



DEPURATION STUDIES ON KADUNA REFINERY WASTEWATER USING  
MODIFIED Cu-DOPED GOETHITE CATALYST

BY

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MODIFIED Cu-DOPED GOETHITE CATALYST

BY

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DECEMBER, 2016

## DECLARATION

I declare that the work in this dissertation entitled DEPURATION STUDIES ON KADUNA REFINERY WASTEWATER USING MODIFIED Cu-DOPED GOETHITE CATALYST has been carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Hambali Umar HAMBALI  
Name of Student Signature

\_\_\_\_\_  
Date

## CERTIFICATION

This dissertation titled “Depuration Studies on Kaduna Refinery Wastewater Using Modified Cu-Doped Goethite Catalyst” meets the regulations governing the award of Masters of Science Degree in Chemical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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## ABSTRACT

Undoped and copper doped goethite catalysts were synthesized and applied in Fenton depuration of Kaduna refinery wastewater. The percentage of copper in the doped catalysts are 0.2 wt% copper in Cu-doped (A), 1.6 wt% copper in Cu-doped (B) and 3.3 wt% copper in Cu-doped (C), respectively. Characterization of the catalysts were done using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Absorption Spectrophotometer (AAS) and Surface Area Analysis. An experimental design matrix was used to evaluate the individual and combined effects of the process variables. Response surface methodology (RSM) was applied with a central composite design (CCD), and models were developed. The optimal conditions are pH of 3, 360 minutes reaction time, catalyst loading of 55mg/L and hydrogen peroxide dosage of 1.1g/L. Astonishingly, appreciable depuration percentage was achieved at near neutral pH, 67.44% was achieved by the undoped goethite catalyst, 79%, 82.56% and 83.72% were achieved by the Cu-doped A, B and C goethite catalysts, respectively. The obtained models for the undoped and doped catalysts gave R-square ( $R^2$ ) values of 0.9471, 0.9794, 0.9371 and 0.9407, respectively which showed that the experimental data fitted the model fairly well, depicting the viability and reliability of the model. It was observed that the Cu-doped goethite catalysts yielded improved depuration, confirming that the doped catalysts have great potential as an efficient tool for Fenton depuration of petroleum refinery wastewater.

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## **LIST OF ABBREVIATIONS**

AAS	Atomic Absorption Spectrophotometer
AOP	Advance Oxidation Process
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
JCPDS	Joint Committee on Powder Diffraction Standard
PRW	Petroleum Refinery Wastewater
SEM	Scanning Electron Microscope
TDS	Total Dissolved Solid
XRD	X-Ray Diffraction

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Preamble

Petroleum refining process is associated with the generation of voluminous wastewater (0.4-1.6 times the volume of the oil processed) (Diya'uddeen *et al.*, 2012). The wastewater is predominantly of toxic and recalcitrant aromatic compounds such as benzene, toluene, ethyl benzene, and xylene which are among the most hazardous compounds released into the environment (Aranda *et al.*, 2010). Environmental deterioration and the increase in demand for water consumption in the industry necessitate the development of wastewater treatment technologies for the petroleum industry (Diya'uddeen *et al.*, 2012).

The conventional wastewater treatment methods (primary and secondary) used for treating refinery effluents include mechanical and physiochemical processes such as oil water separation, sedimentation, coagulation, and dissolved air flotation with further biological treatment (Diya'uddeen *et al.*, 2011). However, biological processes are not efficient for treating wastewater with high toxicity and bio-refractory compounds (Saien and Nejati 2007). Therefore, it is imperative to introduce newer treatment technologies capable of effectively treating petroleum refinery wastewater. The newer technologies include advanced oxidation processes (AOP), filtration, nutrient removal and toxic elements or chemicals removal among others (Chunli, 2013).

Advanced oxidation processes are characterized by hydroxyl radicals ( $\bullet\text{OH}$ ) generation, which can effectively destroy a wide range of toxic and bio-refractory compounds. Among these are the homogenous and heterogeneous Fenton oxidation process which is an advanced oxidation process that utilizes the highly reactive  $\bullet\text{OH}$  to destroy organic

contaminants. It possesses environmental and economic benefits coupled with effective depuration of most wastewater organic compounds. The main parameters that determine the efficiency of the oxidation process are the structure of the organic compounds, oxidant, catalyst type and concentrations, the initial solution pH and the reaction contact time (Basheer *et al.*, 2011). Astonishingly, hydrogen peroxide is an environment friendly oxidant which could oxidize any organic pollutants efficiently and economically. The standard reduction potentials (1.77V) of hydrogen peroxide imply that it is a strong oxidant in both acidic and basic solutions. Catalytic decomposition of hydrogen peroxide can oxidize many kinds of organic contaminants in wastewater directly. In the case of catalyst, iron oxides are commonly applied in heterogeneous Fenton process.

Iron oxides play an important role in organic pollutants depuration as they represent strong sorption surfaces for pollutants and catalyze numerous redox transformations (Stiers and Schwertmann, 1985). Among the sixteen known iron oxides and hydroxides, goethite ( $\alpha$ -FeOOH), magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) and hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ) are the frequently used heterogeneous Fenton catalysts (Yan *et al.*, 2009). Goethite is a synthetic or naturally occurring iron oxide that consists of double chains of  $\text{FeO}_3(\text{OH})_3$  octahedral extending along the crystallographic Z-axis and is composed of about 80 to 90 percent  $\text{Fe}_2\text{O}_3$  and approximately 10 percent water and forms hematite when dehydrated and upon hydration becomes limonite (Ohtani, 2011).

The hydrated surface of goethite is highly reactive and further improves with the doping of metal ions in its crystals. In the past decade, several studies were performed to determine the surface properties of goethite. Researchers suggested that inclusion of minute quantity

of metals like  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  may have notable effect on the chemical and physical properties of goethite and hematite (Subrt *et al.*, 2000).

In this work, goethite and copper doped goethite catalysts were synthesized and used as heterogeneous Fenton catalysts. Effect of copper inclusion on the surface of the goethite catalyst and its performance on depuration of Kaduna refinery wastewater were evaluated.

## 1.2 Problem Statement

- i. Voluminous petroleum refinery wastewater generated contain highly toxic and large amount of organic contaminants, and the current treatment techniques have many drawbacks such as inefficient treatment of wastewater with high toxicity among others.
- ii. An attractive option is the homogenous Fenton process which yields substantial depuration rate. However, its pH adjustment requirements and large sludge generation are subject to many ongoing research efforts.
- iii. Heterogeneous Fenton process which uses solid catalyst such as goethite, among others, has the potential to address the problems.
- iv. Doped goethite catalyst is expected to improve Fenton process efficiency. However, research works are scanty on its development and application.

## 1.3 Aim and Objectives

The aim of this research work is to study the depuration of Kaduna refining wastewater using modified copper doped goethite catalyst.

The specific objectives are to:

- i. Characterize Kaduna refinery wastewater.

- ii. Synthesize and characterize goethite and copper doped goethite catalysts using XRD, SEM and surface area analysis.
- iii. Investigate the depuration of Kaduna refinery wastewater using the synthesized goethite and copper doped goethite catalysts.
- iv. Establish optimal conditions for the depuration of Kaduna refinery wastewater.
- v. Investigate the stability of the copper doped goethite catalyst.

#### **1.4 Scope of the Work**

This work is limited to the following:

- i. To synthesize and characterize goethite and copper doped goethite catalyst.
- ii. To depurate Kaduna refinery wastewater using the copper doped goethite catalyst.
- iii. Stability analysis of the copper doped goethite catalyst.

#### **1.5 Research Justification**

- i. Heterogeneous Fenton process is environment friendly and an efficient form of wastewater treatment that generates small amount of sludge.
- ii. Little work has been done on goethite doped catalyst development and application.
- iii. The amount of energy utilized in this technology is low, as the depuration process is carried out at atmospheric conditions.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Petroleum Refinery Wastewater

Petroleum refinery is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene and liquefied petroleum gas. The crude refining process releases numerous air pollutants and a notable odor which normally accompanies its operations. Aside from air pollution impacts there are also wastewater concerns, risks of industrial accidents such as explosion and industrial noise (Basorun and Olamiju, 2013).

Crude oil is a complex mixture of several polycyclic aromatic compounds and other hydrocarbons. The major hydrocarbon classes found in crude oil are the normal alkanes (rapidly degraded), branched alkanes and cycloalkanes (difficult to identify), the isoprenoids (very resistant to biodegradation), the aromatics (fairly identified and much more soluble than the other hydrocarbons), and finally the polar ones containing mainly sulphur, oxygen and/or nitrogen compounds. Non-hydrocarbon compounds may also be found in crude oil and they include porphyrins and their derivatives (Callot and Ocampo, 2009).

Globally, crude oil demand is expected to rise to 107mbpd over the next two decades, and will account for 32% of the world's energy supply by 2030. Bio fuels, including ethanol and biodiesel, are expected to account for 5.9 mbpd by 2030, and the contributions from renewable energy sources like wind and solar power are estimated to be 4–15% (Molina *et al.*, 2012). These data clearly indicate that petroleum refinery effluents will continually be produced and discharged into the world's main water bodies (Ortizet *al.*, 2008). However,

the petroleum refining industry consumes approximately 246 to 340 liters of water for every barrel of crude petroleum it refines. Most of this water is used for steam production and cooling towers. Approximately 10 percent of this supply water (plus additional blow down flows from the steam production and cooling tower systems) is used for process units, where it might be contaminated with pollutants (Kersten *et al.*, 2009).

Consequently, the volume of wastewater generated during petroleum refining process is 0.4–1.6 times the amount of the crude oil processed (Coelho *et al.*, 2006). Due to the ineffectiveness of purification systems, wastewater may become dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem (Bay *et al.*, 2003).

### **2.1.1 Wastewater composition and effects**

Wastewater is a liquid or water-borne waste polluted or fouled from household, commercial, or industrial operations, along with any surface water, storm water, or groundwater infiltration. Therefore, wastewater is defined as any water that has been adversely affected in quality by anthropogenic activities from residential and non-residential sources (Thomas, 2001).

Wastewater is polluted by numerous causes leading to severe effects as highlighted in Table 2.1. However, wastewater receives a disproportionately low and often poorly targeted share of development aid and investment in developing countries. At least 1.8 million children under five years die every year due to water-related diseases, or one every 20 seconds (Aremuet *et al.*, 2012).

Table 2.1: Causes and Effects of Wastewater Pollution

<b>Causes</b>	<b>Effects</b>
Metals and organic materials	Aesthetic inconveniences, toxic effect, death and bio accumulation in the food chain
Bacterial infections	Typhoid, cholera ,fever and bacillary dysentery diseases
Viral Infections	Infectious hepatitis and poliomyelitis diseases
Protozoan infections	Amoebic dysentery diseases

Source: (Chunli, 2013;Coelho et al., 2006;Sangodoyin, 1995)

The effects of several chemicals found in PRWare petrochemical carbons which causes mutagenic activity, aromatic and poly aromatic hydrocarbon compounds that causes genotoxicity, high nitrate and phosphate concentrations which may lead to the eutrophication of aquatic environments such as lakes, rivers, and coastal ecosystems. During eutrophication, the quality of water may show very high concentrations of nutrients that stimulate the growth of algae and aquatic plants. This in turn induces a negative feedback system by depleting dissolved oxygen from the increased amount of dead and decaying organic matter. As a result, aquatic life is strongly affected, potentially leaving a severely limited and perturbed ecosystem (Smith and Schindler 2009).

The contamination of natural water bodies by industrial activities has emerged as a major problem challenge in developing and densely populated countries like Nigeria. The wastewater from the industries can alter the physical, chemical and biological nature of the receiving water body. Similarly, estuaries and inland water bodies, which are the major

sources of drinking water in Nigeria, and are often contaminated by the activities of the adjoining populations and industrial establishments (Sangodoyin, 1995).

### **2.1.2 Sources of refinery wastewater**

Refinery wastewater originates from numerous sources and varies according to the quantity and degree of contamination (Pignatello *et al.*, 1992). It contains oil which is the major contaminant in the wastewater being composed of a range of different hydrocarbons and other organic compounds present in the crude oil, and chemical substances produced by the refinery process such as sulphides, mercaptans, cyanides, ammonia, phenols, inorganic salts, and traces of some heavy metals (Lettinga *et al.*, 1980). Table 2.2 shows the unit wise wastewater generation in petroleum refinery, with 350 m<sup>3</sup>/hr wastewater generated. The major wastewaters from petroleum refineries are sour water from multiple processes, scrubber water from reformer catalyst regeneration, spent potassium hydroxide stream from alkylation, desalting wastewater, and caustic wash water from isomerization (Basheer *et al.*, 2011). Furthermore, wastewater emanates from quench wastewater, rainwater run-off from paved areas in the processing units and cooling water leaking into the hydrocarbon stream of the heat exchanger (Mota *et al.*, 2008).

### **2.1.3 Refinery wastewater characterization**

To reduce the polluting effect on wastewater, it is essential to know the quality of the wastewater (Diya'uddeen *et al.*, 2012). Table 2.3 shows the characteristics of the refinery wastewater. Liquid wastes generated in petroleum refineries vary considerably in terms of quantity and quality as a function of the type of crude oil processed, the processing units of the refinery, and the mode of operation of these units.

Table 2.2: Petroleum Refinery Process Wastewater

Units/ Processes in Refinery	Wastewater flow rate (m <sup>3</sup> /hr)
Crude / Vacuum Distillation Unit	171.04
Catalytic Reforming Unit	5.70
Hydrocracker Unit	16.22
Naphtha/Diesel Hydrotreater Unit	31.93
Catalytic Cracking Unit	15.20
Hydrogen Generation Unit	1.23
Asphalt Plant/ Bitumen Blowing Unit	13.07
Product Blending	87.44
Sulfur Recovery Unit	0.26
Isomerization Unit	3.26
MEK Dewaxing Unit/ Solvent Unit	0.01
Aromatic Extraction Unit	2.14
Lube Oil/Specialty Processing Unit	2.06
Tank drawdown/ Washings	0.76

(Source: Srikumar and Papita, 2015)

The problem with petroleum refinery effluents is the great diversity of different chemicals and their isomers in the wastewaters, which makes it difficult to efficiently reduce different pollutants from the wastewater. However, organic components present in refinery wastewaters are mostly hexanes, heptanes, higher alkanes, benzene, xylenes, acetonitrile,

acrylonitrile, methanol, butanol, ethyleneglycol, phenol and formaldehyde. (Danana *et al.*, 1985).

Basically, the quantity of organic compounds in wastewater is evaluated by total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD). The TOC gives the amount of total carbon in a water sample, while COD quantifies organic contaminants, and the basis is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. The BOD value, on the other hand, is the quantity of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a water sample at certain temperature and time. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20°C and is often used as a robust surrogate of the degree of organic pollution of water. The TOC, COD, and BOD reflect the organic pollution in the wastewater. However, they cannot reflect the kinds of organic matter and composition of the water and, therefore, cannot reflect the total amount of the same total organic carbon pollution caused by different consequences (Chunli, 2013). Furthermore, the measurement of temperature is necessary because most wastewater treatment schemes include processes that are temperature-dependent. Increase in temperature leads to evaporation, thereby increasing the concentrations of dissolved solids and nutrients in the water system. These effects, in turn, increase turbidities due to algal blooms and nuisance weed growth. Similarly, the temperature of wastewater also differs with respect to season and geographical location where, in cold regions, the temperature ranges from about 7 to 18°C and in warmer regions the temperature may vary from 13 to 24°C (Marsh *et al.*, 2006).

### 2.1.3.1 Heavy metals

Heavy metals are those metals and metalloids having densities greater than  $5 \text{ gcm}^{-3}$  and are mostly associated with pollution and toxicity. Primary sources of pollution is from the burning of fossil fuels, mining, and melting of metallic ferrous ores, municipal wastes, fertilizers, pesticides, and sewage sludge. The most common heavy metals are cadmium, chromium, copper, lead, nickel, and zinc (Adriano, 2001).

### 2.1.3.2 Phenols

Phenols are chemical compounds consisting of a hydroxyl group (-OH) bonded directly to an aromatic hydrocarbon group. The phenol in wastewater comes mainly from the coking plant, refining, insulation material manufacturing, paper making and phenolic chemical plant. However, phenol and phenolic derivatives presence in wastewater even at low concentration causes toxicity, persistence and bioaccumulation in plant and animal organisms and is a risk factor for human health. Furthermore, phenol also has the potential to decrease growth and reproductive capacity of the aquatic organisms (Chunli, 2013).

Generally, phenolic compounds are priority pollutants, often occur in the aqueous environment due to their widespread application in several industrial processes. Phenols, even at concentrations below  $1 \mu\text{g/L}$ , do affect odor and taste of water (Pera *et al.*, 2004). Thus, it necessitated identification and monitoring of these compounds at trace level in drinking water and surface waters are of great importance. Chlorophenols, on the other hand, represent an essential class of very common water pollutants, it is a toxic and non-biodegradable organic compound and can often be found in high quantity in the wastewaters from various industrial sectors (Augugliaro *et al.*, 2006).

Table 2.3: Characteristics of Refinery Wastewater

Parameter	Limits	
	Minimum	Maximum
Temperature (°C)	22	41
pH	6.2	10.6
Conductivity (ms/cm)	5.2	6.8
BOD (mg/L)	17	280
COD (mg/L)	140	3340
Sulphides (mg/L)	0	38
Phenol (mg/l)	11	14
N-Hexane (mg/l)	1.8	1.85
Sulphate (mg/l)	14.5	16
Total dissolved solid (g/l)	3.8	6.2
Total suspended solid (g/l)	0.03	0.04
Hardness as CaCO <sub>3</sub> (mg/L)	139	510
Alkalinity as CaCO <sub>3</sub> (mg/L)	77	356
Oil (mg/L)	23	200
Phosphorus (mg/L)	0	97
Ammonia (mg/L)	0	120
Chlorides (mg/L)	19	1080
Sulphates (mg/L)	0	182

(Source: Mota *et al.*, 2008)

### 2.1.3.3 Total dissolved solids

Dissolved solids in refinery wastewater consist mainly of carbonates, chlorides, and sulfates. Public Health Service Drinking Water Standards for total dissolved solids are set at the discharge point to be approximately 575.15mg/l (Wasserman *et al.*, 2006). Sulphur and nitrogen components present in effluents are highly toxic, and are represented in the form of hydrogen sulphide and ammonia respectively. Hydrogen sulphide in aqueous form exists in equilibrium with bisulphide and sulphide and the latter sulphide is the most reduced form (Altas and Büyüküngör, 2008).

## 2.2 Wastewater Treatment Methods

Almost all industrial processes produce contaminated water as a by-product. Treatment is then necessary before the water can be discharged to the environment or to a municipal wastewater treatment plant treatment. In many developing countries, more than 70 percent of industrial wastes are dumped untreated into waters where they pollute the usable water supply. Industrial discharge contains a wide range of contaminants and originate from a myriad of sources. Some of the biggest generators of toxic industrial waste include mining, pulp mills, tanneries, sugar refineries, and pharmaceutical production (WWAP, 2009).

