'+k1'+k3'}\ e - k3'\ t\ + \frac{-K2'}{K1'+K2'+K3'}\ e - (K2'\ +\ K3') \qquad (4.7)$$

The logarithmic form of (4.6) becomes the following:

$$ln\ CC6H5OH/CC6H5OHo\ \ = ln\ \ (K1')/(K2')\ -\ ln(K1'\ +\ K2')t \qquad (4.8)$$

The derived Kinetic model equations 4.8 for the isothermal temperature of 25 ℃, the calculations described in Appendix A4

$$lnCC6H5OH = -25.36 - ln(t) \qquad (4.9)$$

From the plot, $-ln\ \frac{CC6H5OH}{CC6H5OHo}$ versus time(Figure 4.15), the rate constants were determined and the computed rate constant values were marginally different suggesting that the reaction Phenol conversion which into intermediates proceeded at the same rate as the conversion of intermediates to CO_2 and H_2O.

Table 4.12. FKM and GLKM kinetic rate constants and statistical data

Parameter	kinetic model	
	FKM	GLKM
Kinetic rate constant		
K_1'(min^{-1})	na	0.491
K_2 '(min^{-1})	na	0.514
K_3' (min^{-1})	0.0045	ng
Statistical indicator		
R^2	0.9808	0.9808
SSE	0.00418	0.00418

na: not applicable; ng: negligible.

4.5.3. Goodness-of-Fit Statistics.

Two descriptive statistical indicators were used to appraise the prediction performance of the proposed models and the produced error in accounting for the kinetic reaction constants and assessing the fit between the experimental data from the models evaluated. The examined indicators were the sum of squares due to error (SSE), and the adjusted R^2.

Based on the results summary (Table 4.12), it is assumed that there were very small deviations in descriptive performance indices of all the models. GLKM only marginally varied with FKM and demonstrated a slightly superior predictive performance on the estimation of mineralization kinetics. Based on the R^2 statistic measure, it is evident that the fit successfully accounted for a greater proportion of variance as all the models explained ≈ 98.49 % for temperature 25 ℃ of the total variation in the data. Only 1.51 % of the total variations were not explained by FKM and GLKM. However, as GLKM contained more coefficients than the FKM, the adjusted R-square statistic, a generally accepted best indicator of the fit is used. Results for SSE show that the total deviation of the response values from the fit-to-the response values measured was acceptable. The lowest values of SSE (0.00418) for GLKM and FKM indicated that the model performed better. This indicated that the model had a smaller random error component and that the fit would be more useful for prediction.

In summary, the results suggest that both the models adequately describe the kinetics. However, the limitation imposed on FKM does not translate to the real-world description of the process. For instance, mineralization was very fast with respect to the other step, as the kinetic rate constant (K_1') is maximum. This clearly indicates that the initial oxidation step leading to transitional conversion of phenol to intermediates is significantly yet not captured in its entirety in FKM (0 min−1). In the same vain, ate constant of the intermediates mineralization to the final products preceded fast too (K_2'). Finally, the direct conversion of phenol to end products step (K_3') which was not possible to be captured was found to be appreciable. It is worth noting that mineralization would not have been possible at the rate computed from

FKM, especially when steady mineralization was observed within 180 min of oxidative treatment period for fast phenol mineralization.

The use of generalized lumped models becomes necessary in certain reactions. This assertion has been collaborated by several researchers who have elucidated that use of FKM cannot adequately describe the kinetics in systems being continuously fed with H_2O_2 (Basheer et al., 2014) for example, monitoring Fenton oxidation in a semi-continuous reactor where the overall amount of H_2O_2 is distributed as a continuous feed upon the reaction time (W. chum, et al., 2005). This study provides useful information on complex synthetic phenol solution treatment by heterogeneous Fenton system, specifically phenol.

5. Conclusion and recommendation

5.1. Conclusions

Rapid population growth coupled with urbanization and industrialization has led to stricter legislation which adds pressure on adequate management of the huge quantities of organic pollutant released from different industries. Phenol is considered as one of the most hazardous organic pollutants due to their poor biodegradability, high toxicity, and ecological aspects. Oxidation processes may destroy phenol and is constituents through oxidation and reduction reactions. The employment of recent technologies with the generic term "advanced oxidation processes" leads to the decomposition and mineralization of many groups of organic materials including phenol. Depending on the chemical structure of the pollutant molecules, AOPs mineralize numerous pollutants into ultimately harmless substances like CO_2 and H_2O. Advanced Oxidation Process using Fenton's process is very effective in the removal of many hazardous organic pollutants from water. In the sense of avoiding ferrous ion precipitation and allowing catalyst recovery, use of solid catalysts in the Fenton's process is endorsed. Therefore, heterogeneous Fenton process which requires supportive material of the catalyst for regeneration is important to overcome this drawback. These improvements were achieved by synthesizing an effective iron impregnated solid catalyst that is active for the mineralization reactions.

The fundamental objective of this study was to the synthesize iron stability, and high by reusability bentonite-based iron catalysts that have high activities for mineralization reactions. However, The high stability of the clay. Condition and its good catalytic performance for the potential of bentonite to adsorb phenol from its synthetic solution. The synthesized catalyst was physically and chemically characterized using pH_{pzc}, bulk density, Fourier Transform-Infrared spectroscopy (FT-IR), X-ray diffractogram (XRD), and Atomic Absorption Spectrometer (AAS).

The mineralization activity of phenol was tested with the major factor that affects the heterogeneous Fenton reaction. Experimental design based three-level-four-full factorial design was employed. All samples were analyzed by using UV-Vis

spectrophotometry using 420 methods at 510 nm. Based on the analysis of experimental results, it was found that all the process variables exhibited a significant interaction effect on the percentage removal of phenol. This shows that the capability of the experimental to successfully capture the effects. A total phenol removal of 98.64 % was obtained at concentration of hydrogen peroxide of 4136.99 mg/L, catalyst dosage of 1445.18, reaction time of 85.45 min and pH of a solution 3.43. The experimental tests were performed to determine the significance of independent variables on the response function. The ANOVA showed a satisfactory prediction second-order regression model and a high determination coefficient value (R^2= 0.9977, Pred R^2= 0.9892, Adj R^2 = 0.9953) for the removal of phenols. The ANOVA analysis showed that the removal efficiency of phenol of was highly affected by the concentration of hydrogen peroxide with catalyst dosage, the concentration of hydrogen peroxide with reaction time and concentration of hydrogen peroxide with a solution of pH. The overall results obtained showed that bentonite is a cheap and easily available material in large quantity which can be used as an iron support catalyst for the removal of phenols from its synthetic solution. Bentonite support iron catalyst employed in this heterogeneous process has been shown to be a potential catalyst for the removal of phenol from synthetic solution.

5.2. Recommendations

Further studies are needed to better understand the behavior and to investigate the Commercial application of the bentonite support iron catalyst (Fe/bent), such as

- The selection of prepared catalyst were performed only based on iron leachate, reusability and D-optimal experimental design with the ratio of iron to bentonite and calcination temperature optimization of the catalyst but selection of the catalyst based, on the surface area, pore size and the activity each catalyst in the reaction by varying different process variables like pH, calcination time are very important concepts not covered in this study which needs further investigations.
- More research is necessary to predict the performance of bentonite support iron catalyst for phenol removal from actual effluent under a wide range of operation conditions.
- Other factors which are not addressed by this study such as temperature, shaking speed and initial concentration of phenol that had been taken as constant can be considered and thermodynamic evaluation can be conducted.
- It is suggested to perform preliminary design, economic feasibility study and establish an economic scale for bentonite support iron catalyst manufacturing unit.