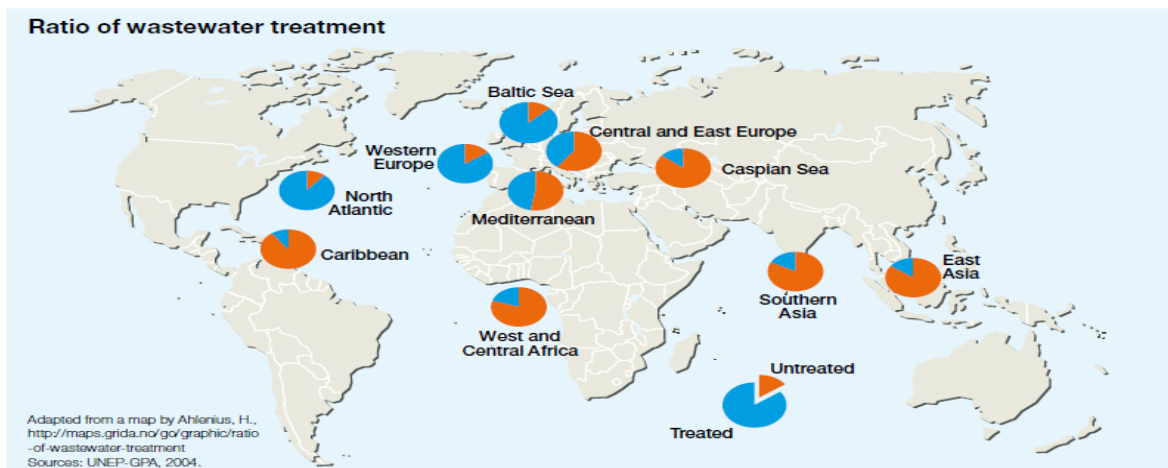


Figure 2.1: The ratio of treated to untreated wastewater (UN Water, 2008).

Wastewater treatment methods are used in the purification of wastewater until its characteristics achieve the required objective, generally related to environmental, health or economic matters. There are numerous treatment methods for treating industrial wastewater ranging from primary, secondary and tertiary treatment methods. Wastewater treatment processes are designed to remove organic and inorganic aqueous pollutants that are of great harm or that pose a risk to human health and natural aquatic resources (Mahmoud, 2002).

### **2.2.1 Primary treatment method**

Preliminary treatment is a physical separation process that involves the removal of large particles as well as solids found in the wastewater and generally removes 40 percent of the suspended solids and 30 to 40 percent of the BOD in the wastewater. The objective of primary treatment methods is to protect further treatment units and protect water bodies from receiving these solids. In a typical refinery wastewater treatment system, the primary treatment step consists of screen of bars, grit chambers, clarifiers and sedimentation tanks to remove floating and settleable solids, including oil and grease. This gross primary separation process produces wastes in the form of macro-solids, organic-rich sludge, and scum (Hammer, 2005). These wastes are then sent for further treatment often including dewatering, by filtration, and anaerobic/aerobic digestion or composting (Bitton 1994).

The primary treatment steps involve:

- a) Screening to remove large objects, such as stones that could plug lines or block tank inlets.
- b) Grit chamber to slow down the flow in order to allow grit to fall out.

- c) Sedimentation which is mostly achieved in a settling tank or clarifier, the settleable solids settle out and are pumped away, while oils float to the top and are skimmed off.

### **2.2.2 Secondary treatment methods**

Secondary treatment methods are types of wastewater treatment used to convert dissolved and suspended pollutants into a form that can be removed, producing a relatively highly treated effluent. It normally utilizes biological treatment processes, followed by settling tanks and will remove approximately 85 percent of the BOD and TSS in wastewater (Hammer, 2005).

#### *2.2.2.1 Biological treatment method*

The biological treatment eliminates organic matter through biological action by means of bacteria, fungi, algae, protozoa and others (Hammer, 2005). Biological treatment methods are among the most cost effective treatment methods. However, they are only suitable for organic wastes with relatively low toxicity. Furthermore, biological processes do not completely destroy the organic materials, and may lead to inactivation of the microbiological processes due to the toxicity of these wastewaters (Méndez *et al.*, 2009).

#### *2.2.2.2 Biodegradation of organic compounds*

Biodegradation is the process of using microorganisms, green plants, fungi and their enzymes to remove numerous pollutants from natural environment or transform them harmless. The degree and rate of biodegradation depends on the characters of the substance. Pollutants like organic matter, organophosphorus pesticide, which have relatively high water solubility and low acute toxicity, are bioavailable and easy to be degraded. However, effluents from pharmaceuticals and other sources which possess a

higher bioaccumulation, biotoxicity and biomagnification properties, are reluctant to biodegradation in the natural condition (Scott and Ollis,1995).

#### *2.2.2.3 Aerobic biodegradation process*

In aerobic biodegradation, oxygen is needed by organisms in degradation at two metabolic sites namely the initial attack of the substrate and at the end of respiratory chain. Classic aerobic biodegradation reactors include activated sludge reactor and membrane bioreactor (Pedro, 2006).

Aerobic biodegradation is a simple, inexpensive and environmentally sound way to degrade wastes. Critical factors in the optimal degradation are temperature, pH, moisture, nutrients and aeration rate that the bacterial culture is exposed to, where temperature and aeration are the most critical parameters that determine the degradation rates by the microorganism (Oller, 2011).

The aerobic biodegradation processes is used for BOD reduction and is ten times faster than anaerobic microbial reactions. The major disadvantage of aerobic bioprocesses relative to anaerobic processes is the large amount of sludge produced. Other disadvantage of aerobic biodegradation includes toxic effect on the microorganisms which is caused by effluents constituents (Turgay, 2011).

#### *2.2.2.4 Activated sludge reactor*

Activated sludge is a process for treating wastewater using air and a biological floc composed of bacteria and protozoa. Air or oxygen is fed into a mixture of primary treated or screened wastewater and organisms to form a biological floc which eventually reduces the organic content of the wastewater, which predominantly comprises of microorganisms such as saprotrophic bacteria, nitrobacteria and denitrifying bacteria. Subsequently,

the biological floc is used to degrade the wastewater and to bio-transform the ammonia in wastewater. The process, in general, involves adsorption and biological oxidation steps (Low *et al.*, 2000). However, the activated sludge treatment method effectively removes organic matters, nitrogenous matters and phosphate in the wastewater when there is enough oxygen and hydraulic retention time. The wastewater is always short of oxygen, which may lead to sludge bulking. Therefore, the aeration device in the system increases oxygen concentration (Low *et al.*, 2000).

#### 2.2.2.5 Membrane bioreactor

Membrane methods generally has its advantages and disadvantages as discussed in Table 2.4, the membrane process is achieved by the use of the membrane bioreactor (MBR) which is a combination of membrane processes such as microfiltration or ultrafiltration with a suspended growth bioreactor used in treating wastewater. Membrane degradation of PRW in a cross-flow membrane system was reported by Rahman and Al-Malack (2006), the result showed COD reduction of 93 percent. The MBR method uses the membrane to achieve the separation, which is more efficient and less dependent on oxygen concentration of the water. However, the MBR has a higher organic pollutant and ammonia removal efficiency compared to the activated sludge process. Besides, the MBR process effectively treat wastewater with higher mixed liquor suspended solids concentrations compared to activated sludge process, thereby reducing the reactor volume to achieve the same loading rate (Ahmed and Lan, 2012). However for large volumes of effluent, it has been established that the use of a membrane is unsuitable (Basheer *et al.*, 2011). Furthermore, membrane fouling greatly affects the performance of MBR, because fouling significantly increases transmembrane pressure, thereby increasing the hydraulic resistance time as well

as the energy requirement of the reactor. Alternatively, frequent membrane cleaning and replacement is therefore necessary, but it significantly increases the operating cost (Ahmed and Lan, 2012).

#### *2.2.2.6 Anaerobic biodegradation process*

Anaerobic biodegradation is a series of processes in which microorganisms break down biodegradable materials in the absence of oxygen (Pedro, 2006).

There are four principles of the anaerobic degradation which are as follows:

- a) The insoluble organic pollutant breaks down into soluble substance, making them available for other bacteria.
- b) The acidogenic bacteria convert the sugars and amino acid into carbon dioxide, hydrogen, ammonia and organic acid;
- c) The organic acids convert into acetic acid, ammonia, hydrogen and carbon dioxide;
- d) The methanogens convert the acetic acid into hydrogen, carbon dioxide and methane, a kind of gaseous fuel.

Generally, anaerobic biodegradation processes are considered to be slow and inefficient compared to aerobic degradation. However, anaerobic processes can efficiently and economically treat organic wastewaters (Pedro, 2006).

##### *2.2.2.6.1 Upflow anaerobic sludge blanket reactor*

The upflow Anaerobic Sludge Blanket Reactor (UASB) system was developed by Lettinga and his co-workers in Holland in the early 1970s. The upward flow anaerobic flow process is illustrated in Figure 2.2, the liquid waste moves upward through a thick blanket of anaerobic granular sludge suspended in the system.

Table 2.4: Advantages and Disadvantages of Membrane Methods

Process	Target pollutants	Separation efficiency	Advantages	Disadvantages
Biological Reactor Membrane	-COD -Activated Sludge	-96% - - -	Generally for membrane methods: -Lower energy consumption -Separation with no need to use material	-Higher membrane fouling -High fixed costs
Ultrafiltration	-COD - TOC - Polymers -Benzene, Toluene and Xylene -Heavy metals (copper, etc.) - Solids -Petroleum compounds	- 90% - 98% - - - - - 54% - 95% - 73% - 54	-Performing separation at ambient temperature -Low weight and size of separation equipment -Simple installation and operation -Minimum need for control, inspection and maintenance -Ease of access and possible use of separate phases	Generally for membrane methods: -Membranes becoming dirty and decreased flow rate -Sensitivity to operating parameters and feed characteristics -Requiring constant cleaning and parts replacement
Microfiltration	- Suspended materials - Q & G - Suspended solids	- Very good - >5 mg/ l - >1 mg/l		
Nanofiltration	- COD - TOC - Oil	- 90% - 98% - Remained < 1%		
Reverse osmosis	- Separation of all compounds - Water - Ions (K <sup>+</sup> , Na <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> )			

(Source: Low *et al.*, 2000).

Mixing of sludge and wastewater is achieved by generation of methane within the blanket and hydraulic flow. The triphase separator prevents biomass loss of the sludge through the gas emission and water discharge (Leitinga and Hulshoff, 1991). However, the advantages of the UASB is that it contains a high concentration of naturally immobilized bacteria with excellent settling properties, and could remove the organic pollutants from wastewater efficiently (Leitinga and Hulshoff, 1991).

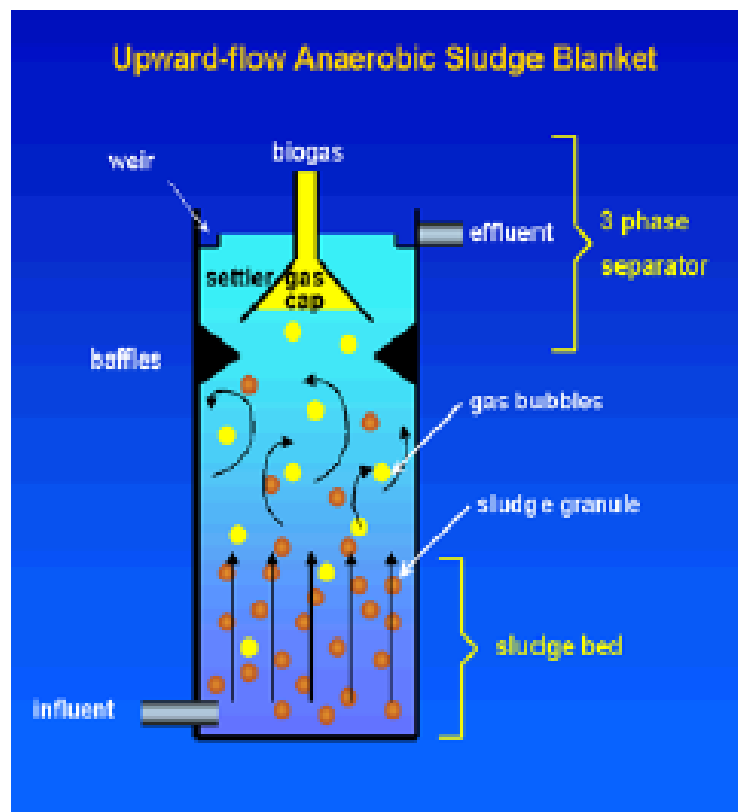


Figure 2.2: The upward flow anaerobic sludge bed (UASB) reactor concept

#### 2.2.2.6.2 Anaerobic biofilter

Anaerobic biofilter is a form of high efficient anaerobic treatment equipment, which uses inert support materials to provide a surface for the growth of anaerobic bacteria and to

reduce turbulence to allow unattached populations to be retained in the system. The organic matter of wastewater is degraded in the system, and produce methane gas, which will be released from the pool from the top (Kassabet *al.*, 2010).

Anaerobic biofilter system has numerous advantages such as:

- a) The filler provides a large surface area for the growth of the microorganisms, and the filler also increases hydraulic retention time of the wastewater;
- b) The system provides a large surface area for the interaction between the wastewater and film.
- c) The fact that microorganisms grow on the filler reduces the run of the degraders.

The major setback to treatment using anaerobic biofilter is that the system could be blocked when dealing with effluents with high concentration organic water, especially in the water inlet parts. And no simple and effective way for filter washing has been developed yet (Kassabet *al.*, 2010).

### **2.3 Advanced Oxidation Processes**

Nowadays, due to the increasing presence of molecules, refractory to the microorganisms in the wastewater streams, the conventional treatment methods (Primary and Secondary methods) cannot be used for complete treatment of the effluent. Therefore, it is imperative to introduce newer treatment technologies to convert effluents into less harmful or lower chain compounds (Chunli, 2013). The newer technologies include microscreening, precipitation, adsorption, ion exchange, reverse osmosis, electro dialysis, chlorination and ozonation and others as shown in Figure 2.3. Advanced oxidation processes (AOP) is also known as tertiary treatment method, and is any level of treatment beyond

secondary treatment, such as filtration, nutrient removal and toxic elements or chemicals removal among others as listed in Table 2.5.

Glaze and Chapin (1987) defined AOP as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (hydroxyl radicals) in sufficient quantity to effect water purification. The AOP mostly involve the use of metal salts to precipitate phosphate and chlorine, ozone or ultraviolet light is used to destroy the potential disease causing pathogenic microorganisms. (Hammer, 2005).

Generally, AOP is one of the newer treatment processes which utilize chemical oxidant ( $H_2O_2$ ,  $O_3$ ,  $K_2MnO_4$ ,  $K_2FeO_4$  and others) to oxidize pollutant to slightly toxic, harmless substances or transform it into manageable form. Similarly, AOP constitute the use of oxidizing agents such as ozone and hydrogen peroxide, exhibit lower rates of degradation.

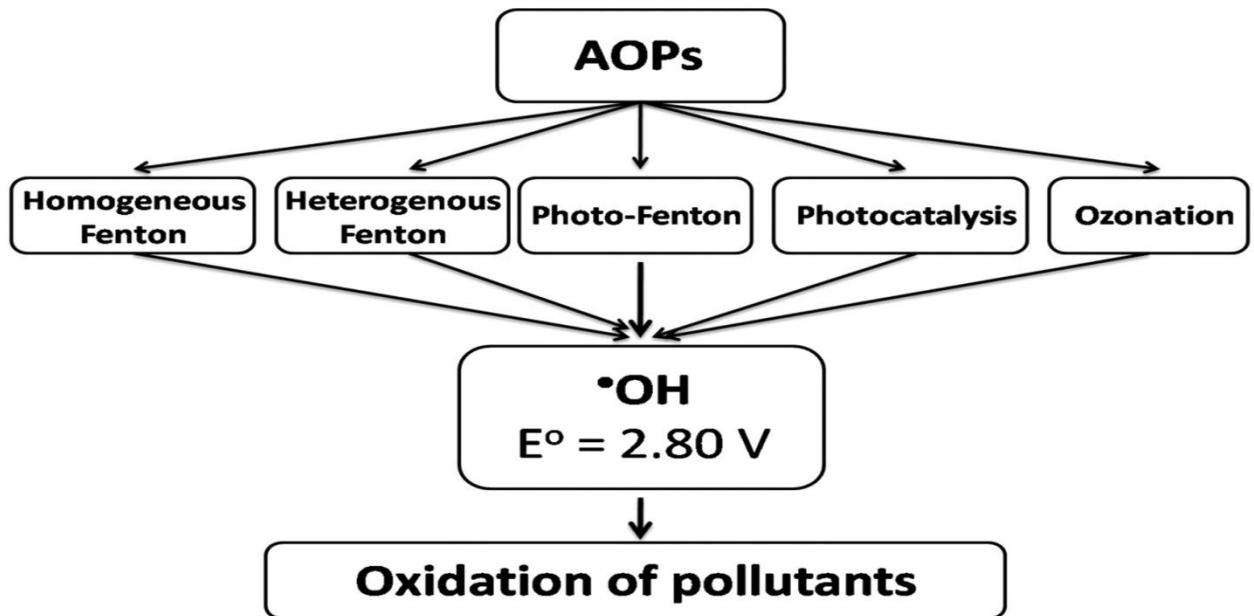


Figure 2.3: Advanced oxidation process (Source:Glaze and Chapin,1987)

Table 2.5: Description of Some AOP Technologies

AOP	Brief Description	System Components	Advantages	Disadvantages
H <sub>2</sub> O <sub>2</sub> /UV	The ·OH radical route is the predominant removal mechanism.	-UV Lamp -H <sub>2</sub> O <sub>2</sub> storage and injection system -Reaction chamber -In line mixer -Temperature controller -Pumps and piping -Monitoring and control system	-No potentials for bromate formation - Can be used for full scale water treatment -No off gases treatment required -Not limited by mass transfer	-Turbidity can interfere with UV light penetration -Less stoichiometrically efficient at generation ·OH -Interfering components (eg nitrate) can absorb UV light
H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub>	The ·OH formed can oxidize most dissolved organic matters to form byproducts	- H <sub>2</sub> O <sub>2</sub> injection and storage systems. -O <sub>3</sub> generators and diffuses -Contactor and mixing vessels -O <sub>3</sub> off gas catalytic decomposer -Pumps and piping -Monitoring and control system	-Supplemental disinfectant - More effective than UV or H <sub>2</sub> O <sub>2</sub> alone -Established technology for remediation applications	- May require treatment for excess H <sub>2</sub> O <sub>2</sub> due to potential for microbial growth - May require ozone off gases treatment
O <sub>3</sub> /UV	-The ·OH are generated with UV light is applied to ozonated water. -Destruction of organic compounds ·OH reactions occupied with direct photolysis and oxidation by molecular ozone	-UV Lamp -H <sub>2</sub> O <sub>2</sub> storage and injection system -Reaction chamber -In line mixer -Temperature controller -Pumps and piping -Monitoring and control system	-Supplemental disinfectant - More effective than UV or O <sub>3</sub> alone -More efficient at generating ·OH than H <sub>2</sub> O <sub>2</sub> /UV process for equal oxidant concentrations	- Energy and cost intensive - potential for bromate formation -Turbidity can interfere with UV light penetration - May require ozone off gases treatment - Interfering components (eg nitrate) can absorb UV light

(Source: Hoigne, 1998).