Reference

Ajemba, R. O. (2016). *Kinetics and equilibrium modeling of lead (II) and chromium (III) ions ' adsorption onto clay from Kono-bowe , Nigeria*. (2014), 455–479.

Albergamo, Vittorio, Blankert, Bastiaan, Cornelissen, R, E, De. (2019). Removal of polar organic micropollutants by pilot-scale reverse osmosis drinking water treatment. *Water Research*, *148*, 535–545.

Araújo, B., Miguel, Alagador, Diogo, Cabeza, Wilfried. (2011). Climate change threatens European conservation areas. *Ecology Letters*, *14*(5), 484–492.

Ayaria, F, E, Srasrab, M, Trabelsi, & Ayadi. (2005). Characterization of bentonitic clays and their use as adsorbent. *Desalination*, *185*(1–3), 391–397.

Babuponnusami, Arjunan, Muthukumar, & Karuppan. (2014). Journal of Environmental Chemical Engineering A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering*, *2*(1), 557–572.

Baker, J., M., Trevisan, Júlio, Bassan, Paul,L. (2014). Using Fourier transform IR spectroscopy to analyze biological materials. *Nature Protocols*, *9*(8), 1771–1791

Banat, F.A., Al-Bashir, B., Al-Asheh, S.,O. (2000). Adsorption of phenol by bentonite - ScienceDirect. *Environmental Pollution*, *107*(3), 391–398. Basheer, Aziz, Abdul, Raman, Abdul, Mohd, Ashri. (2014). *Kinetic Modeling of a Heterogeneous Fenton Oxidative Treatment of Petroleum Refining Wastewater*. *2014*.

Bravo, Suárez, J, Juan, Chaudhari,V, & Raghunath. (2013). *Design of heterogeneous catalysts for the conversion of biomass-derived compounds into fuels and chemicals*.

Busca, Guido, Berardinelli, Silvia, Resini, Carlo,Laura. (2008). *Technologies for the removal of phenol from fluid streams : A short review of recent developments*. *160*, 265–288.

Centi, G, Ciambelli, P, Perathoner, S, P. (2002). *Environmental catalysis : trends and outlook*. *75*(x), 3–15.

Chaplin, B. P. (2014). Critical review of electrochemical advanced oxidation processes for water treatment applications. *Environmental Sciences: Processes and Impacts*, *16*(6), 1182–1203.

Charoenbut, Pattaraporn, Klaewkla, Jeeranun, Srisorrachatr, & Suwat. (2018). *Workplace and individual factors influence eating practices of Thai factory workers*. *24*(3), 417–426.

Chedeville, Olivier, Tosun, Bayraktar, Ayse, Porte, & Catherine. (2005). *Modeling of Fenton Reaction for the Oxidation of Phenol in Water*. *2005*(2), 31–36.

Chen, Yizhong, Zhao, Honghai, Tian, Peipei, .Liang. (2018). Game-based analysis of energy-water nexus for identifying environmental impacts during Shale gas operations under stochastic input. *Science of the Total Environment*, *627*, 1585–1601.

Ciambelli, Paolo, Ruiz, & Patricio.(2002). *Outlooks for environmental catalysis*.*75*, 1–2.

Commission, & European. (n.d.). *Pollutants in urban waste*.

Djeffal, Lemya, Abderrahmane, Sihem, Benzina, Mourad, Sophie. (2014). Efficient degradation of phenol using natural clay as heterogeneous Fenton-like catalyst. *Environmental Science and Pollution Research*, *21*(5), 3331–3338.

Faisal, I, & Btihage. (2009). *Oxidation of Phenolic Wastewater by Fenton â€™ s Reagent*. *10*(2), 1–5.

Falconer, R, I., Chapman, F, H., Moore, R, M., Geetha. (2006). *Endocrine-Disrupting Compounds : A Review of Their Challenge to Sustainable and Safe Water Supply and Water Reuse*. 181–191.

Feng, Jiyun, Hu, Xijun, Yue, & Lock, P. (2005). Discoloration and mineralization of Orange II by using a bentonite clay-based Fe nanocomposite film as a heterogeneous photo-Fenton catalyst. *Water Research*, *39*(1), 89–96.

Fenton, H. J. H. (1894). Oxidation of Tartaric Acid in Presence of Iron. *Journal of the Chemical Society*, *Vol. 65*, 899–910.

Frontistis, Z., Meriç, S., Mantzavinos, D., Antonopoulou, M., Özkal, C. B., & Konstantinou, I. (2017). Removal of antibiotics in a parallel-plate thin-film-photocatalytic reactor: Process modeling and evolution of transformation by-products and toxicity. *Journal of Environmental Sciences*, *60*, 114–122.

Gao, Y., Guo, Y., & Zhang, H. (2016). Iron modified bentonite : Enhanced adsorption performance for organic pollutant and its regeneration by heterogeneous visible light photo-Fenton process at circumneutral pH. *Journal of Hazardous Materials*, *302*, 105–113.

Gao, Yaowen, Guo, Yongzhao, Zhang, & Hui. (2016). Iron modified bentonite: Enhanced adsorption performance for organic pollutant and its regeneration by heterogeneous visible light photo-Fenton process at circumneutral pH. *Journal of Hazardous Materials*, *302*, 105–113.

Garrido, Ramírez, G., E, Theng, K.G., M. (2010). Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions - A review. *Applied Clay Science*, *47*(3–4), 182–192.

Gil, Antonio, Korili, A., Sophia, Trujillano, Angel. (2010). Pillared clays and related catalysts. In *Pillared Clays and Related Catalysts*.

Gilmour, C. (2012). *Water Treatment Using Advanced Oxidation Processes : Application Perspectives by*. (September).

Green, Ben, Griffiths, Emily, Almond, & Solomon. (2017). Neuropsychiatric symptoms following metal-on-metal implant failure with cobalt and chromium toxicity. *BMC Psychiatry*, *17*(1), 1–5.

Gunst, Richard, F., Myers, Raymond, H., C. (2006). Response Surface Methodology: Process and Product Optimization Using Designed Experiments. *Technometrics*, *38*(3), 285.

Huang, W. (2013). *Homogeneous and heterogeneous Fenton and photo-Fenton processes : impact of iron complexing agent ethylenediamine-N , N ' -disuccinic acid (EDDS) Wenyu Huang To cite this version : HAL Id : tel-00788822 Diplômée de Master Homogeneous and heterogeneous F*.

Jarrah, Nabeel, Zubair, Mukarram, Alagha, & Omar. (2017). *Removal of Phenolic Compounds from Water Using Sewage Sludge-Based Activated Carbon Adsorption : A Review*. 1–34.

Kaolinite, I. (2002). *Chapter 6 Porosity Studies of Kaolinite and Bentonite Clay*. *5*.

Katzer, J. R. (2005). Catalytic Oxidation of Phenol in Aqueous Solution over Copper Oxide. *Industrial & Engineering Chemistry Fundamentals*, *17*(3), 234–234.