Advanced oxidation processes (AOPs) with the potentials of exploiting the high reactivity of hydroxyl radicals in driving oxidation have emerged a promising technology for the treatment of wastewaters containing refractory organic compounds. Several technologies like Fenton, photo-Fenton, wet oxidation, ozonation, Photocatalysis, etc. are included in the AOPs and their main difference is the source of radicals.

### **2.3.1 Adsorption treatment methods**

Adsorption is the process by which a solid adsorbent can attach a component dissolved in water to its surface and form an attachment through physical or chemical bonds, thereby removing the component from the fluid phase. Adsorption is nearly always an exothermic process. However, adsorption treatment technique offers a cleaner technology free from sludge handling problems and produces a high quality effluent. Over the last few decades, adsorption has effectively been used in wastewater treatment. Industrially, adsorption is used for many purposes of separation and purification, such as removal of metals, coloured and colourless organic pollutants from industrial wastewater (Chunli, 2013).

### **2.3.2 Activated carbon treatment method**

Activated carbon is a form of carbon processed to have small, low volume pores that increase the surface area available for chemical reactions and adsorption commonly in wastewater treatment. Because during the adsorption, the pollutants are removed by accumulation at the interface between the activated carbon and the wastewater, where the adsorbing capacity of activated carbon is always associated with very high surface area per unit volume (Hammer, 2005). Activated carbon are produced from carbonaceous material such as including coal, peat, wood, or nutshells. However, the manufacturing process consists of carbonization and activation phases. Generally, granular activated carbon

systems are composed of carbon contactors, virgin and spent carbon storage, carbon transport systems, and carbon regeneration systems (Chunli, 2013).

The carbon contactor consists of a lined steel column or a steel or concrete rectangular tank in which the carbon is placed to form a filter bed. Then, wastewater is applied at the top of the column and flows downward through the carbon bed, and is withdrawn at the bottom of the column. Subsequently, the carbon is held in place with an underdrain system at the bottom of the contactor. Provisions for backwash and surface wash of the carbon bed are required to prevent buildup of excessive headloss due to accumulation of solids and to prevent the bed surface from clogging (Chunli, 2013). However, the activated carbon treatment removal efficiency is dependent on particle size, selected catalyst and its activation practice. Wastewater constituents such as organic hydrocarbons, some heavy metals, biodegradable organic compounds and other components not responsive to conventional biological treatment are suitable for activated carbon treatment. Also components toxic to conventional biological treatment like pesticides, phenols, and organic dyes can be treated in the activated carbon treatment, according to Hameed *et al.*, (2008) the activated carbon wastewater treatment is efficient in removal of phenol from the waste solution. Furthermore, the activated carbon can also remove soluble components such as benzene, toluene and xylenes. The problem is that the activated carbon does not remove nitrogen and other metals (Marsh *et al.*, 2006).

### **2.3.3 Zeolites**

Zeolites are minerals or synthetic resins that have ion exchange capabilities (Thomas, 2001). There are several types of zeolites such as MCM-22, ZSM-5, ZSM-22, BETA, and Y. Studies showed that synthetic zeolites have higher adsorption capacity than the natural

zeolites for the removal of pollutants such as ink, dye, and others from wastewater. The use of zeolites as an alternative adsorbent in wastewater treatment offers solution to the drawback encountered in activated carbon due to its high regeneration and production cost. (Chunli, 2013).

#### **2.3.4 Natural materials**

Natural materials are materials such as certain waste products from industrial or agricultural operations that have potential as effective and inexpensive adsorbents. Natural materials availability, abundance and low cost make them good adsorbents for the removal of various pollutants from wastewaters. However, agricultural waste biomass currently is gaining importance. Rice husk which contains 20 percent silica has been reported as a good adsorbent for the removal of heavy metals, phenols, pesticides, and dyes. Grisdanurak *et al.*, (2003) evaluated the adsorptive capacity of rice husk silica and its adsorption capacity for chlorinated volatile organic compounds, and was found to be higher than that of commercial activated carbons.

#### **2.3.5 Photocatalysis**

Photocatalysis is a promising and very attractive wastewater treatment method. However, the process is achieved using titanium dioxide ( $\text{TiO}_2$ ) for water splitting after UV irradiation, it has been shown that this can encompass a wide range of reactions, especially the oxidation of organic compounds. Therefore, several studies on photo degradation of substances such as halogenated hydrocarbons, aromatics, nitrogenated heterocyclic, hydrogen sulfide, surfactants and herbicides, and toxic metallic ions, among others has clearly shown that the majority of organic pollutants present in waters can be mineralized or at least partially destroyed. The photocatalytic activity is dependent on the surface and

structural properties of the semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density (Ahmed *et al.*, 2010).

Several variety of semiconductor powders such as oxides and sulfides, acting as photocatalysts have successfully been utilized. However, TiO<sub>2</sub> has mostly been considered due to its high photocatalytic activity having a maximum quantum yields, its resistance to photo corrosion, its biological immunity and low cost. Basically, there are two types of reactors, namely reactors with TiO<sub>2</sub> suspended in the reaction medium and reactors with TiO<sub>2</sub> fixed on a carrier material (Li *et al.*, 2009). A very promising method for solving problems concerning the separation of the photocatalyst from the reaction medium is the application of photocatalytic membrane reactors (PMRs), having other advantages such as the realization of a continuous process and the control of a residence time of molecules in the reactor (Mozia, 2010). Therefore, the self-assembly of TiO<sub>2</sub> nanoparticles was established through coordinance bonds with (OH) functional groups on the membrane surface, improving reversible deposition, hydrophilicity and flow and diminishing the irreversible fouling (Mansourpanah *et al.*, 2009). TiO<sub>2</sub> functionalized membranes may be obtained by different methods, but the sol gel process is used because it has numerous exceptional features such as purity, homogeneity, control over the microstructure, ease of processing, low temperature and low cost (Alphonse *et al.*, 2010).

#### **2.4 Fenton Oxidation**

Fenton oxidation is an advanced oxidation process that utilizes the highly reactive hydroxyl radical to effectively destroy organic contaminants, it possesses environmental and economic benefits coupled with effective mineralization of most wastewater organics.

The main parameters which determine the efficiency of the oxidation process are structure of the organic compounds, hydrogen peroxide and catalyst concentrations, and the initial solution pH and the reaction contact time (Basheer *et al.*, 2011). Astonishingly, the hydrogen peroxide is an environment friendly oxidant which could oxidize any organic pollutants efficiently and economically.

The standard reduction potentials (1.77V) of hydrogen peroxide imply that it is a strong oxidant in both acidic and basic solutions. It can oxidize many kinds of organic contaminants in wastewater directly. However, the classical Fenton oxidation process has the advantages of being nonselective and effective in the treatment of several wastewaters. Furthermore, it is a cost effective treatment method by using hydroxyl radicals and easy to handle reagents, and treats wastewater with COD of more than 500mg/l. The disadvantages in using the Fenton reagent include the production of a substantial amount of  $\text{Fe}(\text{OH})_3$  precipitate, need for pH adjustment before and after oxidation and residual catalyst in the treated effluent which requires further purification (Di Iaconi *et al.*, 2010).

#### **2.4.1 History of Fenton oxidation**

H.J.H. Fenton discovered in 1894 that hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) could be more reactive by the use of Fe (II) salts to oxidize tartaric acid. Subsequently, iron catalyzed  $\text{H}_2\text{O}_2$  activation became known as Fenton's oxidation. Research was later done considering different metals to investigate their potentials in terms of power to generate hydroxyl radical ( $\bullet\text{OH}$ ) and their electron transfer properties which eventually improve the use of  $\text{H}_2\text{O}_2$ . Pignatello *et al.*, (2006) made a thorough review on history of Fenton oxidation covering the century of its existence. Laboratory investigations were the final phase of the trend in Fenton oxidation which promoted interest in the process as the strength and frugal

benefit of the technique was established. Therefore, it directly accounted for its pervasiv utilization in treating several wastewater, the efficiency of the process was thus further established (Pignatello *et al.*, 2006).

### 2.4.2 Fenton process

Fenton oxidation basic principle has been extensively studied and elaborated by several researchers (Umar *et al.*, 2010), the summary of trends of the process is listed in Table 2.6. Basically, the process is an oxidative cycle shown in Figure 2.4 with a multipurpose oxidant ( $H_2O_2$ ) induced via catalytic decomposition of  $H_2O_2$  by ion ( $Fe^{2+}$ ) as shown in 2.5, and ion ( $Fe^{3+}$ ) are also produced. The cycle is completed by the reduction of ferric iron by  $H_2O_2$  and the subsequent generation of per hydroxyl radicals and ferrous iron (Lucas *et al.*, 2007).

The series of the Fenton reactions are as follows:

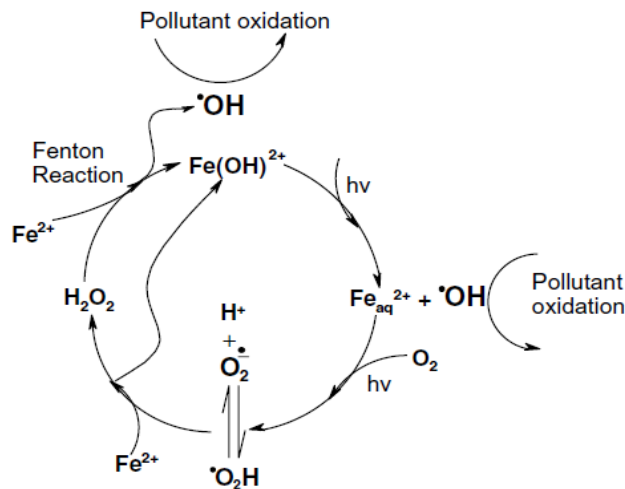


Figure 2.4: Schematic diagram of photo-assisted Fenton oxidation (Rodríguez *et al.*, 2005).

Table 2.6: Summary of the Trends in Fenton Oxidation Evolution

Researcher(s)	Findings/Highlights	Year
Fenton	Correspondence to the journal editor of Chemical News describing a violet colour emanating from the reaction between H <sub>2</sub> O <sub>2</sub> , tartaric acid, an Fe(II) salt and a base as a test for tartaric acid	1876
Fenton	Identifying the violet colour as arising from a complex formed between iron and the oxidation product of tartaric acid	1881
Fenton	Pioneered the Fenton oxidation by the discovery that Fe(II) salts could activate H <sub>2</sub> O <sub>2</sub> and potentially oxidize tartaric acid in a characteristic way, providing a new and valuable oxidizing agent	1894
Haber and Weiss	Proposed that the active oxidant generated by the Fenton reaction is •OH	1934
Barb and coworkers	Proposed the chain reaction mechanism in the Fenton oxidation as “classical” or “free radical” after several years of investigation on organic compounds	1949-1951
Eisenhauer	Application of Fenton oxidation in small-scale industry	1964
Walling and co-workers	Novel work on the free radical pathway of the Fenton oxidation. The reported results were central to the understanding and subsequent Proliferation of research in varied branches of the Fenton oxidation.	1975
Buxton and co-workers	Documented over 1700 rate constants for •OH reactions with organic and inorganic compounds in aqueous solution	1988
Several Workers	The beginning of extensive research on the applications of Fenton oxidation for waste treatment in academic laboratories	1990 -

(Source: Pignatello *et al.*, 2006; Krzysztof, 2009)

Mineralization of the RH component of the wastewater induces free organics as transient intermediates, and are subsequently oxidized to produce more stable products by hydroxyl radicals, hydrogen peroxide, oxygen and ions (Fe<sup>3+</sup>, Fe<sup>2+</sup>) as shown in equations (2.4-2.8) (Umar *et al.*, 2010).



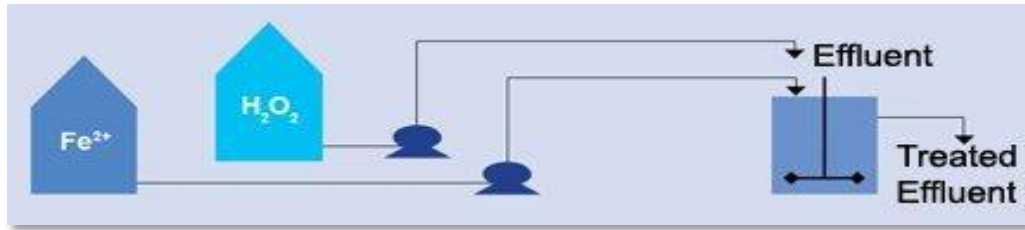


Figure 2.5: The Fenton process (Umar *et al.*, 2010).

Generally, in the presence of UV radiations (photo-Fenton process), an additional number of HO. Radicals are produced both through direct H<sub>2</sub>O<sub>2</sub> photolysis and through UV radiations interaction with the iron species in aqueous solutions (Eq. 2.9-2.11) (Pignatello, 1992)



### 2.4.3 PRWdeputation by Fenton oxidation

Depuration is the process of freeing wastewater of impurities or contaminants. PRW contains oil which is the major contaminant in the wastewater being composed of a range of different hydrocarbons and other organic compounds present in the crude oil, and chemical substances produced by the refinery process such as sulphides, mercaptans,

cyanides, ammonia, phenols, inorganic salts, and traces of some heavy metals. Generally, PRW treatment is achieved in two stages namely, a series of pre-treatment steps, in which suspended matter, oil and grease are reduced, and the advanced stage where the contaminants are reduced to allowable discharge limits as shown in Figure 2.6. For Fenton oxidation in particular, reported PRW mineralization is low (Basheer *et al.*, 2011).

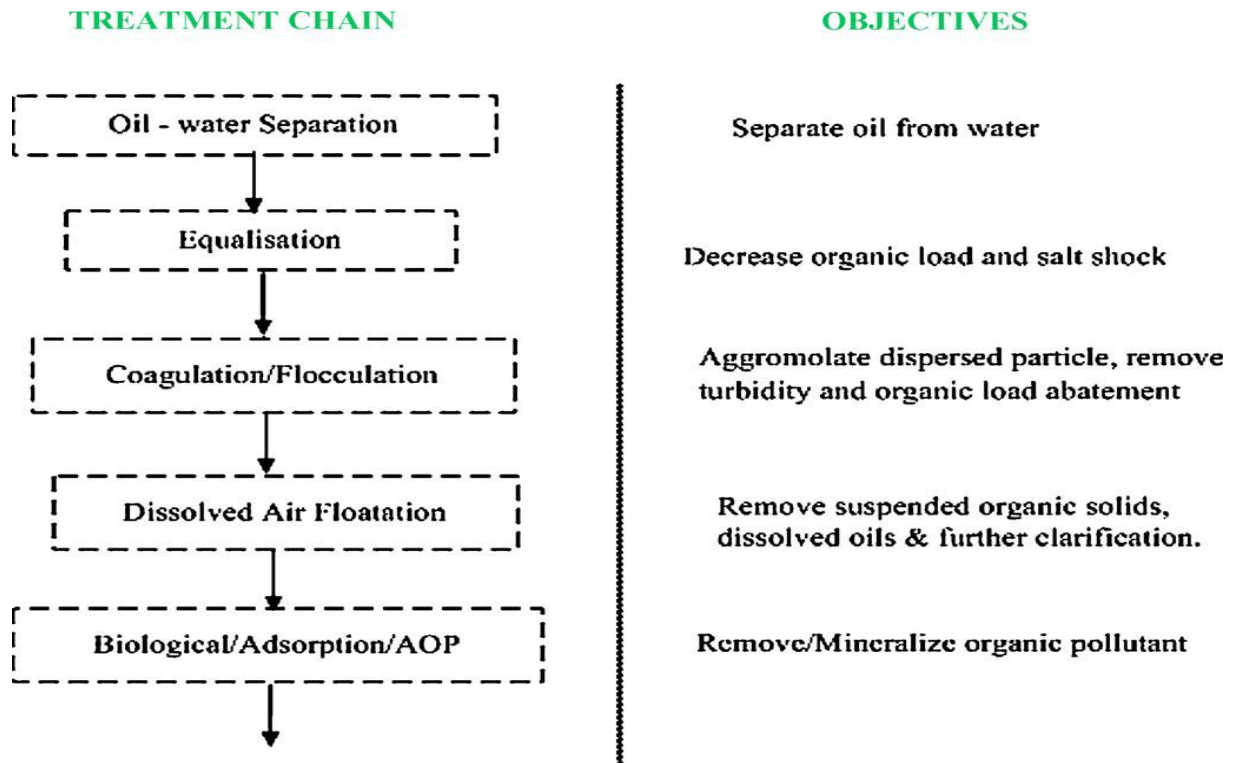


Figure 2.6: Schematic diagram of generic sequence for treating petroleum refinery effluent (Basheer *et al.*, 2011)

Astonishingly, researchers have started findings on PRW treatment. Diya'uddeen *et al.*, (2012) conducted a research on the oxidative mineralization of petroleum refinery effluent using Fenton-like process, and under optimal conditions, maximal TOC and COD reduction achieved within 30 min of oxidation reaction were 70% and 98.1%,

respectively. The obtained models had correlation coefficients of 0.9984 and 0.9916 for TOC and 0.9636 and 0.8835 for COD, respectively. At a pH of 3, corresponding optimal oxidation conditions were found to be 1008.0 mM for hydrogen peroxide and 686.0 mg for (Fe<sup>3+</sup>). That is, the molar ratio of hydrogen peroxide to PRE is 12 and 5 is the mass ratio of hydrogen peroxide to iron (Fe<sup>3+</sup>) (Diya'uddeen *et al.*, 2012).

Photo catalytic degradation of wastewater was investigated as listed in Table 2.7. Tony *et al.*, (2012) studied the application of AOP in treating PRW and COD removal of approximately 50% was obtained by the use of photo Fenton process. However, COD removal of 75% was obtained when preceded by physiochemical treatment. Furthermore, Yasmin *et al.*, (2013) worked on the removal of oil from wastewater by photo Fenton oxidation process, COD removal of 72% was obtained at the optimal condition.

Table 2.7: Photo-catalytic Degradation of PRW

Reference	Parameters investigated	Highlights
Li <i>et al.</i> , (2009)	COD	Reduction in COD level of 80%, 88.9% and 93.0% COD at 30, 60 and 120 min, respectively
Adams <i>et al.</i> , (2008)	COD	85% COD reduction in 10 min, eliminated need for aeration through mechanical mixing
Tony <i>et al.</i> , (2012)	COD	50% removal and 75% when preceded by physiochemical treatment
Yasmin <i>et al.</i> , (2013)	COD	72% removal efficiency at 1000 mg/L dosage ratio

#### 2.4.4 Sludge generation in Fenton oxidation

Generation of sludge is a deficiency for any wastewater treatment technique, because of high cost of sludge treatment. Di Iaconi *et al.*, (2010) reported that approximately 1-2 Euro/m<sup>3</sup> of wastewater is spent on sludge treatment. Characterization and quantification of

Fenton sludge was researched by Mahiroglu *et al.*, (2009) and reported that the sludge generated may not hinder utilization of the process. Generally, the coagulation potentials of catalyst brought about sludge generation in Fenton oxidation, due to the precipitation of the catalyst ( $\text{Fe}^{3+}$ ) during neutralization (Kirilet *et al.*, 2010). As such, it leads to the generation of sludge in the form of iron oxyhydroxides (Umar *et al.*, 2010).