Kavitha, V., Palanivelu, & K. (2005). Destruction of cresols by Fenton oxidation process. *Water Research*, *39*(13), 3062–3072.

Khelifi, S. (2016). *Chemical Engineering & Process Technology Synthesis and Characterization of Heterogeneous Catalysts and Comparison to Iron-ore.7*(5).

Klauck, C. R., Giacobbo, A., Altenhofen, C. G., Silva, L. B., Meneguzzi, A., Bernardes, A. M., & Rodrigues, M. A. S. (2017). Toxicity elimination of landfill leachate by hybrid processing of advanced oxidation process and adsorption. *Environmental Technology and Innovation*, *8*, 246–255.

Krishnan, S., Rawindran, H., Sinnathambi, C., M., W. (2017). Comparison of various advanced oxidation processes used in remediation of industrial wastewater laden with recalcitrant pollutants. *IOP Conference Series: Materials Science and Engineering*, *206*(1).

Kuan, Chi, C., Chang, Sin, Yuen, Schroeder, & L.M., S. (2015). Fenton-like oxidation of 4-chlorophenol: Homogeneous or heterogeneous? *Industrial and Engineering Chemistry Research*, *54*(33), 8122–8129.

Kulik, N. (2008). *The Application of Fenton-Based Processes for Wastewater and Soil TreatmentNiina Kulik Tallinn 2008*.

Kuma, P. (2010). *Remediation of High Phenol Concentrations Using Chemical and Biological Technologies*. (September).

Kurnik, Katarzyna, Treder, Krzysztof, Skorupa, Kłaput, Jarosław. (2015). Removal of Phenol from Synthetic and Industrial Wastewater by Potato Pulp Peroxidases. *Water, Air, and Soil Pollution*, *226*(8).

Liu, Q., Yang, M., Zou, J., Wang, K., Zhu, L., Ma, J., & Komarneni, S. (2015). Visible light photocatalytic activity enhancement of Ag 3 PO 4 dispersed on exfoliated bentonite for degradation of rhodamine B. *Applied Catalysis B: Environmental*, *182*, 26–32.

Ltd, I. C. (2001). Pollutants in urban waste and sewage sludge. In *Reproduction*.

Madeira, L. M. (n.d.). *Use of Pillared Clay-Based Catalysts for Wastewater Treatment Through Fenton-Like Processes*.

Martin, K., A., Milne, A., J., Moberly, & P. (2005). The origin of urinary aromatic compounds excreted by ruminants. *British Journal of Nutrition*, *49*(1), 87.

Martínez, Huitle, A., Carlos, Ferro, & Sergio. (2006). Electrochemical oxidation of organic pollutants for the wastewater treatment: Direct and indirect processes. *Chemical Society Reviews*, *35*(12), 1324–1340.

Matavos, Aramyan, Sina, Moussavi, & Mohsen. (2017). *Advances in Fenton and Fenton Based Oxidation Processes for Industrial Effluent Contaminants Control-A Review*. *2*(4).

Mehrjouei, M. (2012). *Advanced oxidation processes for water treatment : Reactor design and case studies*. (September 1977).

Miao, Xiaozeng, Dai, Huiwang, Chen, Jianxin, Jianxi. (2018). Separation and Puri fi cation Technology The enhanced method of hydroxyl radical generation in the heterogeneous UV-Fenton system with α -FeOOH as catalyst. *Separation and Purification Technology*, *200*(December 2017), 36–43.

Mora. (2016). *Fenton-Like Processes Using Iron Oxide Magnetic*. (May).

Mora, E. G. G.-R. and B. K. . T. and M. L. (2010). Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions. *Applied Clay Science*, *47*, 182--192.

Moreau, & Kathi. (2012). *Home schooled vs. public schooled: Specific differences in the educational outcomes of those students who are home schooled vs. students in a traditional school setting*. 1–34.

Muruganandham, M., Suri, R. P. S., Jafari, S., Sillanpää, M., Lee, G., Wu, J. J., & Swaminathan, M. (2014). *Recent Developments in Homogeneous Advanced Oxidation Processes for Water and Wastewater Treatment*. *2014*.

Navalon, Sergio, Alvaro, Mercedes, Garcia, & Hermenegildo. (2010).Heterogeneous Fenton catalysts based on clays, silicas and zeolites. *Applied Catalysis B: Environmental*, *99*(1–2), 1–26.

Nawrocki, J., & Kasprzyk-hordern, B. (2010). Applied Catalysis B : Environmental The efficiency and mechanisms of catalytic ozonation. *"Applied Catalysis B, Environmental," 99*(1–2), 27–42.

Ncibi, M. C., & Matilainen, A. (2018). *Advanced oxidation processes for the removal of natural organic matter from drinking water sources : A comprehensive review*. *208*.

Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater.*, *98*, 33–50.

Nidheesh, P. V. (2015). RSC Advances Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution : a review. *RSC Advances*, *5*(6), 40552–40577.

Onyekwere, F., Oluwaseun, N., Ajala, J., Motunrayo, R., Bukola, O., & Raheem, G. (2018). Preparation and characterization of adsorbents derived from bentonite and kaolin clays. *Applied Water Science*, *8*(7), 1–10.

Pariente, Isabel, M., Martínez, Fernando, Botas, Ángel, J., Antonio. (2015). *Extrusion of Fe $_2$ O $_3$ / SBA-15 mesoporous material for application as heterogeneous Fenton-like catalyst*. *2*(2), 154–168.

Pawar, V., & Gawande, S. (2015). *An overview of the Fenton Process for Industrial Wastewater JSPM ' S Rajarshi Shahu College Of Engineering , Pune -33 , Maharashtra , India*. 127–136.

Perathoner, S., & Russo, P. (2002). *Environmental catalysis : trends and outlook*. *75*(x), 3–15.

Petr, K., Št, H., Kou, K., Št, J., Procházka, V., Jan, H., & Med, I. (2013). *Bentonite / Iron Oxide Composites : Preparation and Characterization by Hyperfine Methods*. *2013*.

Pigatto, Gisele, Lodi, Alessandra, Finocchio, Elisabetta, Attilio. (2013). Chitin as biosorbent for phenol removal from aqueous solution: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering and Processing: Process Intensification*, *70*, 131–139.

Pines, E. (2003). *The Chemistry of Phenols, Chapter 7*.

Plgnatello, J. J. (1992). *Dark and Photoassisted Fe3+-Catalyzed Degradation of Chlorophenoxy Herbicides by Hydrogen Peroxide*. *26*(5), 944–951.

Pozan, G. S., & Kambur, A. (2014). Effect of operating parameters and titanium source on photodegradation of phenol. *Indian Journal of Chemical Technology*, *21*(4), 272–279.

Rey, D. R. (2015). *Master Study of Chemical Engineering Application of Heterogeneous Fenton Oxidation for The Removal of Pollutants From*. (May).

Rey, & Rodríguez, D. (2015). *Master study ofChemical Engineering Application of Heterogeneous Fenton oxidation for The Removal of Pollutants from*. (May).

Rietjens, M, C., M, C., Rietjens, M, Ivonne, Karsten. (2016). *The potential health effects of dietary phytoestrogens Correspondence Professor Ivonne*

Rizzo, & Luigi. (2011). Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. *Water Research*, *45*(15), 4311–4340.