Generally, sludge formed from Fenton processes have a unique feature of low sludge settling velocity (SSV) and sludge settling index (SVI) values, which indicates ease of settling and dewatering with high density and highest settling velocity ( $v_s$ ), thus no further conditioning of the sludge is required (Mahiroglu *et al.*, 2009). However, unlike in other treatment processes where sludge generation is expensive and voluminous (between 40 and 180 mg/L), thereby amounting to 35-50% of the total operating costs, in Fenton oxidation, sludge generation is minimal (Dewil *et al.*, 2005). Literature reports on Fenton sludge characterization indicate that sludge are easily formed and handled and are of good quality. Furthermore, Fenton and Fenton-like reactions was investigated at low iron concentrations to achieve oxidation of commercial azo dyes, only a small amount of sludge was produced and it met the standards of local effluent disposal limits, which needed no further treatment (Hsueh *et al.*, 2005). Therefore, it is justified that the Fenton sludge is effective when recycled back into the treatment system as it does not add to the organic loading of the coagulation step (Yoo *et al.*, 2001).

## **2.5 Goethite Catalyst**

Goethite ( $\alpha\text{-FeOOH}$ ), is a hydrated iron oxide that occurs abundantly in nature, as a constituent of terrestrial soils, sediments, and major weathering product of all type of rocks as shown in Figure 2.7. Goethite was named after of Johann Wolfgang von Goethe, a

mineralogy enthusiast. It was first described in 1806 for occurrences in the Mesabi iron ore district of Minnesota U.S.A. (Prasad *et al.*, 2006).



Figure 2.7: Natural Goethite (Prasad *et al.*, 2006)

Generally, the naturally occurring iron oxide minerals are goethite ( $\alpha$ -FeOOH), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), lepidocrocite ( $\gamma$ -FeOOH), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O or Fe<sub>5</sub>HO<sub>8</sub>·4H<sub>2</sub>O) (Schwertmann and Taylor, 1989). All iron oxides including goethite, are the weathering products, formed from the reactions of Fe<sup>2+</sup> ion, released from Fe (II) silicates and sulfide minerals through protolysis and oxidation (Cornell and Schwertmann, 1996). Their formation and transformation subsequently depends on factors such as temperature, pH, moisture, organic matter and ionic conditions. Copper on the other hand, is a ductile metal with very high thermal and electrical conductivity, and an essential trace element in living systems.

### 2.5.1 Composition and properties of goethite

Goethite is composed of about 80 to 90 percent Fe<sub>2</sub>O<sub>3</sub> and approximately 10 percent water, and is thermodynamically unstable at room temperature. When goethite is dehydrated, it

forms hematite and upon hydration, goethite becomes limonite. The properties of goethite are listed in Table 2.8. The structure of goethite is illustrated in Figure 2.9, it consists of double chains of  $\text{FeO}_3(\text{OH})_3$  octahedra extending along the crystallographic Z-axis. These octahedra are bound to neighboring double chains by Fe-O-Fe and H bonds. However, synthetic goethites are mostly acicular or needle like crystals, but this morphology is often less well developed in soils. Fibrous goethite and grassy types of goethite aggregates have also been reported to occur in some soils (Cornell and Schwertmann, 1996).

Table 2.8: Properties of Goethite

<b>Property</b>	<b>Description</b>
Color	Yellow to reddish to dark brown or black
Luster	Earthy to dull for massive forms and metallic for crystals
Crystal System	Orthorhombic; 2/m
Transparency	Crystals are opaque
Crystal Habits	Include prismatic and platy crystals, massive and aggregate forms include internally radiating or fibrous; reniform, botryoidal and stalactitic.
Cleavage	Perfect in one direction {010}
Fracture	Uneven to splintery
Hardness (Mohs Scale)	5.0 to 5.5
Specific Gravity	3.3 to 4.3
Solubility	HCl soluble
Streak	Brown, brownish yellow to orange yellow

(Source: Ford *et al.*, 1997)

Furthermore, natural goethite is an imperfectly crystalline material, with large surface area and open channel structure when formed under the influence of different pathogenic factors. The preexisting metal cations like  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and others get incorporated into the crystal structure of goethite as a substitute for  $\text{Fe}^{3+}$  ion (Ford *et al.*, 1997). Therefore, this impure form of goethite consisting of substituted metal cations of varying valances for  $\text{Fe}^{3+}$  ion are referred to as metal ion doped goethite.

Goethite has a highly reactive surface due to complete hydroxylation which makes it an efficient sorbent and is significant in mobility control of trace contaminants, plant nutrients, soil aggregation, soil classification and pedogenesis (Prasad *et al.*, 2006). Like other metal oxides, it also possesses pH dependent surface charges and thus, in an aqueous medium its surface may either be positively or negatively charged. At a certain pH value the magnitude of positive and negative charges on the surface become equal, as a result, the net charge on the surface is zero (Mcbride, 1989).

The hydrated surface of goethite is highly reactive and further improves with the doping of metal ions in its crystals. Therefore, the surface properties of metal-doped goethite become particularly important due to its widespread occurrence and abundance in natural environment. In the past decade a number of studies have been performed to determine the surface properties of goethite (Mohapatra *et al.*, 2006). Researchers suggests that the inclusion of minute quantity of metals may have notable effect on the chemical and physical properties of goethite and hematite.

### 2.5.2 Occurrence of goethite

Goethite is present in rocks by means of varied compartments of the ecosystem, and occurs in almost every soil type and climate region and is thought to be responsible for the yellowish to brown color of many soils and weathered materials (Schwertmann and Taylor, 1989).

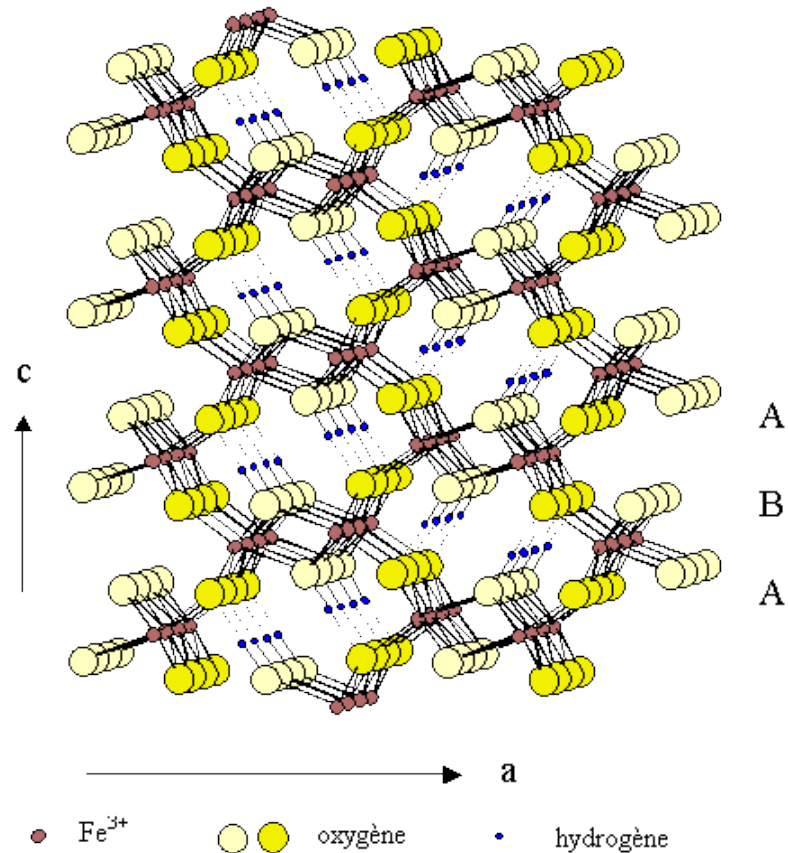


Figure 2.9: The structure of Goethite (Mohapatra *et al.*, 2006)

Goethite formation was reported to occur through deprotonation and hydrolysis of Fe(III) in dissolved state, which is later followed by nucleation and crystallization. The mechanism of goethite formation involving Fe(II) as a precursor, is even more complicated. Cornell and Schwertmann, (1989) discussed on the formation and transformation mechanism, and the effect of experimental conditions on the properties of

goethite. These oxides are secondary minerals and are formed from the primary minerals through reactions of  $\text{Fe}^{2+}$  ions released from Fe(II)-bearing silicates upon weathering. In Nigeria, goethite is abundant in million of tones. Goethite is predominantly found in areas, such as in Ota-Efun and Oshogbo in Osun state, Kotonkarfi in Kogi state and Birnin gwari in Kaduna State of Nigeria (Abdusalam and Adekola, 2005).

Astonishingly, goethite can also be synthesized in the laboratory in the form of needle-like (acicular) particles of submicrometer size with a very high specific surface area. Numerous methods of preparation and experimental conditions have been proposed for developing goethite samples with different specific surface areas and morphologies (Subrt *et al.*, 2000). The main variables that affect the surface area and morphologies of goethite are:

- a) Fe precursor (nitrate, chloride, and sulfate etc.)
- b) Final pH
- c) Catalyst dosage
- d) Temperature (40–90 °C)
- e) Time (a few hours to a few weeks) allowed for crystallization.

### **2.5.3 Uses of goethite**

Goethite marks its worth by being used as an iron ore, and is often acknowledged as a brown iron ore, for the reason that it has significant use as a clay earth pigment. It does not hold a status of a phenomenally beautiful mineral specimen, and hence, it is often brought to use in forming the backdrop for other minerals like vanadinite.

The following is a list of some of its benefits and uses:

- a) In eliminating chemical elements and other contaminants from liquid industrial effluents.
- b) As a divination element in meditation, offering insight into future occurrences.
- c) After hematite, goethite is the most important ore of iron.
- d) For treating deficiency of red blood cells, and health problems associated with the digestive system and convulsions.

Therefore, it wouldn't be wrong to conclude that goethite is one of the most prominent minerals on the face of the Earth (Subrt *et al.*, 2000).

#### **2.5.4 The concept of doping in goethite**

Doping is the isomorphous substitution of  $\text{Fe}^{3+}$  in goethite by another cation. The presence of cations other than  $\text{Fe}^{3+}$  in goethite crystals, substantially affect the physical and chemical properties of goethite (Stiers and Schwertmann, 1985).

Unit cell parameters of synthetic doped goethite were investigated by Gerth, (1990) using  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  or  $\text{Pb}^{4+}$  as dopants. Mohapatra *et al.*, (2005) reported that the suitable percentage of element in doped iron oxide materials is 0.15-4.0%. He related the systematic changes of the unit-cell b-dimension with increasing substitution to the ionic radii of incorporated metals. The octahedra of the goethite structure became distorted along the crystallographic a-axis by incorporation of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ .

The distortion along a in case of Zn- and Cd-goethite, was reported to be due to the smaller ionic size which both of these metals exhibited in the tetrahedral coordination. Thorium was found to be incorporated by non-structural incorporation while uranium was not incorporated at all. It was postulated that the higher a-dimension in case of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  was the result of structural defects and did not indicate the formation of a separate

mineral phase. Copper in the goethite structure strongly favors the H<sub>2</sub>O<sub>2</sub> decomposition with radical as intermediates as shown in equation 2.13.



## 2.6 Depuration of PRW Using Copper Doped Goethite Catalyst

Goethite is one of the most thermodynamically stable iron oxides. It is often modified by dispersing it on a supporting material or doped with some cations. Doping cations are added to principally assist special redox processes, such as the Fenton reaction. In order to minimize the amount of the ferric hydroxide sludge forming in the homogeneous reaction, iron oxides such as goethite are used instead.

Muruganandham *et al.*, (2007) investigated the decomposition of dissolved ozone in the presence of granular goethite to reduce the residual ozone in treated water and the decomposition of ozone increased from 53.2% to 98% as the goethite loading increased from 2 to 30 g/l. The results indicated granular goethite is a promising catalyst for the decomposition of ozone in aqueous medium. Oxalate and salicylate have a competitive adsorption on goethite, however, the existence of oxalate improved the photo degradation of salicylate by reacting with goethite producing OH radicals (Kryśa *et al.*, 2011)

Generally, goethite is the commonly used iron oxide among Fe (III) bearing minerals for catalytic Fenton degradation or photo degradation of organic pollutants (Hanna, 2008) due to numerous factors such as:

- a) Ability to operate in a wide range of pH
- b) Positive performance with sun light

- c) Higher stability thermodynamically
- d) Being relatively low priced and environmentally friendly (Ortiz *et al.*, 2008).

However, a reported investigation depicted that for half lives ( $t_{1/2}$ ) of photodegraded sulfadiazine which is the time required for degradation of 50% of initial sulfadiazine concentration, for various studied iron oxides namely fatite , maghemite , lepidocrocite and goethite (Wanget *al.*, 2010) that shows better catalytic performance of goethite. Despite the fact that iron oxides provide acceptable scores for contaminant degradation in Fenton-like reactions with uncontrolled pH values, several works have been put in practice to improve their efficiency and increase decomposition rate of probe molecules through some modifications in their structure.

### 2.6.1 Goethite as an adsorbent

Adsorption is the accumulation of gas, vapor or liquid molecules on an interface. Frequently, adsorption method is utilized in the removal of soluble metals and organic substances from aqueous phase and depends upon the surface properties of the adsorbent. Goethite like other metal oxides possesses pH dependent surface charges in aqueous medium which changes with pH according to the following reactions (Sun *et al.*, 1999):



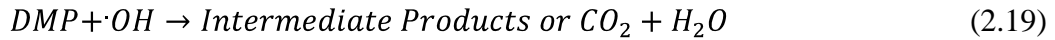
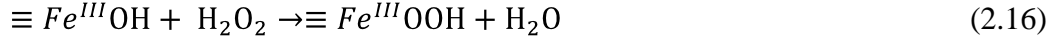
In aqueous medium, the surface of goethite is, either positively or negatively charged. At a certain pH value, the positive charge on the surface becomes equal to the negative charge, whereby the net charge on the surface is zero and this pH value is referred to as the point of zero charge (Mcbride, 1989).

Goethite is an ideal adsorbent due to features such as its well known surface chemistry and natural abundance in the earth's surface. Surface site density is an important factor in determining the adsorption capacity of material. Villalobos *et al.* (2003) investigated the surface site density of goethite by adsorption of proton and carbonate, indicating an inverse relationship between sorption capacity for protons and carbonate ions and specific surface area of goethite for three synthetic goethite preparations.

However, the adsorption capacity of adsorbents can be improved by the modification of its surface functional groups by incorporating foreign organic and inorganic compounds. Mohapatra *et al.*, (2006) reported that Cu, Ni or Co doped goethite was a better adsorbent for arsenic than the pure goethite itself.

Generally, in heterogeneous Fenton reactions, the electrostatic interaction between the surface of the catalyst and the probe molecule is a very important factor and removal of probe molecule from reaction solution is accounted by its adsorption on surface of transition metal substituted ironoxides (Yanget *al.*, 2009). Therefore, the organic contaminant and the heterogeneous iron catalyst are stirred together for a period of 2 to 3 hour to achieve adsorption equilibrium (Hanna, 2008). Several factors such as pH, contact time, initial concentration of contaminant and physiochemical properties affect the adsorption capacity of the catalyst. In UV/Si-FeOOH/H<sub>2</sub>O<sub>2</sub> system (Yuan *et al.*, 2011). For example, the surface charge of the catalyst and dimethyl phthalate (DMP) hydrolysis was found to be pH dependent. Electron-donating groups in DMP induces negative charge to DMP at pH values higher than zero potential charge of Si-FeOOH (8.4) and on the other side, at pH <8.4, the surface of the catalyst is positively charged which is desirable for DMP adsorption. In this study, pH of 5 improved DMP removal by 10 to 15%. The

reactions involved in DMP degradation under UV irradiation has been summarized as follows:



Under the influence of UV irradiation, both produced holes from Si-FeOOH semiconductor and the electron hole pairs, could react with adsorbed hydrogen peroxide or ( $\cdot OH$ ) anion and yield ( $\cdot OH$ ) radicals. Moreover, other strong oxidizing species such as ( $\cdot O_2^-$ ) also were produced from the reduction of adsorbed  $O_2$  on the catalyst surface over conduction band electrons (Yuan *et al.*, 2011).

### 2.6.2 Cation adsorption

Generally, the possibility of adsorption on goethite to metal ions have been documented and the strength of some of them on goethite in decreasing order of  $Cu > Pb > Zn > Cd > Co > Ni > Mn$ . The affinity of cations for goethite is strongly dependent on the temperature of the system and on the time allowed for adsorption. It was proposed that the process involved rapid adsorption on the external surface surfaces of crystals followed by slow diffusion into the internal sites, possibly along the domain boundaries, with finally, adsorption on internal sites (Cornell and Schwertmann, 1996). Most of previous investigations have suggested that humic substance promoted the adsorption of metal ions at low pH, such as the report of Ali and Dzombak (1996). However, the increase of adsorption was attributed to the adsorption of anions/organic acid on the mineral surface followed by the interaction of heavy metal ions with modified surface and generally

formed ternary adsorption. Therefore, goethite is playing an important role in the water/particles system on the adsorption/desorption of metal ions, which is also affected in the presence/absence of natural organic matter, such as humic acid and fulvic acid.

### **2.6.3 Anion adsorption**

Adsorption of various anions like arsenate, arsenite, silicate, tungstate, vanadate, antimonite, carbonate, phosphate, sulfate and chromate among others on the surface of goethite has been studied extensively. However, in comparison to the cations, detailed studies involving the adsorption of anions are rather few. Furthermore, to their more likelihood in natural environment, competitive adsorption studies in case of anions cover most of the reported literature. Moreover, a number of anions, like phosphate, sulphate, arsenite, antimonite, vanadate and carbonate have been studied both individually and in competitive adsorption systems. Goethite has also been used as a model sorbent to examine the effect of pH, temperature, background electrolyte concentration, presence of other species in solution. Therefore, competitive adsorption on goethite also has been the subject of much research because the competitive adsorption results at least to some extent, affects the bioavailability of nutrients and immobilization of toxic chemicals, such as the competitive adsorption between phosphate and sulphate/arsenate (Gao and Mucci, 2003).

## **CHAPTER THREE**

### **MATERIALS AND METHODS**

#### **3.1 Materials**

The main materials(analytical grade from BDH Chemical England) used in this work include:

1. Ferric Sulphate (98%).
2. Copper (II) Sulphate (99%).
3. Cetyltrimethyl Ammonium Bromide.
4. Sodium Hydroxide (98%).
5. Hydrochloric Acid (36.5%).
6. Nitric Acid (65%).
7. Deionized Water.
8. Hydrogen Peroxide (30%).
9. Ethanol (98%).
10. Distilled Water (obtained from Chemical Engineering Department, A.B.U Zaria).