Rokhina, E. V. (2009). *Heterogeneous Ruthenium-Based Catalytic Systems in Wet Peroxide Oxidation of Organic Compounds*.

Rossi, A. (2014). *Fenton's Process Applied to Wastewaters Treatment*.

Ruiz, C. S. (2015). *Fenton reactions*. (November).

Ryan, Daniel, Leukes, Winton, Burton, & Stephanie. (2007). Improving the bioremediation of phenolic wastewaters by Trametes versicolor. *Bioresource Technology*, *98*(3), 579–587.

Saitoh, Tohru, Sugiura, Yusuke, Asano, Kotaro, Masataka. (2009). Reactive & Functional Polymers Chitosan-conjugated thermo-responsive polymer for the rapid removal of phenol in water. *Reactive and Functional Polymers*, *69*(10), 792–796.

Saleh, S., Aye, Younis, Alaa, Ali, Reham, Eman. (2019). Phenol removal from aqueous solution using amino modified silica nanoparticles. *Korean Journal of Chemical Engineering*, *36*(4), 529–539.

Shah, I., Adnan, R., Saime, W., Ngah, W., & Mohamed, N. (2015). *Iron Impregnated Activated Carbon as an Efficient Adsorbent for the Removal of Methylene Blue : Regeneration and Kinetics Studies*. 1–23.

Shokri, & Aref. (2018). Application of Sono – photo - Fenton process for degradation of phenol derivatives in petrochemical wastewater using full factorial design of experiment. *International Journal of Industrial Chemistry*, *9*(4), 295–303.

Silva, Larissa, S, L., Moreira, G, C., Curzio, V, F. (2017). *Micropollutant Removal from Water by Membrane and Advanced Oxidation Processes -A Review*. 411–431.

Stern, A., W., Lewis, J., R., Thompson, & S., K. (2014). Toxic Smoke Inhalation in Fire Victim Dogs. *Veterinary Pathology*, *51*(6), 1165–1167.

Tekindal, Mustafa, Agah, Hulya, Baypark, Berrin, Genc. (2012). Box- Behnken Experimental Design in Factorial Experiments : the Importance of Bread for Nutrition. *Turkish Journal of Field Crops*, *17*(2), 115–123.

Tengrui, Long, Anas, Al, Harbawi, Jun, Ming. (2007). *reaction time.pdf* (pp. 724–727). pp. 724–727.

Tomul, & Fatma. (2016). The effect of ultrasonic treatment on iron-chromium pillared bentonite synthesis and catalytic wet peroxide oxidation of phenol. *Applied Clay Science*, *120*, 121–134.

Toor, M. K. (2010). *Enhancing Adsorption Capacity of Bentonite for Dye Removal : Physiochemical Modification and Characterization Thesis submitted for the degree of Masters in Engineering Science School of Chemical Engineering October 2010*. (October).

Toulouse, I. N. P. (2016). *Doctorat De L â€™ Université De Toulouse Délivré Par*.

U.o.aroke, & A. A., & R.O.Ogubunka. (2001).

Andrés Almeida, J. M. (2012). A ferrous oxalate mediated photo-Fentonsystem:

Toward an increased biodegradability of indigo dyed wastewaters. *Journal of Hazardous Materials*, *243*, 293–301. Retrieved from

Vessal, A. (2017). *Iron Removal from Acid Mine Drainage Using Activated Bentonite Clay*. *II*.

Vimonses, Vipasiri, Lei, S., Haomin, Jin, Bo, Chris. (2009). Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. *Chemical Engineering Journal*, *148*(2–3), 354–364.

Wang, S. (2008). A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. *Dyes and Pigments*, *76*(3), 714–720.

Wu, Kaiqun, Xie, Yinde, Zhao, Jincai, Hisao. (1999). Photo-Fenton degradation of a dye under visible light irradiation. *Journal of Molecular Catalysis A: Chemical*, *144*(1), 77–84.

Xiong, Xingaoyuan, Wang, Bing, Zhu, Wei, Huan. (2018). A Review on Ultrasonic Catalytic Microbubbles Ozonation Processes: Properties, Hydroxyl Radicals

Generation Pathway and Potential in Application. *Catalysts*, *9*(1), 10.

Xu, Huan-yan, He, Xiu-lan, Wu, Ze, … Wei-dong. (2009). *Iron-loaded Natural Clay as Heterogeneous Catalyst for Fenton-like Discoloration of DyeingWastewater*. *30*(10).

Ywet, Maleterova, Ta, Martina, Matejkova, Katerina, Solcova. (2016).

Biodegradation of Phenol Adsorbed on Soil in The Presence of Polycyclic Aromatic Hydrocarbons. *3*(1), 87–98.

Zeni, & Leiliane. (2012). Analytical Methods for Performing Pesticide Degradation Studies in Environmental Samples. *Pesticides - Formulations, Effects, Fate*, (January 2011).

Zepp, G, Richard, Faust, C, Bruce, .Juerg. (1992). Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction. *Environmental Science & Technology*, *26*(2), 313–319.

Appendix

Appendix A1. Absorbance of the standard phenol solution used to plot a calibration curve

Label	Concentration (mg/l)	Absorbance
0	0	0
1	20	0.252
2	40	0.255
3	60	0.403
4	80	0.526
5	90	0.577

Appendix A2. Batch Experiment Results

Lable	Absorbance	Final concentration of phenols	Dilution factor	Removal efficiency of phenol (%)
1	0.075	11.3846	113.846	85.76
2	0.141	21.5384	215.384	73.07
3	0.077	11.6923	116.9230	85.38
4	0.119	18.1538	181.5384	77.30
5	0.103	15.6923	156.923	80.38
6	0.085	12.9230	129.230	83.84
7	0.061	9.2307	92.307	88.46
8	0.041	10	100	92.30
9	0.038	5.6923	56.923	92.88
10	0.088	13.3846	133.8461	83.26

11	0.112	17.077	170.77	78.65
12	0.106	16.1538	161.5384	79.8
13	0.049	7.3846	73.846	90.76
14	0.059	8.923	89.2307	88.84
15	0.073	11.077	110.77	86.15
16	0.064	9.6923	96.9230	87.88
17	0.062	9.3846	93.846	88.26
18	0.043	6.461	64.615	91.92
19	0.005	0.6153	6.1538	99.23
20	0.044	6.6153	66.1538	91.73
21	0.123	18.769	187.6923	76.53
22	0.132	20.1538	201.538	74.8
23	0.046	6.9230	69.230	91.34
24	0.063	9.5384	95.3846	88.07
25	0.081	12.307	123.076	84.42
26	0.056	8.4615	84.6153	89.42
27	0.081	12.307	123.076	84.61
28	0.129	19.6923	196.923	75.38
29	0.134	20.4615	204.6153	74.42