### **3.2 Apparatus**

The apparatus used in this work are:

1. Conical flasks (250, 500,1000ml)
2. Measuring cylinders (100ml, 200ml)
3. Plastic funnels
4. Retort stand and G-Clamp
5. Thermometer (0-360°C)
6. Plastic spoons
7. Rubber gloves
8. Nose masks
9. Sample bottles (plastic)
10. Burette (50ml)
11. Pipette (25ml)
12. Filter paper (12.5cm)

### **3.3 Equipment**

The major equipment employed in this work are:

1. Electronic Weighting scale (0-100kg Range),WEDA Holland (AB 204) from Chemical Engineering Department, A.B.U, Zaria.
2. Oven, Gallenkamp England (TMOV – 420) from Chemical Engineering Department, A.B.U, Zaria.
3. Digital pH meter, Crison(AB 204) from Multi User Laboratory, A.B.U, Zaria.
4. X-Ray Diffraction (XRD) Machine, PANanalytical, England (Empyre) from National Geological Research Laboratory (NGRL), Barnawa, Kaduna
5. Hot Plate with Magnetic Stirrer (0-300°C), Stuart, England(C1202)from Chemical Engineering Department, A.B.U, Zaria.
6. Scanning Electron Microscopy (SEM) Machine, JENWAY (3510) from Chemical Engineering Department, A.B.U Zaria.
7. Centrifuge,Baird and Tatlock (BT115) from Chemistry laboratory A.B.U, Zaria.

### 3.4 Experimental Procedures

Block diagram of the experimental procedure followed in the course of this work is shown in Figure 3.1.

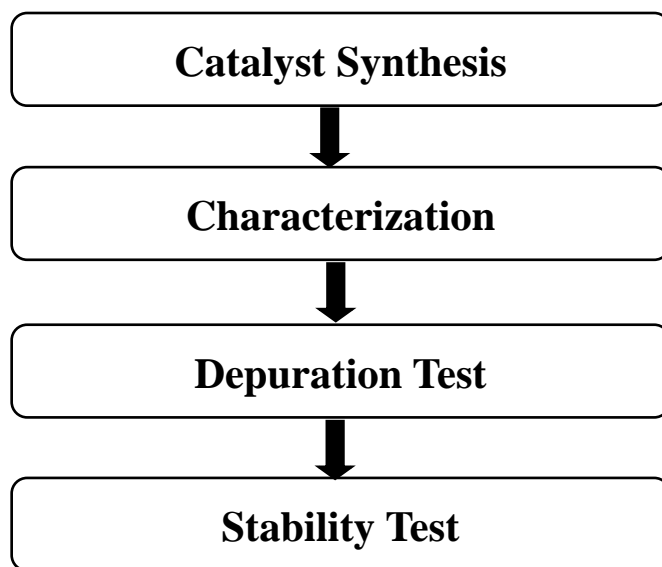


Figure 3.1: Block diagram of the experimental procedure

#### 3.4.1 Catalyst preparation

A precipitation technique was employed in this work, being the most efficient chemical pathway to obtain iron oxide particles and large amount of nanoparticles (Mohapatra *et al.*, 2005). Pure goethite was synthesized by dissolution of ferric sulphate (0.01M) and cetyltrimethyl ammonium bromide (CTAB) (0.015M) in 50ml deionized water then stirred and heated at temperature of 80°C for 30 minutes to effectively dissolve CTAB into a homogenous mixture. However, for the copper doped goethite synthesis which is the same as in goethite synthesis as shown in Figure 3.2, copper (II) sulphate (0.00029M, 0.00073M, 0.00103M) was used as the copper precursor (Mohapatra *et al.*, 2006).

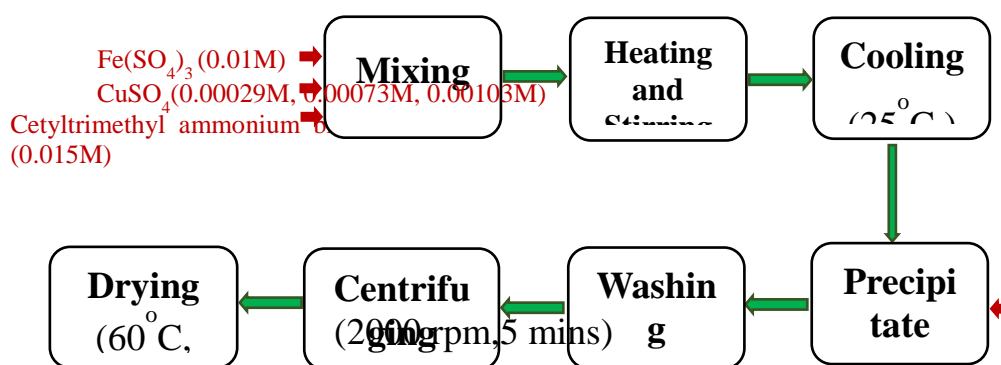


Figure 3.2: Catalyst synthesis block flow diagram

Subsequently, the obtained solution was cooled down to room temperature and the pH was adjusted to 10 using sodium hydroxide. Then the suspension was kept for 24 hours, and a clear brown precipitate was formed at the bottom. The solid products obtained were washed three times with hydrochloric acid, ethanol and deionized water, respectively and were subsequently centrifuged. Finally, the products were oven dried at 60°C for 24 hours, grinded, weighed, and stored in plastic containers.

### 3.4.2 Samples characterization

#### 3.4.2.1 XRD analysis

X-Ray Diffraction (XRD) patterns of the synthesized samples were recorded using an England Philips diffractometer at the National Geological Research Laboratory (NGRL), Barnawa Kaduna with a crystal monochromator at an accelerating voltage of 40kV with 100-mA flux. The X-ray source was CuK $\alpha$ 1 with a wavelength of 1.5406Å.

#### 3.4.2.2 Atomic Absorption Spectrophotometer analysis

The concentration of metal ions were estimated by Atomic Absorption Spectrophotometer (AAS). 33 mg samples were digested in hydrochloric acid and the solutions obtained were analyzed volumetrically for iron and copper using the standard procedure (Vogel,1991).

#### 3.4.2.3 Surface area analysis using Sear's method

The surface area was estimated using Sear's method by agitating 1.5 g of powdered sample in 100 ml of diluted hydrochloric acid at pH of 3, 30 g of sodium chloride was then added with a constant stirring and the volume was made up to 150 ml with deionized water. The solution was titrated with (0.10N) NaOH and the volume needed to raise the pH from 4 to 9 was recorded. Then the surface area of synthesized undoped and doped catalysts were estimated (Sears, 1981).

The volume (V) required to raise the pH from 4 to 9 was noted and the surface area computed from the following equation:

$$S(m^2 \cdot g^{-1}) = 32V - 25 \quad (3.1)$$

Where S and V are the specific surface area in m<sup>2</sup>g<sup>-1</sup> and volume of NaOH in cm<sup>3</sup> respectively

#### 3.4.2.4 Scanning Electron microscopy (SEM)

The SEM of the synthesized samples for microstructures and morphologies were determined using a PHENON PRO-X machine in Chemical Engineering Department, A.B.U., Zaria.

### 3.5 Depuration Experiments

The wastewater was obtained from Kaduna refinery and petrochemical plant (KRPC) located along Kachia road Kaduna State, Nigeria. The wastewater samples were collected in a 120 mL plastic container, at the inlet point to the pre-treatment unit. The plastic containers were placed in an ice box and immediately conveyed to the laboratory and stored in a cold room maintained at 4°C to avoid composition change through probable biological activities or photolysis.

The heterogeneous Fenton depuration experiments were carried out in a 500 mL conical flask (containing 100 mL of wastewater). The experimental design and optimization were accomplished using the Design-Expert software, version 6.0.6 (Stat-Ease, Inc., USA). The initial pH (8.16) of the wastewater was adjusted to 3 and 6.5 by H<sub>2</sub>SO<sub>4</sub> and to pH of 10 by NaOH respectively (Zhong *et al.*, 2012).

The oxidant and catalyst were added to the wastewater under stirring and nearly constant temperature, at 25 ± 1°C. (Guimaraes, 2009). At pre-selected time as shown in Table 3.1, samples were removed and then filtered through 0.22 µm membrane and COD analysis of the samples was then carried out. To conduct the stability analysis, the used catalyst was filtered and rinsed with distilled water and dried then used again in depuration tests.

The depuration efficiency was calculated using the expression

$$\text{Depuration (\%)} = \frac{COD_o - COD_t}{COD_o} \quad (3.2)$$

Where  $COD_0$  is the initial COD (mg/L) of the raw wastewater,  $COD_t$  is the wastewater final COD (mg/L) at a certain reaction time,  $t$  in minutes.

Furthermore, a three-factorial central composite design (CCD) was used, as it can adequately provide a reasonable distribution of datapoints throughout the region of interest with minimum runs for four factors of investigation.

Table 3.1: Depuration Test Design Matrix

<b>Run</b>	<b>Catalyst Loading (mg/L)</b>	<b>H<sub>2</sub>O<sub>2</sub> (g/L)</b>	<b>Time (mins)</b>	<b>pH</b>
1	10	0.2	5	10
2	100	0.2	5	10
3	55	1.1	182.5	6.5
4	100	0.2	5	3
5	10	2	360	3
6	55	1.1	182.5	6.5
7	55	2	182.5	6.5
8	55	1.1	182.5	6.5
9	100	2	5	10
10	100	0.2	360	10
11	10	2	360	10
12	10	0.2	5	3
13	100	0.2	360	3
14	10	0.2	360	3
15	55	1.1	182.5	6.5
16	100	2	360	10
17	100	2	5	3
18	55	1.1	182.5	6.5
19	10	0.2	360	10
20	10	2	5	10
21	55	2	182.5	6.5
22	55	1.1	182.5	6.5
23	55	1.1	182.5	3
24	55	1.1	360	6.5
25	100	2	360	3
26	10	2	5	3
27	55	1.1	182.5	6.5

### **3.6 Analysis of the Raw and Treated Water Samples**

#### **3.6.1 Measurement of COD and BOD**

The measurement of COD and BOD values was based on the analytical method. 0.4 g of  $\text{H}_2\text{SO}_4$  was placed into refluxing flask and 20 ml of aliquot was added, then 10 ml of standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and several glass beads previously dried at  $600\text{ }^\circ\text{C}$  for 1 hr, 30 ml  $\text{Ag}_2\text{SO}_4$  - $\text{H}_2\text{SO}_4$  solution was added slowly with gentle swirling, then the flask was connected to the condenser. The blank mixture was prepared and allowed to reflux for 2 hrs, cooled and the condenser was washed with distilled water, the cooled sample was then poured into Erlenmeyer flask and diluted to 150 ml then allowed to cool to temperature and then titrated the excess dichromate with standard using 2 to 3 drops of ferroin as the indicator (Bay *et al.*, 2003).

#### **3.6.2 Measurement of pH**

The electrode meter was set to pH mode and immersed into the liquid sample and the pH reading was recorded.

#### **3.6.3 Measurement of TDS**

The electrode meter was set to TDS mode and immersed into the liquid sample and the total dissolved solid of the sample was then recorded.

#### **3.6.4 Measurement of soluble iron content**

The soluble iron content of the wastewater was analyzed using AAS.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Characterization of Synthesized Catalysts

##### 4.1.1 XRD analysis of the synthesized undoped and doped goethite catalysts

The XRD pattern of the synthesized samples shown in Figures 4.1-4.4 are similar, providing ground for the undoped and copper doped goethite catalyst comparison. The XRD pattern shows that the solids are crystalline in nature and all the diffraction peaks can be well indexed to Goethite ( $\alpha$ -FeOOH) phase structure (JCPDS card no. 29-713).

All the strong and sharp diffraction peaks indicated the good crystallization of the synthesized samples. The drying temperature of 60<sup>0</sup>C was selected based on the work of Ford *et al.*, (1997).

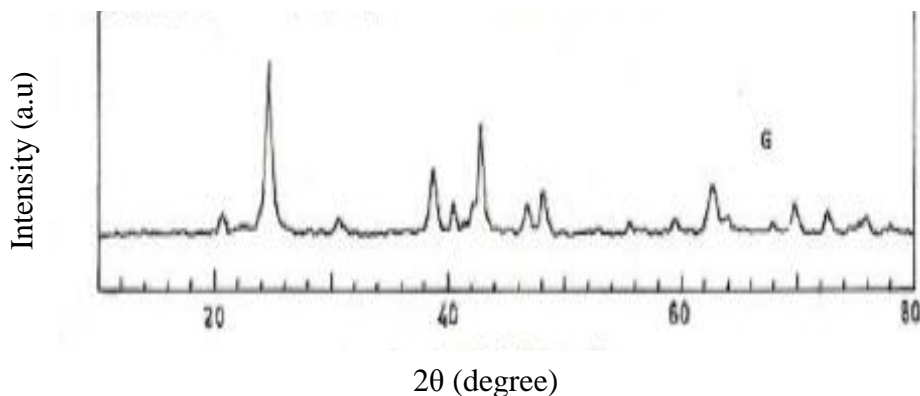


Figure 4.1a: Standard XRD pattern of Goethite (Mohapatra *et al.*, 2006)