Appendix B. Bulk density of raw and calcinated bentonite

$$\text{Bulk density (BD)} = \frac{weight\ of\ the\ sample\ (g)}{volume\ of\ the\ sample\ (ml)}$$

$$BD_{RB1} = \frac{0.903g}{2.0ml} = 0.4515\ \text{g/ml}$$

$$BD_{RB2} = \frac{1.1565g}{2.4ml} = 0.481875\ \text{g/ml}$$

$BD_{RB3} = \frac{1.4359g}{3.0ml} = 0.478633$ g/ml

$BD_{RB4} = \frac{1.7089g}{3.4ml} = 0.502617647$ g/ml

$BD_{CB1} = \frac{0.88665g}{1.8ml} = 0.492583333$ g/ml

$BD_{CB2} = \frac{1.05425\ g}{2.2ml} = 0.479204545$ g/ml

$BD_{CB3} = \frac{1.6339\ g}{3.2ml} = 0.51059375$ g/ml

$BD_{CB4} = \frac{1.98585g}{3.8ml} = 0.522592105$ g/ml

Appendix C. Variation of pHi and ΔpH at 0.1MNaCl concentrations

Raw bentonite (0.1MNaCl)			Bentonite support iron catalyst(0.1MNaCl)	
Phi	Phf	Δph (phi-phf)	Phf	ΔpH (phi-phf
2	4.28	-2.28	2.37	-0.37
4	7.17	-3.17	5.38	-1.38
6	7.65	-1.65	6.65	-0.65
8	7.74	0.16	6.25	1.75
10	8.14	1.86	7.98	2.02

The calculation for Kinetic model

Appendix D. Data used for kinetic models

	Unit	@ 25℃		
Time(min)	min	60	90	120
$\ln\frac{CC6H5OH}{CC6H5OHo}$	$\frac{mg}{l}$	0.227751	0.325735	0.502313

By using the above kinetic model's data drived the following kinetic model equation for the given temperature (@ 25℃) at the initial concentration of phenols=554.0205128 mg/l

From the kinetic model equation(4.7), $\ln \frac{CC6H5OH}{CC6H5OHo} = \ln \frac{K1'}{K2'} - \ln(K_1' + K_2')t$

Slope= 0.0045= $- \ln(K_1' + K_2')$

$K_1' + K_2' = 1.0045104$

Intercept = $ln\frac{K1'}{K2} = -0.0479$

$\frac{K1'}{K2'} = 0.953229105$

$K_1 = 0.953229105\ k_2$

$K_1' + K_2' = 1.0045104$

$0.953229105\ k_2 + K_2' = 1.0045104$

$K_2(0.953229105+1) = 1.0045104$

$K_2 = \frac{1.0045104}{1.953229105} = 0.514281912\ min^{-1}$

$K_1 = 0.953229105k2$

$K_1 = 0.953229105 * 0.514281912$

$= 0.490228487\ min^{-1}$

Then the equation become: $\ln CC_6H_5OH = -25.36 - \ln t$

Appendix E. D- Optimal experiment for selection of mixing ratio and calcination temperature

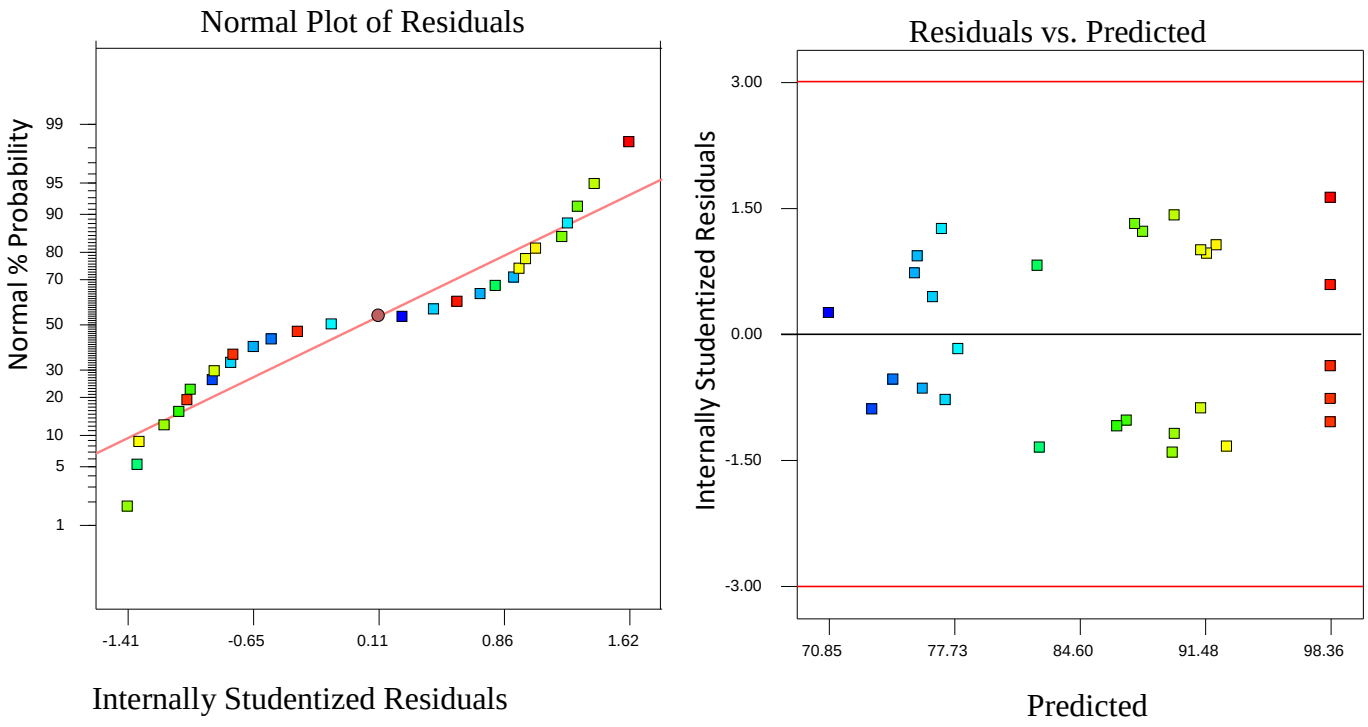
Std	Run	block	Factor 1 A-Temperature	Factor-2 BRatio(Fe:bent, %wt)	Response 1 Removaof phenol (%)	Response 2 TOC Reduction
2	1	Block 1	500.00	0.20	96.35	99.25
10	2	Block 1	400.00	0.03	60.71	91.875
12	3	Block 1	600.00	0.03	63.57	86.875

4	4	Block 1	400.00	0.10	67.44	95.275
3	5	Block 1	600.00	0.20	68.5	89.625
6	6	Block 1	600.00	0.10	64.87	89.71
7	7	Block 1	400.00	0.05	62.07	93.375
11	8	Block 1	500.00	0.03	74.57	95.65
9	9	Block 1	600.00	0.05	61.27	87.35
5	10	Block 1	500.00	0.10	80.05	96.75
1	11	Block 1	400.00	0.20	78.8	92.91
8	12	Block 1	500.00	0.05	79	94.34

Appendix F. Results of the constituted synthetic phenol solution by Box–Behnken design of experiments