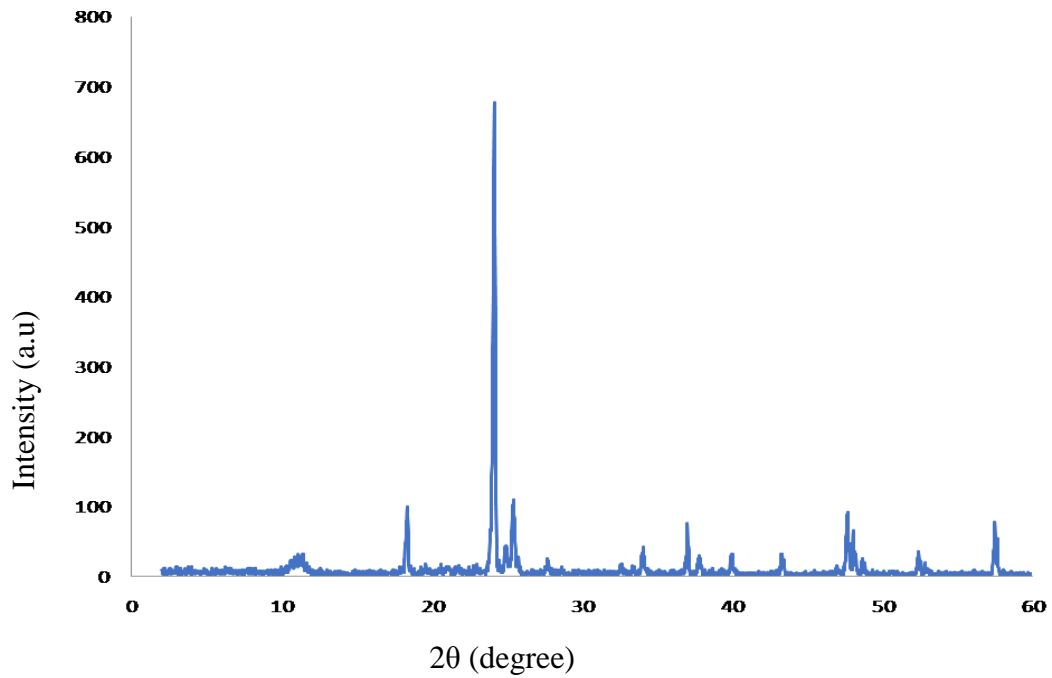


Figure 4.1b: XRD pattern of synthesized Goethite catalyst

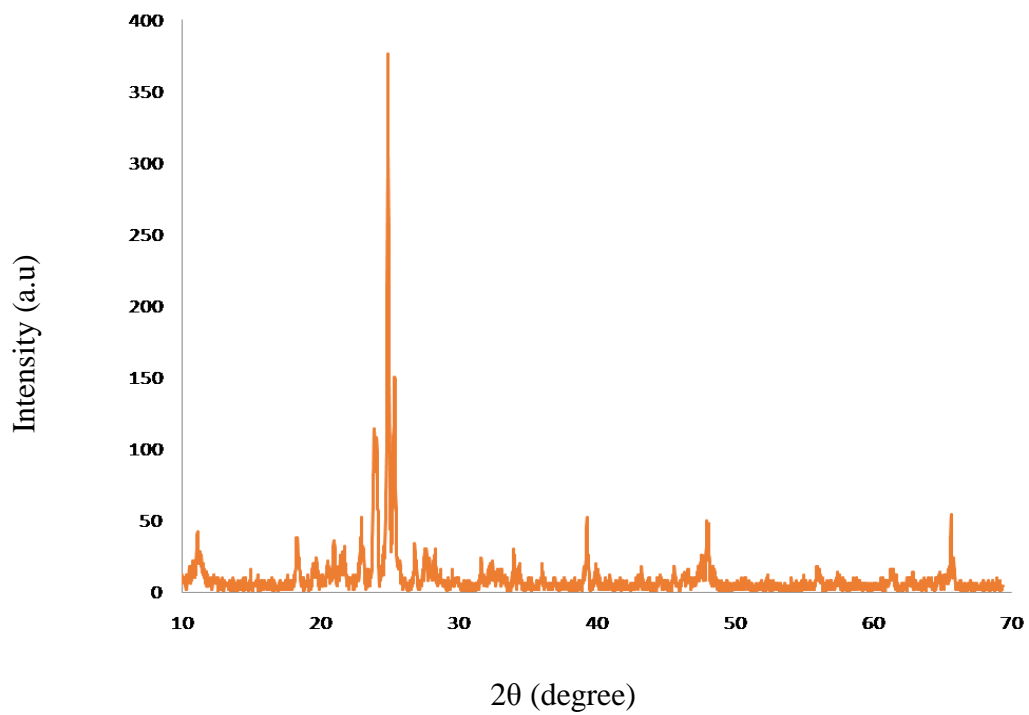


Figure 4.2: XRD pattern of Cu-doped (A) catalyst

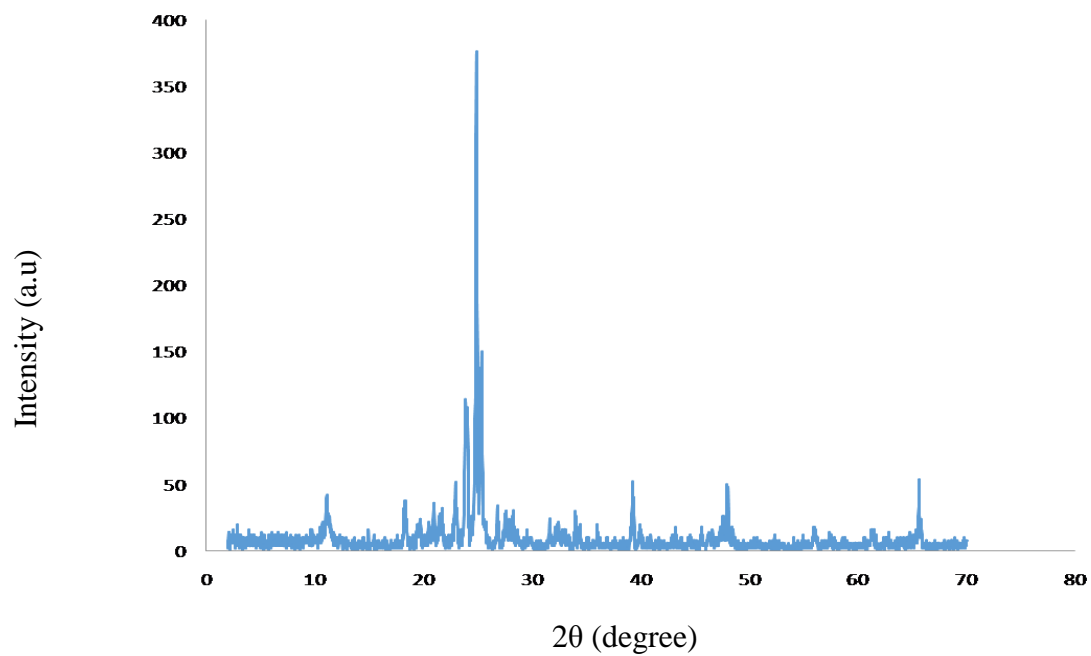


Figure 4.3: XRD pattern of Cu-doped (B) catalyst

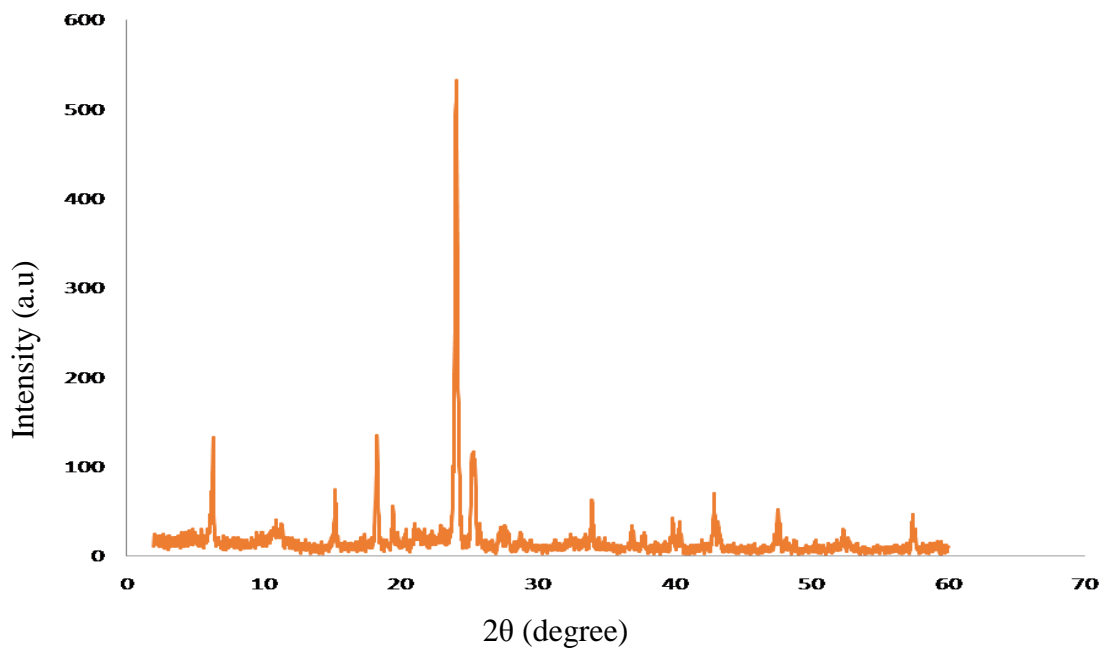


Figure 4.4: XRD pattern of Cu-doped (C) catalyst

### 4.1.2 Composition of synthesized undoped and doped goethite catalysts

The AAS result as shown in Table 4.1, indicate that the main constituents of the synthesized catalysts are mainly elemental iron and copper, which are the active species of the Fenton depuration catalyst. The precursor for iron used in the synthesis of the undoped and doped catalysts was ferric sulphate (0.01M), cupric sulphate (0.00029M, 0.00073M and 0.00103M) was the precursor of copper in the doped catalysts.

Table 4.1:Composition of the Synthesized Catalysts

Sample	Fe(wt %)	Cu(wt %)
Undoped goethite	63.9	-
Cu-doped (A)	62.4	0.20
Cu-doped (B)	59.9	1.63
Cu-doped (C)	58.6	3.25

### 4.1.3 Surface area analysis of the synthesized catalysts

The specific surface areas were measured using the Sear's method. The surface area of the undoped goethite catalyst was  $85.4 \text{ m}^2 \text{ g}^{-1}$ , while the copper doped samples were  $99.8 \text{ m}^2 \text{ g}^{-1}$  for doped (A) goethite,  $106.2 \text{ m}^2 \text{ g}^{-1}$  for doped (B) goethite and  $109.7 \text{ m}^2 \text{ g}^{-1}$  for doped (C) goethite respectively. However, it depicts that copper inclusion in the goethite structure increased the surface area which is likely due to the difference in the ionic radii of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ . The ionic radii of Cu ( $0.73 \text{ \AA}$ ) is approximately 13% greater than Fe ( $0.645 \text{ \AA}$ ). Therefore, presence of the foreign element in goethite structure led to the increase in surface area of the copper doped samples. Mohapatra *et al.*, (2006) reported similar effect of copper doping on the properties of goethite. Furthermore, the surface area of the

synthesized doped samples increased with increase in percentage copper as shown in Figure 4.5. The high surface area may be attributed to a combination of (i) the significant void space between individual crystallites due to insertion of Cu (II) ion in the goethite matrix (ii) the finer goethite particle and (iii) increase in amorphous content of the doped samples (Mcgarvey and Owen, 1998).

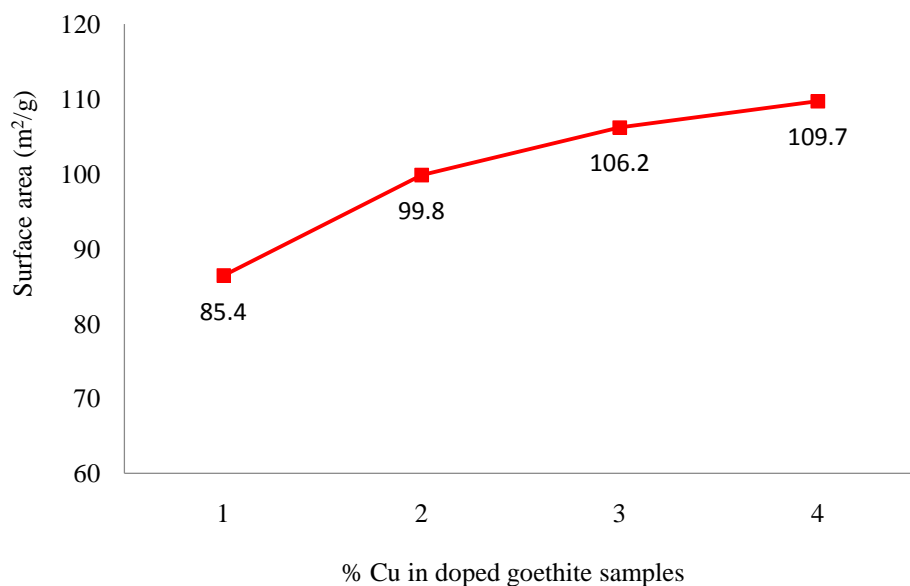


Figure 4.5: Effect of Cu-doping on surface area

#### 4.1.4 Particle size analysis of the synthesized catalysts

The particle sizes of the synthesized undoped and doped catalysts were obtained from the

XRD peaks and calculated using the Debye - Scherrer equation  $D = \frac{k\lambda}{\beta \cos\theta}$  (4.1)

Where  $D$  is the particle size,  $\lambda$  is the wave length of the x – ray radiation (Cu  $K\alpha = 0.1542$  nm),  $k$  is the shape factor ( $k = 0.94$ ),  $\beta$  is the line width at half maximum height and  $\theta$  is the angular position of the maximum peak (Hou *et al.*, 2009).

As could be observed from the results in appendix B, the particle size of the undoped goethite catalyst is 59.80nm and for the doped goethite catalysts were 59.33nm, 59.33nm and 43.60nm, respectively. However, the particle size decreases with increase in the surface. Similar trend was observed in the work of An *et al.*, (2011).

#### **4.1.5 Morphology of the synthesized catalysts**

The morphological characteristics of the synthesized undoped and doped goethite catalyst were investigated by SEM analysis. Undoped goethite catalyst SEM image displayed in Plate 1.0 shows goethite with roughly irregular shape and Cu-doped (C) goethitecatalyst with high percentage of copper, while Plate 2.0 showsCu-doped (A) and Cu-doped (B) goethitecatalyst. However, the limited particle size distribution was largely due to the precipitation technique employed. Furthermore, the SEM image of the doped goethite catalyst shows large crystalsindicating high crystallinity.Most of the particles are aggregated which makes it difficult to determine the exact size and shape of the particle.

#### **4.2 Depuration of Kaduna Refinery Wastewater**

In this study, COD removal was used as the indicator of successful petroleum refinery wastewater depuration. The basis for the choice of COD parameter, is that nearly all organic compounds can fully be oxidized to carbon dioxide with a strong oxidizing agent (Bay *et al.*, 2003).The characteristics of the wastewater used in the work are presented in Table 4.2, and compared with the National Environmental Standards and Regulations Enforcement Agency (NESREA).

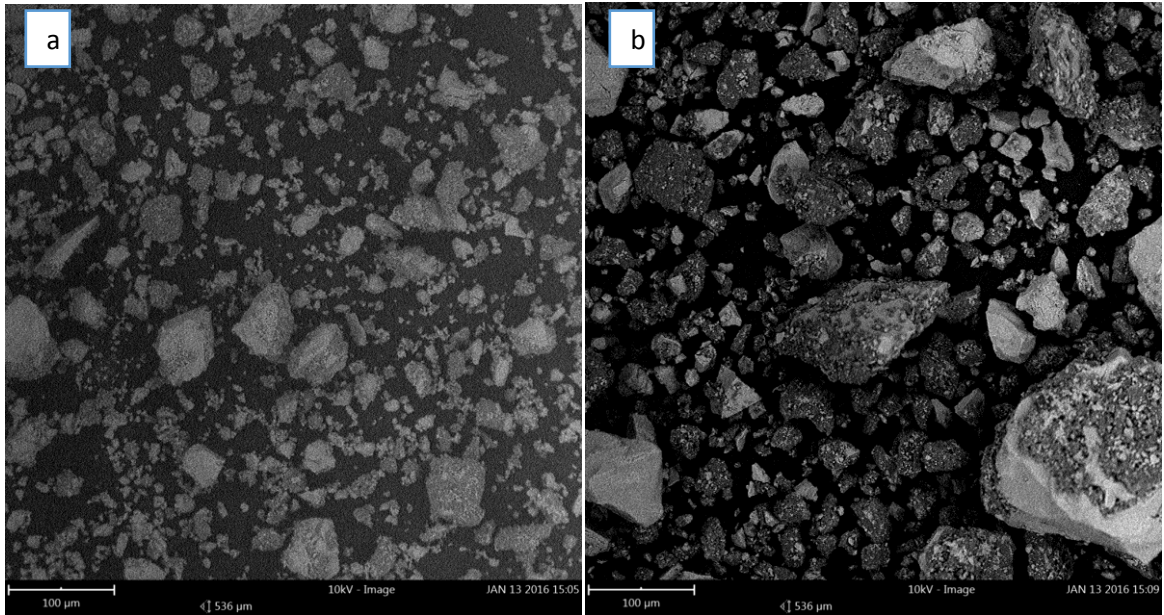


Plate 1.0: SEM image (a) Undoped Goethite catalyst (b) Cu-doped (C) Goethite catalyst

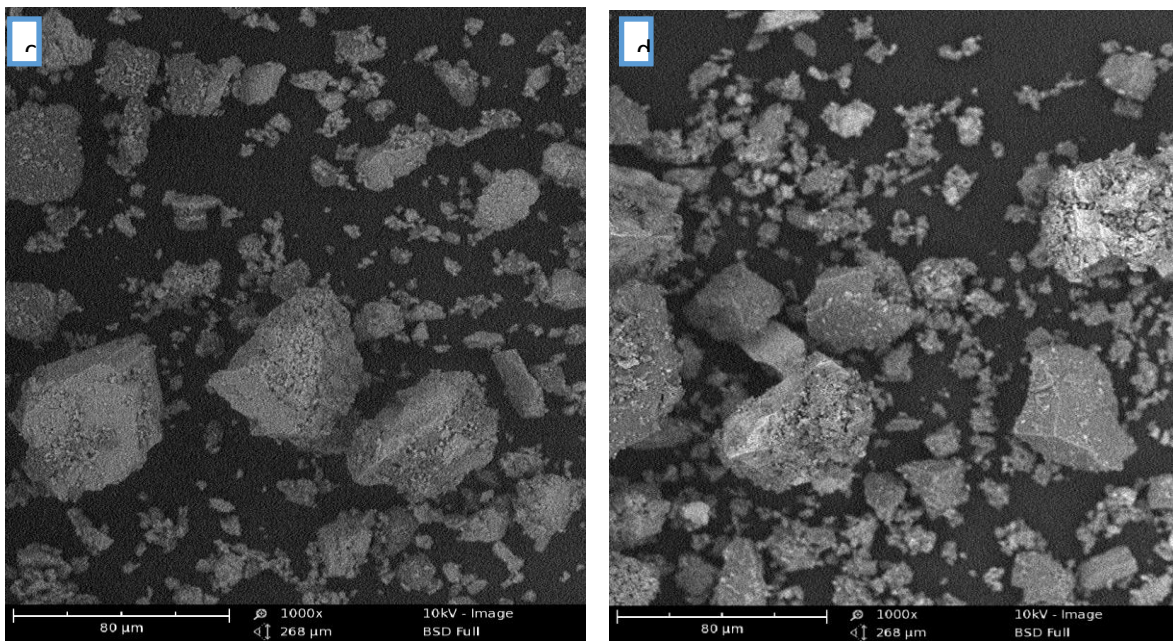


Plate 2.0: SEM image(c) Cu-doped (B) Goethite catalyst (d) Cu-doped (B) Goethite catalyst

The COD results are shown in Table 4.4, and the percentage depuration was calculated using equation 3.2 and the results are shown in Table 4.5. The optimum conditions are 360 minutes reaction time, pH of 3, catalyst loading of 55mg/L and hydrogen peroxide dosage of 1.1g/L. However, copper doped (C) catalyst yielded the highest depuration percentage of 86% at pH of 3, 84% at pH of 6.5 and 72% at pH of 10, respectively.

Table 4.2: Characterization of Kaduna Refinery Wastewater

<b>Parameter</b>	<b>Unit</b>	<b>Value</b>	<b>NESREA (2007)</b>
pH	Dimensionless	8.16	6-9
Chemical oxygen demand (COD)	mg/L	860	150
Fe	mg/L	65	15-20
Biological oxygen demand (BOD)	mg/L	342	50
Total dissolved solids	mg/L	34	25-30

The most widely applied technique in treatment of PRW is the biological process. Although the process is capable of removing some of the organic contaminants, the process have deficiency of incomplete degradation, as reported by Abubakar *et al.*, (2008) where low COD reduction of 22% was achieved in treatment of Kaduna refinery wastewater. Similarly, Usman *et al.*, (2012) used biological process for the treatment of Kaduna refinery wastewater and 56%COD reduction was achieved. Therefore, further clarification of the treated wastewater from the biological process leads to effective treatment as practiced in most Nigerian refineries, but requires high operational and maintenance cost (Anyadiegwu *et al.*, 2015).

The Fenton depuration process is still not being utilized on an industrial scale in refineries, due to drawbacks such as voluminous reagent consumption. The need for pH modulation is required because the initial pH of PRW is 6-9, so before the depuration process is carried out, the PRW pH is modulated to 3 as the Fenton catalyst is active only at pH of 3. Numerous laboratory works have been undertaken, the most recent is work is by Ali *et al.*, (2014), where COD reduction of 46% was achieved using natural goethite catalyst at pH of 3, with large amount of reagents consumed for pH modulation. Astonishingly, appreciable depuration percentage was achieved in this study, at pH of 6.5, with 67.44% for the undoped catalyst, and 79%, 82.56% and 83.72% for the Cu-doped A, B and C goethite catalysts, respectively. It was observed that the Cu-doped goethite catalysts yielded improved performance, affirming the efficacy of the doped catalysts in Fenton depuration of Kaduna refinery wastewater.

The soluble iron content of the treated wastewater is shown in Table 4.3. Depurated wastewater using Cu-doped (C) goethite catalyst had iron content of 10.5 mg/L which is in accordance with NESREA standards. Similarly, the obtained BOD value of 36 mg/L and TDS value of 21 mg/L proves the efficiency of the synthesized catalysts.