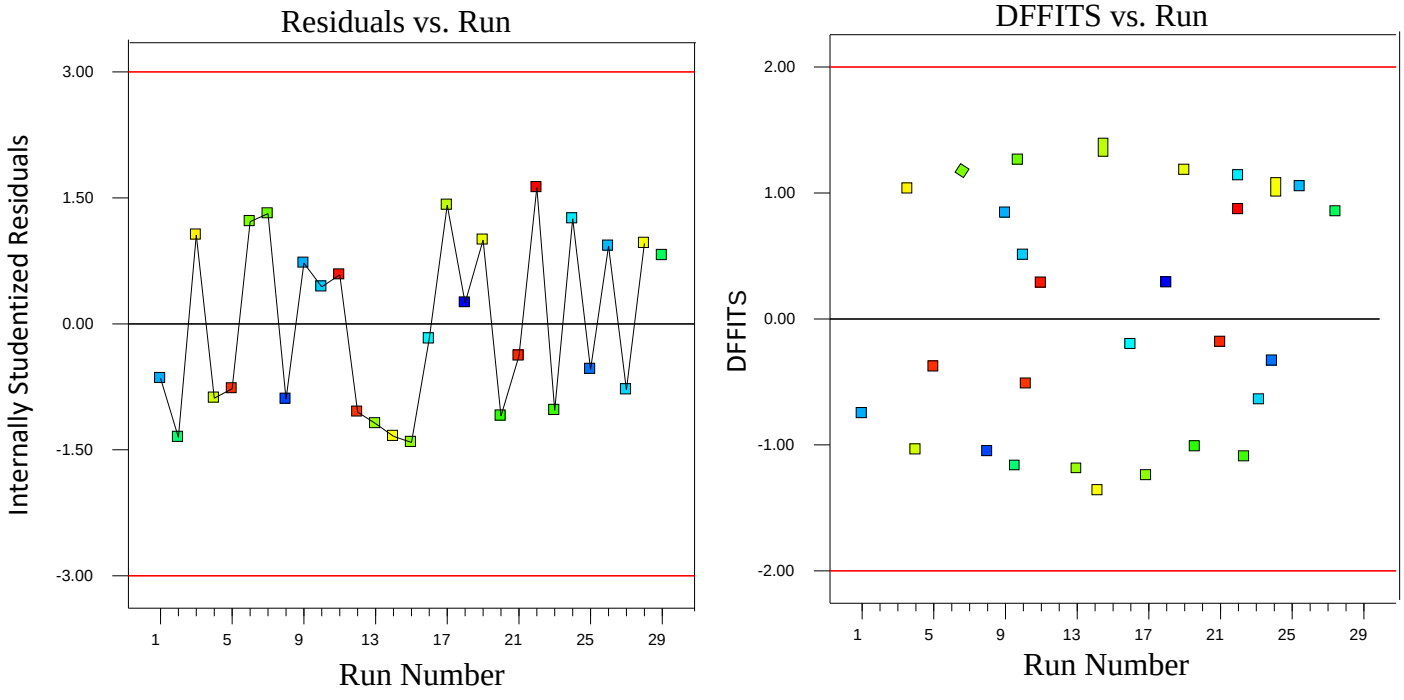
Std	Run	Factor 1 A-H_2O_2	Factor 2 B-catalyst dosage(mg/l)	Factor 3 C-Time	Factor 4 D-pH	Experimentally Removal	Predicted Value	Residual
12	1	6000.00	1500.00	90.00	4.00	85.76	85	0.76
18	2	6000.00	1500.00	60.00	3.50	73.07	74.17	-1.10
5	3	4000.00	1500.00	60.00	3.00	85.38	87.06	-1.68
15	4	4000.00	1000.00	120.00	3.50	77.30	79.66	-2.36
26	5	4000.00	1500.00	90.00	3.50	80.38	78.03	1.77
7	6	4000.00	1500.00	60.00	4.00	83.84	82.16	1.68
23	7	4000.00	1000.00	90.00	4.00	88.46	86.08	2.38
1	8	2000.00	1000.00	90.00	3.50	92.30	94.94	-2.64
9	9	2000.00	1500.00	90.00	3.00	92.88	94.02	-1.14
20	10	6000.00	1500.00	120.00	3.50	83.26	82.57	0.69
27	11	4000.00	1500.00	90.00	3.50	78.65	78.03	0.62
25	12	4000.00	1500.00	90.00	3.50	79.8	78.03	1.77
6	13	4000.00	1500.00	120.00	3.00	90.76	89.57	1.19
13	14	4000.00	1000.00	60.00	3.50	88.84	86.68	2.16
22	15	4000.00	2000.00	90.00	3.00	86.15	87.55	-1.4
10	16	6000.00	1500.00	90.00	3.00	87.88	87.78	0.10
16	17	4000.00	2000.00	120.00	3.50	88.26	91.15	-2.89
11	18	2000.00	1500.00	90.00	4.00	91.92	92.40	-0.48
21	19	4000.00	1000.00	90.00	3.00	99.23	96.30	2.93
24	20	4000.00	2000.00	90.00	4.00	91.73	93.37	1.64
29	21	4000.00	1500.00	90.00	3.50	76.53	78.03	-1.50
28	22	4000.00	1500.00	90.00	3.50	74.8	78.03	-3.23

8	23	4000.00	1500.00	120.00	4.00	91.34	90.06	1.28
19	24	2000.00	1500.00	120.00	3.50	88.07	86.19	1.88
17	25	2000.00	1500.00	60.00	3.50	84.42	84.19	0.23
4	26	6000.00	2000.00	90.00	3.50	89.42	87.39	2.03
3	27	2000.00	2000.00	90.00	3.50	84.61	82.67	1.94
14	28	4000.00	2000.00	60.00	3.50	75.38	73.73	1.65
2	29	6000.00	1000.00	90.00	3.50	74.42	76.58	-2.16



a) **b**)

Appendix G. **Normal Plot of residuals and (b) residual vs. predicted**

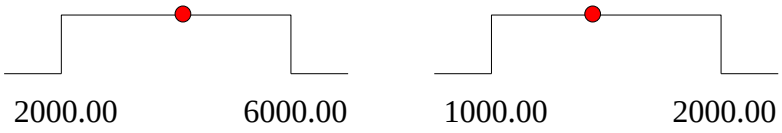


(a) **(b)**

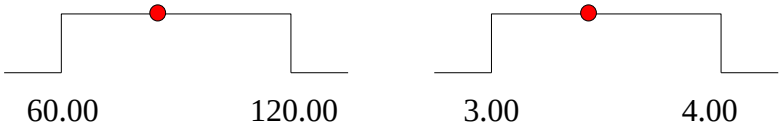
Appendix H. Plots of (a) Residuals vs. Run and (b) DFFITS vs. Run

Appendix I. Sequential Model Sum of Squares [Type I] model fittings

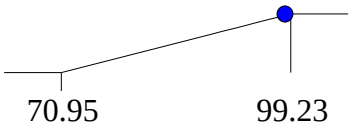
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Mean vs Total	2.136E+005	1	2.136E+005		
Linear vs Mean	88.34	4	22.08	0.26	0.9037
2FI vs Linear	48.76	6	8.13	0.072	0.9981
Quadratic vs 2FI	2023.83	4	505.96	1395.49	< 0.0001
Suggested					
Cubic vs Quadratic	3.67	8	0.46	1.96	0.2134
Aliased					
Residual	1.40	6	0.23		
Total	2.158E+005	29	7439.94		



Hydrogen peroxide = 4137.21 Catalyst dosage = 1445.41



Time = 85.47 pH = 3.43



Desirability = 0.979

Removal of phenol = 98.6369

Report of desirability ramps

Appendix J . Method 420.1: Phenolics (Spectrophotometric, Manual 4-AAP With Distillation**)**

METHOD #: 420.1: Approved for NPDES (Editorial Revision 1978)

TITLE: Phenolics (Spectrophotometric, Manual 4-AAP With Distillation)

ANALYTE: Phenolics:

INSTRUMENTATION: Spectrophotometer

STORET No.: 32730

1 Scope and Application

1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials at the 5 µg/L level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

1.3 The method is capable of measuring phenolic materials that contain more than 50 µg/L in the aqueous phase (without solvent extraction) using phenol as a standard.