Table 4.3: Soluble Iron Content Results

<b>Sample</b>	<b>Iron Content (mg/L)</b>
Undoped	30.1
Doped (A)	11.4
Doped (B)	10.9
Doped (C)	10.5

Table 4.4: Kaduna Refinery Wastewater Depuration COD Results

Run	Catalyst Loading (mg/L)	H <sub>2</sub> O <sub>2</sub> (g/L)	Time (mins)	pH	COD			
					Undoped Goethite	Doped (A)	Doped (B)	Doped (C)
1	10	0.2	5	10	650	560	500	480
2	100	0.2	5	10	650	530	450	460
3	55	1.1	182.5	6.5	700	640	650	600
4	100	0.2	5	3	560	490	480	450
5	10	2	360	3	250	150	130	120
6	55	1.1	182.5	6.5	700	640	650	600
7	55	2	182.5	6.5	720	580	620	450
8	55	1.1	182.5	6.5	700	640	650	600
9	100	2	5	10	620	500	500	480
10	100	0.2	360	10	470	300	270	240
11	10	2	360	10	490	330	290	290
12	10	0.2	5	3	560	420	400	350
13	100	0.2	360	3	260	170	140	130
14	10	0.2	360	3	260	190	140	150
15	55	1.1	182.5	6.5	700	640	650	600
16	100	2	360	10	560	320	280	290
17	100	2	5	3	580	410	370	360
18	55	1.1	182.5	6.5	700	640	650	600
19	10	0.2	360	10	470	330	290	240
20	10	2	5	10	610	490	480	400
21	55	2	182.5	6.5	720	580	620	450
22	55	1.1	182.5	6.5	700	640	650	600
23	55	1.1	182.5	3	440	380	340	300
24	55	1.1	360	6.5	280	180	150	140
25	100	2	360	3	250	170	170	160
26	10	2	5	3	580	420	380	400
27	55	1.1	182.5	6.5	700	640	650	600

Table 4.5: Kaduna Refinery Wastewater Percentage Depuration Results

Run	Catalyst Loading (mg/L)	H <sub>2</sub> O <sub>2</sub> (g/L)	Time		% Depuration			
			(mins)	pH	Undoped	Doped (A)	Doped (B)	Doped (C)
1	10	0.2	5	10	24.42	34.88	41.86	44.19
2	100	0.2	5	10	24.42	38.37	47.67	46.51
3	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23
4	100	0.2	5	3	34.88	43.02	44.19	47.67
5	10	2	360	3	70.93	82.56	84.88	86.05
6	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23
7	55	2	182.5	6.5	16.28	32.56	27.91	53.49
8	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23
9	100	2	5	10	27.91	41.86	41.86	44.19
10	100	0.2	360	10	45.35	65.12	68.6	72.09
11	10	2	360	10	43.02	61.63	66.28	66.28
12	10	0.2	5	3	34.88	51.16	53.49	59.3
13	100	0.2	360	3	69.77	80.23	83.72	84.88
14	10	0.2	360	3	69.77	77.91	83.72	82.56
15	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23
16	100	2	360	10	43.02	62.79	67.44	66.28
17	100	2	5	3	32.56	52.33	56.98	58.14
18	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23
19	10	0.2	360	10	45.35	61.63	66.28	72.09
20	10	2	5	10	27.91	43.02	44.19	53.49
21	55	2	182.5	6.5	16.28	32.56	27.91	47.67
22	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23
23	55	1.1	182.5	3	48.84	55.81	60.47	65.12
24	55	1.1	360	6.5	67.44	79.1	82.56	83.72
25	100	2	360	3	70.93	80.23	80.23	81.4
26	10	2	5	3	32.56	51.16	55.81	53.49
27	55	1.1	182.5	6.5	18.6	25.58	24.42	30.23

From the analysis of variance (ANOVA) results as shown in Table 4.6 to Table 4.9, it suggests that the quadratic model obtained was significant for the depuration of the Kaduna refinery wastewater. R-square ( $R^2$ ) is the proportion of variability in a data set that is accounted for by a statistical model. It describes the fraction of the total variation attributed to the model (John *et al.*, 2015). The obtained  $R^2$  values were 0.9471, 0.9794, 0.9371 and 0.9407 respectively for the synthesized samples. The  $R^2$  values confirm that the data are well fitted in the statistical quadratic model, implying that the total variations in depuration were adequately represented by the model. A modified form of  $R^2$  which is the  $R^2_{adj}$  was also obtained. Therefore, based on  $R^2_{adj}$  values closeness to  $R^2$ , it can be concluded that the experimental data fitted the model fairly well. Furthermore, F-value and P-values obtained were less than 0.001 and 0.05 respectively implying that the model was significant for depuration. As shown in Figure 4.6 to Figure 4.9, the points are randomly dispersed around the horizontal axis. The points formed cloud became funnel shaped in Figure 4.9, thereby showing that the obtained experimental data were appropriate with the model.

Table 4.6: ANOVA Results for the Depuration Using Undoped Goethite Catalyst

Source	Sum of squares	Degree of freedom	Mean Square	F-ratio	P-value
Model	576500	14	41178.91	2.77	<0.0001
Residuals	38702.68	12	3225.22		
Lack of fit	38131.25	5	7626.25	1.42	<0.0001
Pure error	571.43	7	81.63		
			$R^2 = 0.9471$		
			$R^2_{adj} = 0.8637$		
			Adq. Prec. Ratio = 10.751		

Table 4.7: ANOVA Results for the Depuration Using Cu-doped (A) Goethite Catalyst

<b>Source</b>	<b>Sum of squares</b>	<b>Degree of freedom</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Model	721900	14	51564.20	40.97	<0.0001
Residuals	15167.86	12	1263.99		
Lack of fit	3975.00	5	765.00	0.50	0.7704
Pure error	11192.86	7	1598.98		
			$R^2 =$	0.9794	
			$R^2_{adj.} =$	0.9554	
			Adq. Prec. Ratio =	17.770	

Table 4.8: ANOVA Results for the Depuration Using Cu-doped (B) Goethite Catalyst

<b>Source</b>	<b>Sum of squares</b>	<b>Degree of freedom</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Model	576500	14	41178.91	12.77	<0.0001
Residuals	38702.63	12	3225.22		
Lack of fit	38131.25	5	7626.25	0.82	<0.0001
Pure error	571.43	7	81.63		
			$R^2 =$	0.9371	
			$R^2_{adj.} =$	0.8637	
			Adq. Prec. Ratio =	10.751	

Table 4.9: ANOVA Results for the Depuration Using Cu-doped (C) Goethite Catalyst

Source	Sum of squares	Degree of freedom	Mean Square	F-ratio	P-value
Model	567300	14	40520.80	13.60	<0.0001
Residuals	35760.71	12	2980.06		
Lack of fit	4675.00	5	935.00	0.21	0.9474
Pure error	31085.71	7	4440.82		

$R^2 = 0.9407$   
 $R^2_{adj.} = 0.8715$   
 Adq. Prec. Ratio = 10.572

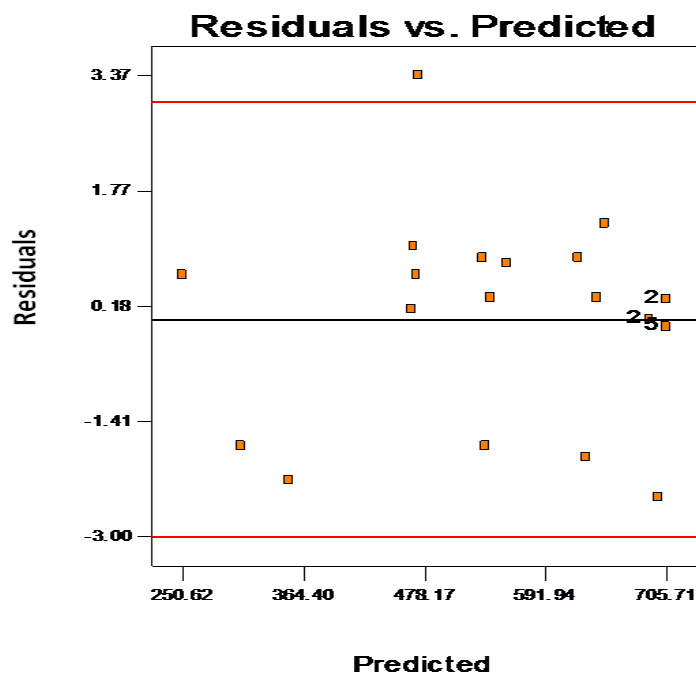


Figure 4.6: Standardized residuals and initial plot for undoped Goethite catalyst

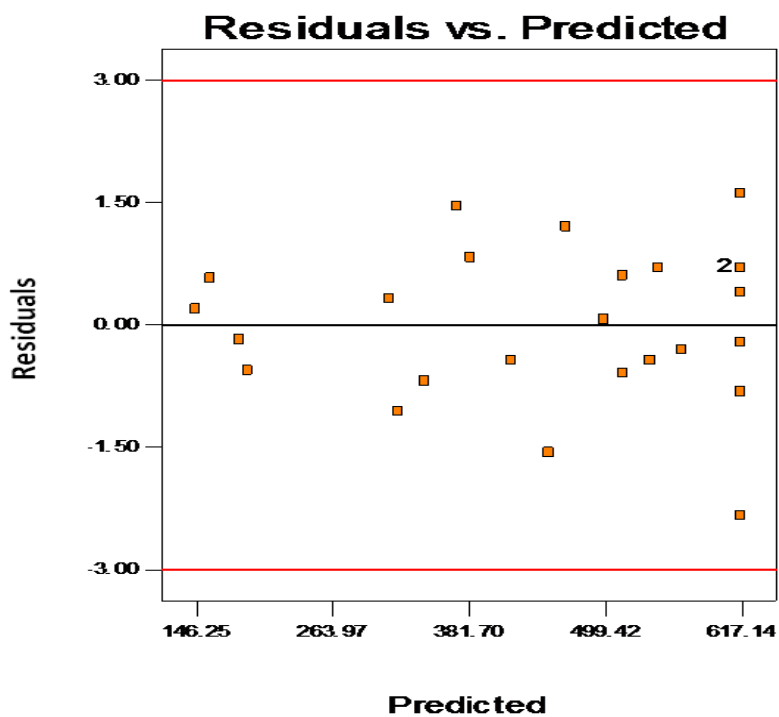


Figure 4.7: Standardized residuals and initial plot for Cu-doped (A) Goethite catalyst

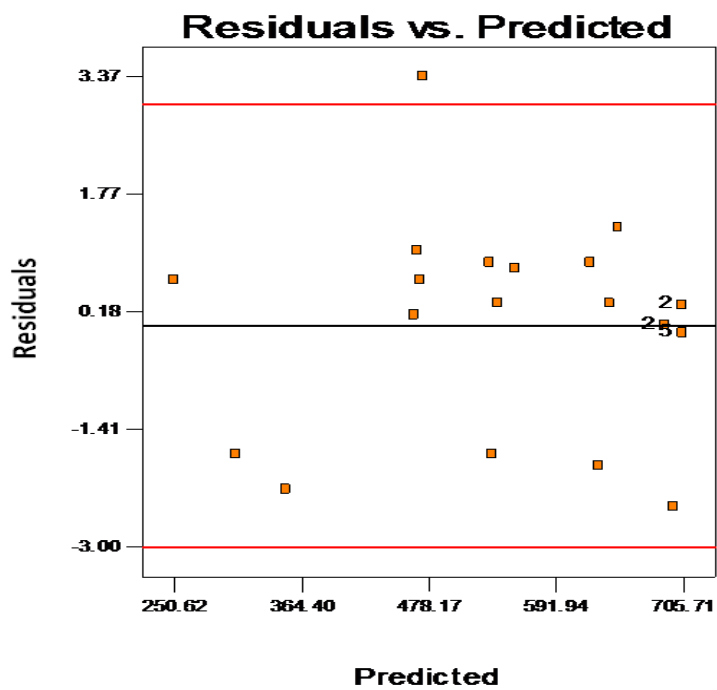


Figure 4.8: Standardized residuals and initial plot for Cu-doped (B) Goethite catalyst

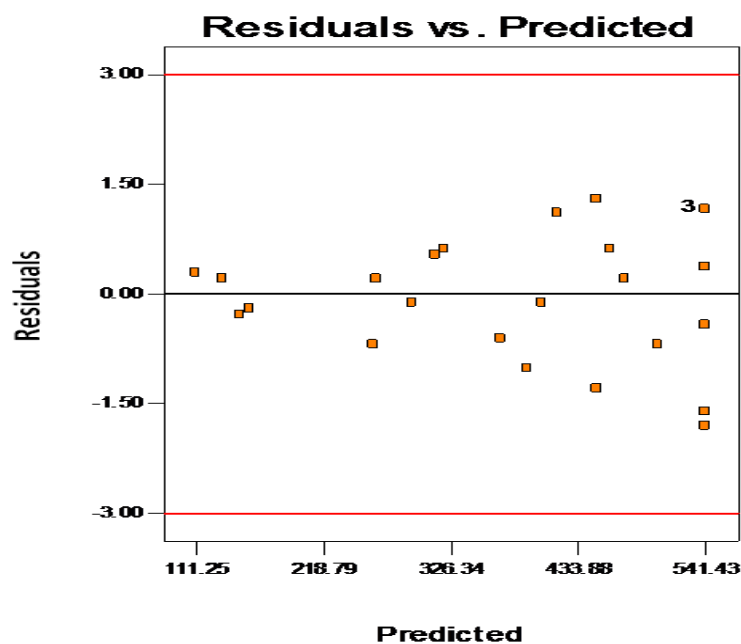


Figure 4.9: Standardized residuals and initial plot for Cu-doped (C) Goethite catalyst

The outlier is also an indicator of experimental error. It can be observed in Figure 4.10 to Figure 4.13 that only few data points lied far away from the true regression line proving that the experimental data fits the model and the model approximation of the response surface was satisfactory and not associated with data recording error (Montgomery, 2009).

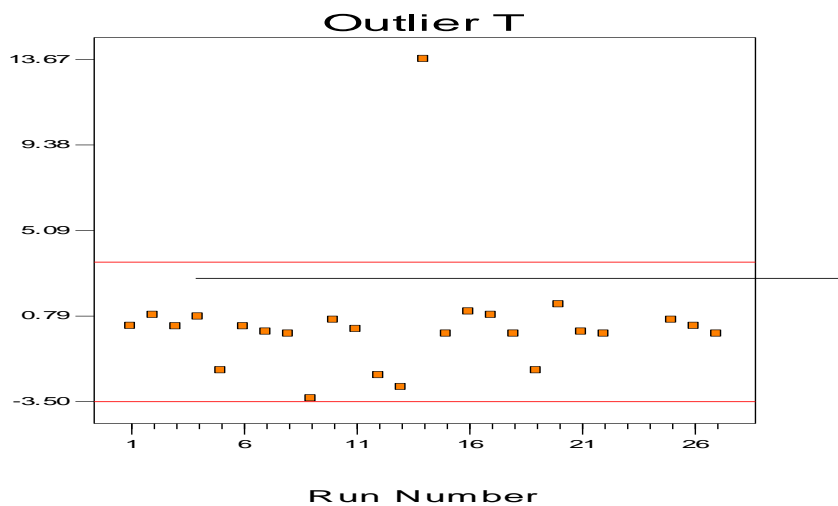


Figure 4.10: Outlier plot for depuration using undoped Goethite catalyst

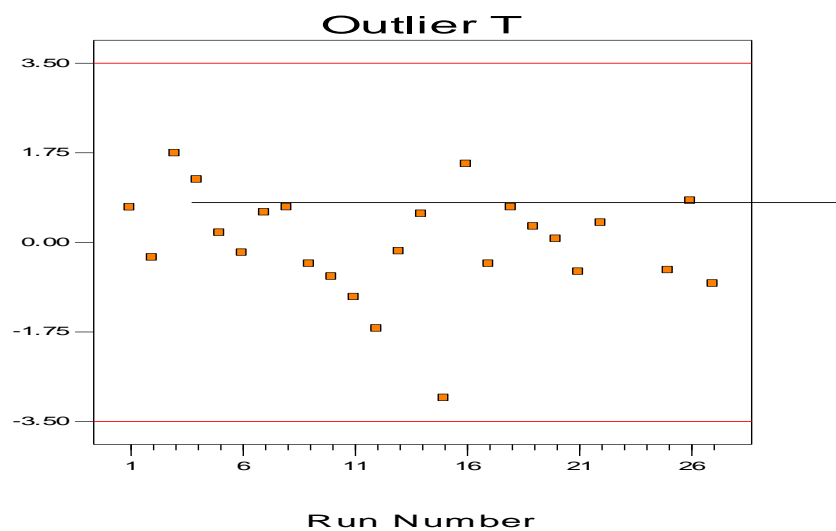


Figure 4.11: Outlier plot for deperation using Cu-doped (A) Goethite catalyst

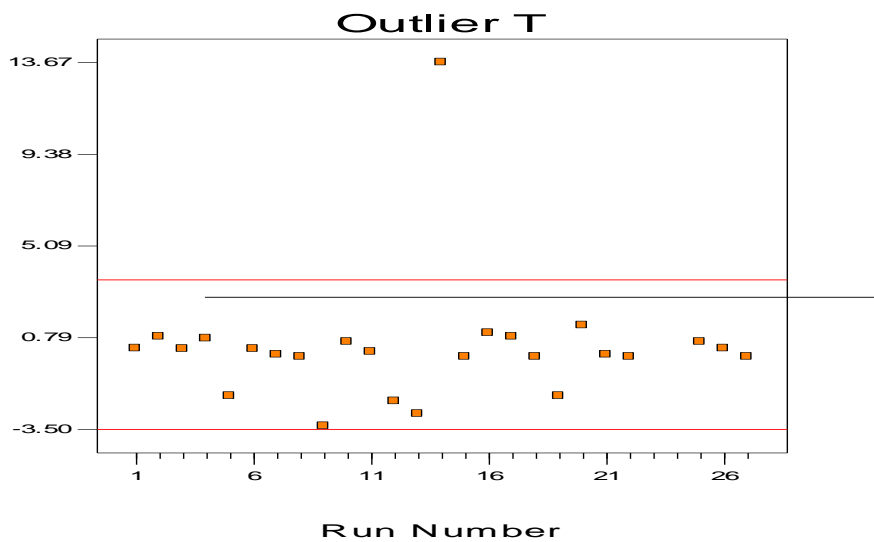


Figure 4.12: Outlier plot for deperation using Cu-doped (B) Goethite catalyst

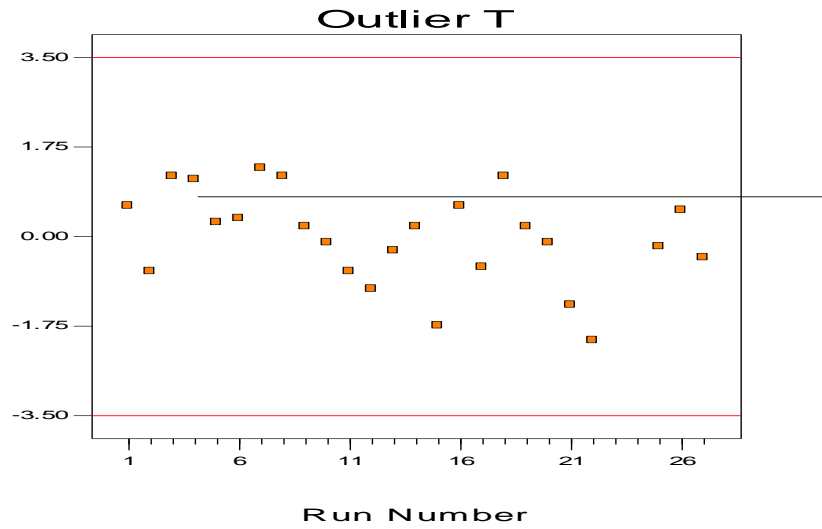


Figure 4.13: Outlier plot for depuration using Cu-doped (C) Goethite catalyst

From Figure 4.14 - 4.17, it was observed that there is a good agreement between the predicted and actual COD values which further confirmed the viability and reliability of the model (Montgomery, 2009).