1.4 It is not possible to use this method to differentiate between different kinds of phenol.

2.0 Summary of Method

2.1 Phenolic materials react with 4-amino anti pyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored anti pyrene dye. The amount of color produced is a function of the concentration of phenolic material.

3.0 Comments

3.1 For most samples a preliminary distillation is required to remove interfering materials.

3.2 Color response of phenolic materials with 4-amino antipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason, phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

4.0 Sample Handling and Preservation

4.1 Biological degradation is inhibited by the addition of 1 g/L of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 4°C and analyzed within 24 hours after collection.

5.0 Interference

5.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_3 PO4 and aerating briefly by stirring and adding $CuSO_4$

5.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (**7.10**). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

6.0 Apparatus

6.1 Distillation apparatus, all glass consisting of a 1 liter Pyrex distilling apparatus with Graham condenser.

6.2 pH meter.

6.3 Spectrophotometer, for use at 460 or 510 nm.

6.4 Funnels.

6.5 Filter paper.

6.6 Membrane filters.

6.7 Separators funnels, 500 or 1,000 mL.

6.8 Nessler tubes, short or long form.

7.0 Reagents

7.1 Phosphoric acid solution, 1 + 9: Dilute 10 mL of 85% H_3 PO_4 to 100 mL with distilled water.

7.2 Copper sulfate solution: Dissolve 100 g CuSO4•5H $_2$O in distilled water and dilute to 1 liter.

7.3 Buffer solution: Dissolve 16.9 g NH_4 Cl in 143 mL conc. NH_4 OH and dilute to 250 mL with distilled water. Two mL should adjust 100 mL of distillate to pH 10.

7.4 Amino anti pyrine solution: Dissolve 2 g of 4AAP in distilled water and dilute to100 mL.

7.5 Potassium ferricyanide solution: Dissolve 8 g of $K_3Fe(CN)6$ in distilled water and dilute to 100 mL.

7.6 Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled distilled water and dilute to 1 liter. 1 mL = 1 mg phenol.

7.7 Working solution A: Dilute 10 mL stock phenol solution to 1 liter with distilled water. 1mL = 10 µg phenol.

7.8 Working solution B: Dilute 100 mL of working solution A to 1000 mL with distilled water. 1 mL = 1 µg phenol.

7.9 Chloroform

7.10 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 mL distilled water containing 1 mL conc. H_2SO_4 and dilute to 1 liter with freshly boiled and cooled distilled water.

8.0 Procedure

8.1 Distillation

8.1.1 Measure 500 mL sample into a beaker. Lower the pH to approximately 4 with 1 + 9 H_3PO_4 **(7.1**), add 5 mL CuSO4 solution (7.2) and transfer to the distillation apparatus. Omit to add H_2PO_4 and CuSO4 if the sample was preserved as described in **4.1**.

8.1.2 Distill 450 mL of sample, stop the distillation, and when boiling ceases add 50 mL of warm distilled water to the flask and resume distillation until 500 mL have been collected.

8.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

8.2 Direct photometric method

8.2.1 Using working solution A (7.7), prepare the following standards in 100 mL volumetric flasks.

mL of working solution A	Conc. µg/L
0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0

8.0	800.0
10.	1000.0

8.2.2 To 100 mL of distillate or an aliquot diluted to 100 mL and/or standards, add 2 mL of buffer solution **(7.3)** and mix. The pH of the sample and standards should be **10 ± 0.2.**

8.2.3 Add 2.0 mL amino anti pyrine solution **(7.4**) and mix.

8.2.4 Add 2.0 mL potassium ferri cyanide solution (**7.5)** and mix.

8.2.5 After **15** minutes read absorbance at **510** nm.

8.3 Chloroform extraction method

8.3.1 Using working solution B **(7.8),** prepare the following standards. Standards may be prepared by pipetting the required volumes into the separatory funnels and diluting to 500 mL with distilled water.

mL of working solution B	Conc. µg/L
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

8.3.2 Place 500 mL of distillate or an aliquot diluted to 500 mL in a separatory funnel. The sample should not contain more than 25 µg phenol.

8.3.3 To sample and standards add 10 mL of buffer solution (7.3) and mix. The pH should be 1O ± 0.2.

8.3.4 Add 3.0 mL amino anti pyrine solution **(7.4**) and mix.

8.3.5 Add 3.0 mL potassium ferricyanide solution **(7.5)** and mix.

8.3.6 After three minutes, extract with 25 mL of chloroform **(7.9).** Shake the separatory funnel at least 10 times, let $CHCl_3$settle, shake again 10 times and let chloroform settle again. Vent chloroform fumes into the hood.

8.3.7 Filter chloroform extracts through filter paper. Do not add more chloroform. Carry out filtration in a hood. Dispose of chloroform in an environmentally acceptable manner.

8.3.8 Read the absorbance of the samples and standards against the blank at 460 nm.

9.0 Calculation

9.1 Prepare a standard curve by plotting the absorbance value of standards versus the corresponding phenol concentrations.

9.2 Obtain concentration value of sample directly from the standard curve.

10.0 Precision and Accuracy

10.1 Using the extraction procedure for the concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3, and 93.5 µg/L. Standard deviations were ±O.99, ±3.1 and ±4.2 µg/L, respectively.

10.2 Using the direct photometric procedure, six laboratories analyzed samples at concentrations of 4.7, 48.2 and 97.0 mg/L. Standard deviations were ±0.18, ±0.48 and ±1.58 mg/L, respectively.

Bibliography

1.Annual Book of ASTM Standards, Part 31, "Water", Standard D 1783-70, p553 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p574-581, Method 510 through 510C, (1975).

Appendix K. Infrared Spectroscopy Correlation Table

Bond	**Type of bond**	**The specific type of bond**	**Absorption peak (cm^{-1})**	**Appearance**
C─H	**Alkyl**	**Methyl**		Strong
				Weak
			2870	
			2960	Medium to Strong
		Methylene	1470	Strong
			2850	Medium to

			2925	Medium to
		Methine	2890	Weak
	Vinyl	**C═CH₂**	900	Strong
			2975	Medium
			3080	Medium
		C═CH	3020	Medium
		Mono substituted alkenes	900	Strong
			990	Strong
		Cis-disubstituted	670–700	Strong
		Trans-di substituted	965	Strong
		Tri substituted alkenes	800–840	Strong to
	Aromatic	Benzene / sub.	3070	Weak
		Mono substituted benzene	700–750	Strong
			690–710	Strong
		Ortho-disub. Benzene	750	Strong
		Meta-di sub. Benzene	750–800	Strong
			860–900	Strong
		Para-di sub. Benzene	800–860	Strong
	Alkynes	Any	3300	Medium
	Aldehydes	Any	2720	Medium
			2820	
C═C	**Acyclic C═C**	Mono sub. Alkenes	1645	Medium
		1, 1-disub. Alkenes	1655	Medium

		Cis-1, 2-disub.	1660	Medium
		Trans-1, 2-disub.	1675	Medium
		Tri sub., tetra sub.	1670	Weak
	conjugated C=C	Dienes	1600	Strong
			1650	Strong
	With benzene ring		1625	Strong
	With C=O		1600	Strong
	C=C (both sp^2)	Any	1640–1680	Medium
	Aromatic C=C	Any	1450	Weak to strong (usually 3 or 4)
			1500	
			1580	
			1600	
	C≡C	Terminal alkynes	2100–2140	Weak
		Di subSt. alkynes	2190–2260	Very weak (often in distinguishable)
C=O	**Aldehyde/ketone**	Saturated aliph./cyclic	1720	
		α,β-unsaturated	1685	
		Aromatic ketones	1685	
		Cyclic 5-membered	1750	
		Cyclic 4-membered	1775	
		Aldehydes	1725	Influenced by conjugation (as
		Saturated carboxylic acids	1710	

	Carboxylic acids/Derivates	Un sat. /aromatic carb. Acids	1680–1690	
		Esters and lactones	1735	Influenced by conjugation and ring size (as with
		Anhydrides	1760	
			1820	
		Acyl halides	1800	
		Amides	1650	Associated
		Carboxylates (salts)	1550–1610	
		Amino acid	1550–1610	
O─H	**Alcohols, phenols**	Low concentration	3610–3670	
		High concentration	3200–3400	Broad
	Carboxylic acids	Low concentration	3500–3560	
		High concentration	3000	Broad
N─H	**Primary amines**	Any	3400–3500	Strong
			1560–1640	Strong
	Secondary amines	Any	>3000	Weak to medium
	Ammonium ions	Any	2400–3200	Multiple broad
C─O	**alcohols**	Primary	1040–1060	Strong, broad
		Secondary	~1100	Strong
		Tertiary	1150–1200	Medium
	Phenols	Any	1200	
	Ethers	Aliphatic	1120	
		Aromatic	1220–1260	

	Carboxylic acids	Any	1250–1300	
	Esters	Any	1100–1300	Two bands (distinct from ketones, which
C─N	**Aliphatic amines**	Any	1020–1220	Often overlapped
	C═N	Any	1615–1700	Similar conjugation
	C≡N (nitriles)	Unconjugated	2250	Medium
		Conjugated	2230	Medium
	R─N─C	Any	2165–2110	
	R─N═C═S	Any	2140–1990	
C─X	**Fluoro alkanes**	Ordinary	1000–1100	
		Tri fluro methyl	1100–1200	Two strong, broad bands
	Chloro alkanes	Any	540–760	Weak to medium
	Bromo alkanes	Any	500–600	Medium to
	Iodo alkanes	Any	500	Medium to
N─O	**Nitro compounds**	Aliphatic	1540	Stronger
			1380	Weaker
		Aromatic	1520	Lower if conjugated
			1350	
P─C	**Organophosphorus**	Aromatic	1440-1460	Medium
P─O	**Phosphorus oxide**	Bonded	1195-1250	Strong
		Free	1250-1300	Strong

Appendix L. Laboratory Equipment's and Samples Photo

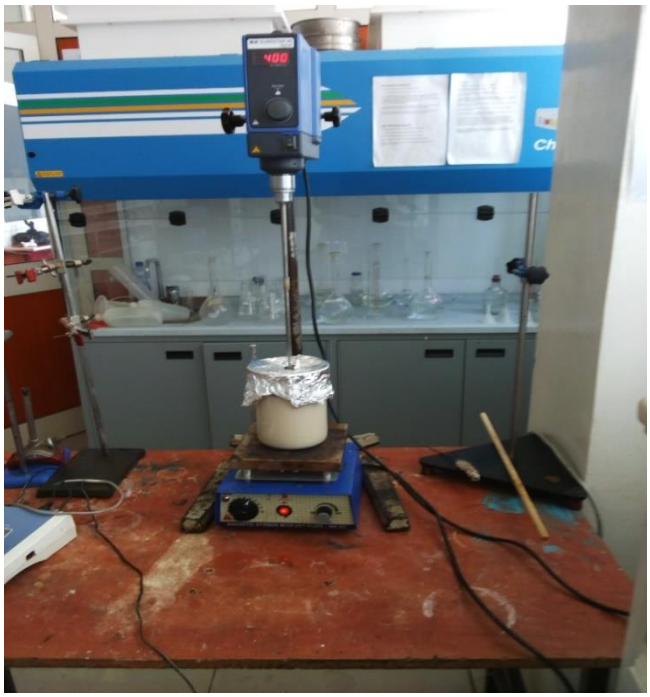


Fig. impregnation of iron and bentonite

Fig. Furnace

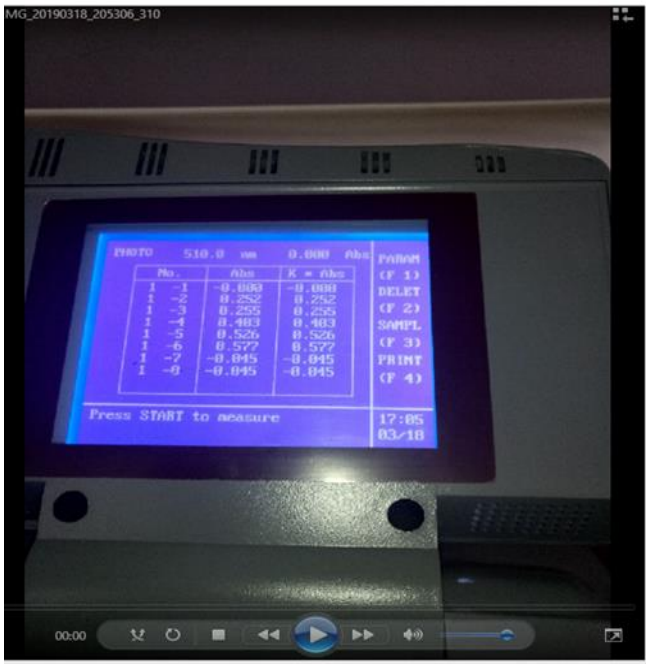


Fig: UV-Vis determination of phenolic compound

GEOLOGICAL SURVEY OF ETHIOPIA	Doc.Number: GLD/F5.10.2	Version No: 1
GEOCHEMICAL LABORATORY DIRECTORATE		Page 1 of 1
Document Title: Complete Silicate Analysis Report	Effective date:	May, 2017

Customer Name:- Dawit Alemu.

Issue Date: - 25/04/2019
Request No: GLD/TR/262/19
Report No: GLD/TR/212/19
Sample Preparation: - 200 Mesh
Number of Sample: Two (2)

Sample type: - Powder.
Date Submitted: - 15/04/2019
Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides
Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS

Collector's code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LOI
Calcinated bentonite	63.64	18.29	2.54	2.84	3.76	2.02	0.10	<0.01	0.02	0.11	<0.01	5.99
Raw bentonite	58.06	13.48	1.40	0.70	3.42	1.76	<0.01	<0.01	0.06	0.08	13.30	6.54

Note: - This result represent only for the sample submitted to the laboratory.

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Checked By: Dessie Abebe

Approved By: Gosa Haile

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