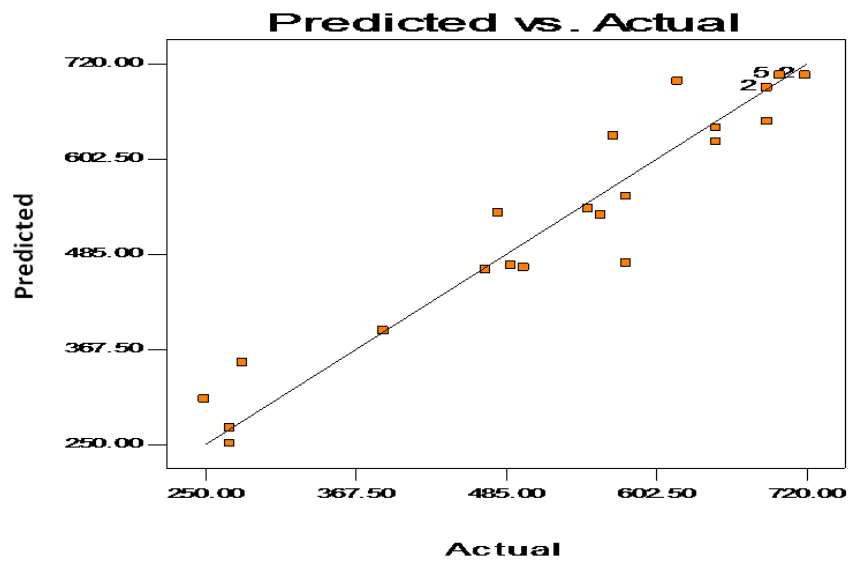


Figure 4.14: Actual responses against predicted for the undoped Goethite catalyst



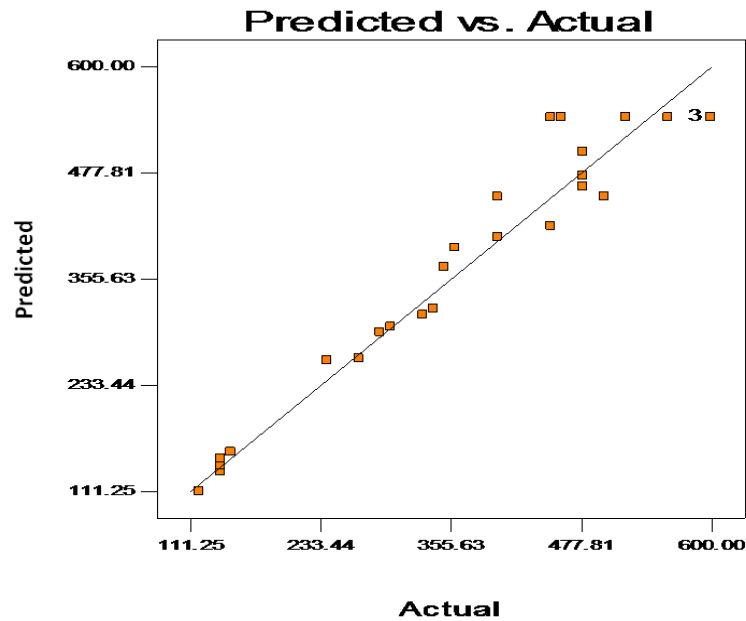


Figure 4.17: Actual responses against predicted for Cu-doped (C) Goethite catalyst

The generated results of the responses from the experimental runs were processed by employing the model equations (Table 4.10), obtained through fitting with a second-order polynomial equation using a multiple regression technique.

#### 4.2.1 Effect of time on COD reduction

The reduction in COD of the PRW is the indicator of successful depuration. Decrease in COD was achieved as shown in Figure 4.18. The optimum depuration was achieved with copper doped (C) goethite catalyst, COD reduction was achieved from 860 to 120 at pH of 3, to 140 at pH of 6.5 and to 240 at pH of 10, respectively. Therefore, from 5 to 360 minutes there was 86.05%, 83.72% and 72.09% at pH of 3, 6.5 and 10, respectively, which depicts the substantial increase in COD reduction percentage.

Table 4.10: Model for Wastewater Depuration Using the Synthesized Catalysts

Sample	Equation
Undoped	$y=705.71-18.12x_1-23.12x_2-96.87x_3+56.88x_4+396.43x_1^2+7.41x_2^2-218.84x_3^2-378.84x_4^2+16.87x_1x_2-11.88x_1x_3+14.37x_1x_4-19.38x_2x_3+24.37x_2x_4+13.12x_3x_4$ .
Doped (A)	$y=617.14+16.25x_1-10.00x_2-115.00x_3+68.75x_4+474.29x_1^2-92.14x_2^2-242.14x_3^2-388.39x_4^2+5.00x_1x_2+2.50x_1x_3+1.25x_1x_4+13.75x_2x_3+5.00x_2x_4+15.00x_3x_4$ .
Doped (B)	$y=705.71-18.13x_1-23.13x_2-96.88x_3+56.87x_4+396.43x_1^2+7.41x_2^2-218.84x_3^2-378.84x_4^2+16.88x_1x_2-11.87x_1x_3+14.38x_1x_4-19.37x_2x_3+24.38x_2x_4+13.13x_3x_4$ .
Doped (C)	$y=541.43+21.25x_1-12.50x_2-102.50x_3+58.75x_4+332.86x_1^2-78.93x_2^2-298.93x_3^2-182.68x_4^2+7.50x_1x_2-2.50x_1x_3+3.75x_1x_4+13.75x_2x_3+5.00x_2x_4+15.00x_3x_4$ .

Where y is the COD removal %,  $x_1$  is catalyst loading,  $x_2$  is  $H_2O_2$  loading,  $x_3$  is pH of the PRW and  $x_4$  is the reaction time.

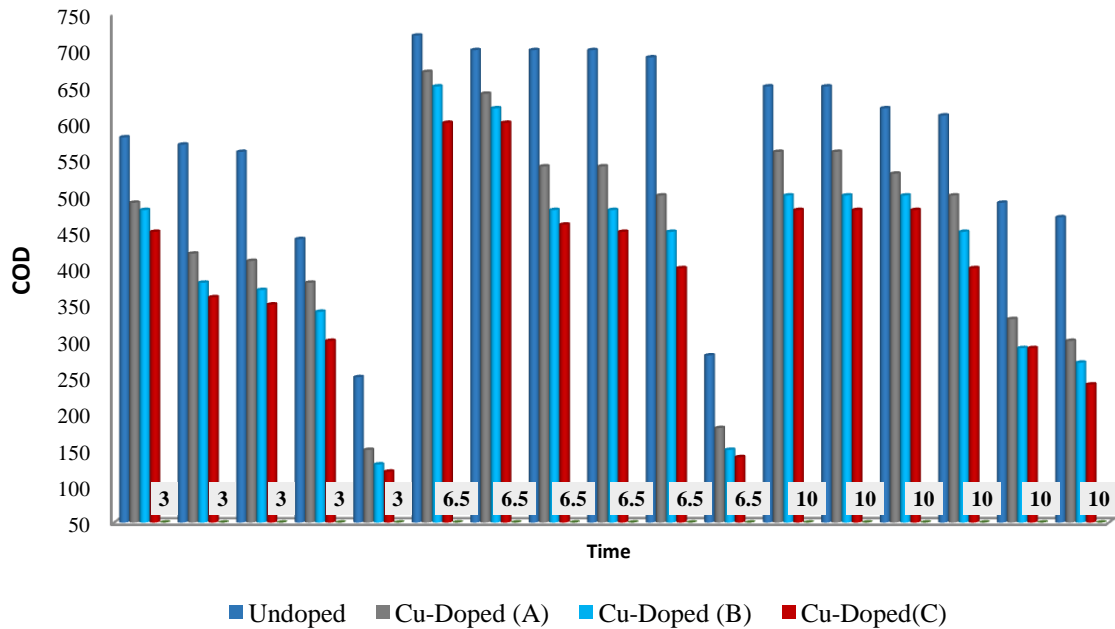


Figure 4.18: COD results for deputation of wastewater

#### 4.2.2 Effect of doping on depuration percentage

The hydrated surface of goethite catalyst further increases catalytic activity by inclusion of metal ion in its structure (Ortiz *et al.*, 2008). The undoped goethite catalyst gave 71, 67 and 45 depuration percentages at pH of 3, 6.5 and 10 respectively. However, Fenton based treatment of PRW with scrap iron catalyst was reported by Ali *et al.*, (2013), where COD depuration of 46 % at pH of 3.0. Astonishingly, the synthesized copper doped (C) goethite catalyst gave higher depuration percentage of 86% at pH of 3, 84% at pH of 6.5 and 72% at pH of 10.

#### 4.3 Stability Test of the Synthesized Samples

The catalyst stability or reusability is an important factor in catalyzed reactions. Therefore, it is necessary to study the stability of the goethite catalyst. Figure 4.19 shows the reusability test results, whereby at the end of the first cycle of depuration process, 84% was achieved and the catalyst was sieved then washed and oven dried. The second cycle gave 72% depuration, and the difference was not much compared to the first cycle.

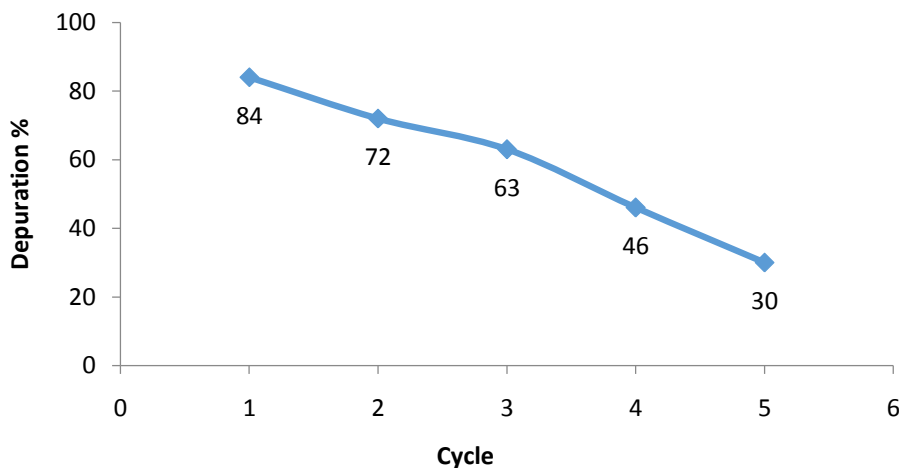


Figure 4.19: Catalyst stability results

Furthermore, the depuration efficiency decreased from 63% in the third cycle to 46% in the fourth cycle. However, there was much decrease in the fifth cycle where depuration percentage of 30% was obtained. Therefore, the stability test results depicts that the synthesized copper doped samples had less catalyst deactivation over the first to the third cycle, and severe deactivation from the fourth to the fifth cycle. Below are the contributions to knowledge from this work:

- a) For the first time, Cu-doped goethite catalyst was used in Fenton depuration of PRW.
- b) Less sludge (10.5 mg/L) is generated, implying that no need for further treatment thereby reducing the cost of the depuration process.
- c) Efficient Fenton depuration (83.72%) of PRW was achieved, confirming that the doped goethite catalysts have great potential in Fenton depuration of petroleum refinery wastewater.

## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

The following conclusions were drawn from the work

1. Undoped goethite catalyst, copper doped (A) catalyst with 0.2 wt% Cu, copper doped (B) catalyst with 1.6wt% Cu and copper doped (C) catalyst with 3.3wt% Cu were synthesized by precipitation method and characterized using XRD, surface area analysis, AAS and SEM techniques.
2. Batchwise depuration of the Kaduna refinery wastewater was achieved at optimum conditions of 360 minutes reaction time, pH of 3, catalyst loading of 55mg/L and hydrogen peroxide dosage of 1.1g/L.
3. Copper doped (C) catalyst yielded the highest depuration percentage of 86% at pH of 3, 84% at pH of 6.5 and 72% at pH of 10, respectively
4. Appreciable depuration percentage was achieved at near neutral pH (pH of 6.5), with 67.44% for the undoped catalyst, and 79%, 82.56% and 83.72% for the Cu-doped A, B and C goethite catalysts, respectively.
5. Cu-doped catalysts yielded improved depuration percentage, depicting that the doped catalysts have great potential as an efficient tool for Fenton depuration of petroleum refinery wastewater.
6. The stability of the synthesized copper doped catalyst had less catalyst deactivation over the first to third cycle. So the catalyst will perform fairly well in practical industrial application.

7. The Depuration process can be used as an efficient, less expensive and environmental friendly technique for petroleum refinery wastewater depuration.

## **5.2 Recommendations**

The following recommendations have been made:

1. Research work should be carried out on kinetic studies and design of a pilot plant for Fentondepuration of petroleum refinery wastewater.
2. Effective and economic methods of natural goethite beneficiations should be investigated.
3. Adequate funding should be provided.

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## APPENDICES

### APPENDIX A

#### SURFACE AREA DETERMINATION

The specific surface areas (SSA) of the samples were determined using Sear's method according to the equation  $S \text{ (m}^2\text{/g)} = 32V - 25$

$$s \left( \frac{\text{m}^2}{\text{g}} \right) = 32V - 25$$

##### 1. Undoped Goethite Catalyst

$$\begin{aligned} \text{Specific surface area} &= 32V - 25 \\ &= 32 * 3.45 - 25 = 85.4 \text{ m}^2/\text{g} \end{aligned}$$

##### 2. Cu-doped (A) Goethite Catalyst

$$\begin{aligned} \text{Specific surface area} &= 32V - 25 \\ &= 32 * 3.9 - 25 = 99.8 \text{ m}^2/\text{g} \end{aligned}$$

##### 3. Cu-doped (B) Goethite Catalyst

$$\begin{aligned} \text{Specific surface area} &= 32V - 25 \\ &= 32 * 4.1 - 25 = 106.2 \text{ m}^2/\text{g} \end{aligned}$$

##### 4. Cu-doped (C) Goethite Catalyst

$$\begin{aligned} \text{Specific surface area} &= 32V - 25 \\ &= 32 * 4.21 - 25 = 109.7 \text{ m}^2/\text{g} \end{aligned}$$

## APPENDIX B

### PARTICLE SIZE ANALYSIS USING XRD

Using Scherrer's equation

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where, D = Particle size, nm.

$$\lambda = 1.542 \text{ \AA}$$

B = Width at Full Width at Half Maximum (FWHM) in radians.

$2\theta$  = Bragg angle.

#### 1. Goethite Catalyst

The values of  $\beta$  and  $\theta$  for Goethite catalyst were obtained from Figure B1.

$$\beta = 24.24^\circ - 24.06^\circ = 0.16^\circ \text{ (0.00244 radian)}$$

$$2\theta = 24.14^\circ \quad \theta = 12.07^\circ \text{ (0.21066 radian)}$$

$$D = \frac{0.94\lambda}{\beta \cos\theta} = \frac{0.94 * 1.542}{0.00244 * \cos(0.21066)} = 56.80 \text{ nm}$$

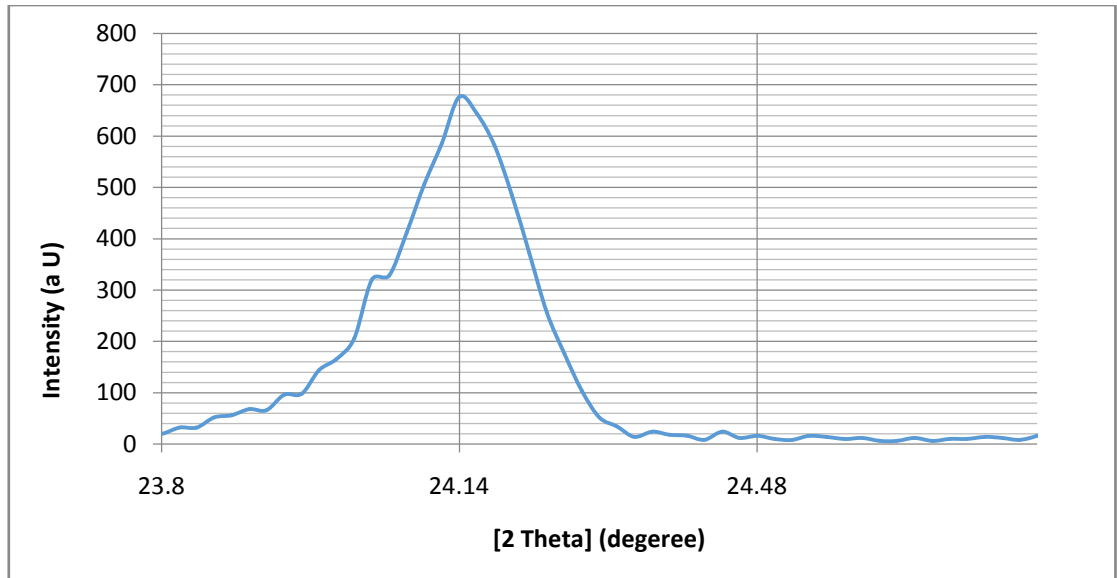


Figure B1: XRD showing the peaks for particle size of Goethite catalyst

## 2. Cu-doped (A) Goethite Catalyst

The values of  $\beta$  and  $\theta$  for Cu-doped (A) Goethite catalyst were obtained from Figure B2.

$$\beta = 24.98^{\circ} - 24.84^{\circ} = 0.14^{\circ} \text{ (0.00244 radian)}$$

$$2\theta = 24.90^{\circ} \quad \theta = 12.45^{\circ} \text{ (0.21729 radian)}$$

$$D = \frac{0.94\lambda}{\beta \cos\theta} = \frac{0.94 * 0.1542}{0.00244 * \cos(0.21729)} = 59.33 \text{ nm}$$

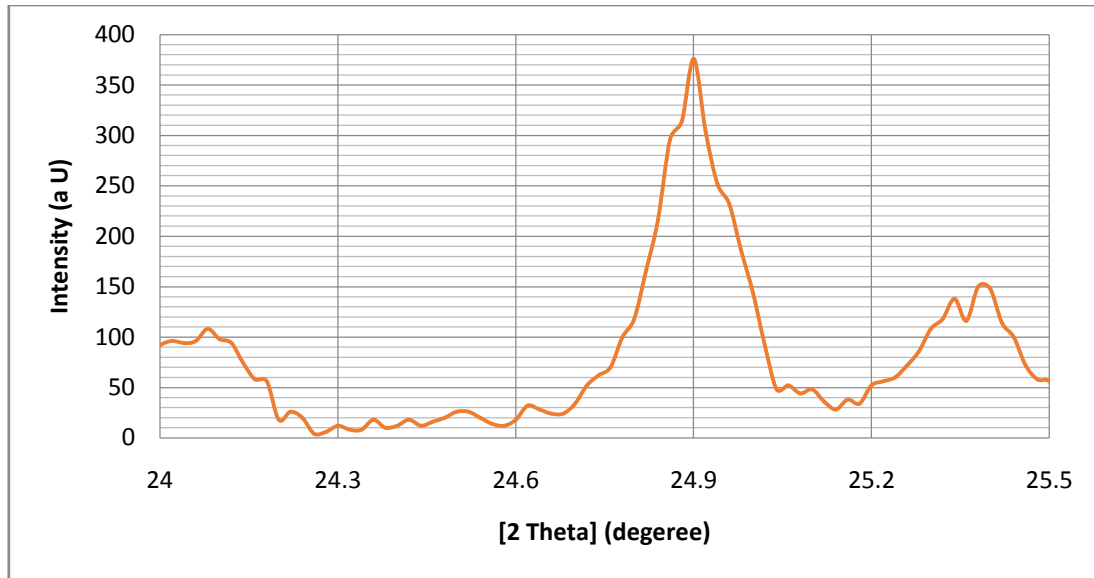


Figure B2: XRD showing the peaks for particle size of Cu-doped (A) Goethite catalyst

### 3. Cu-doped (B) Goethite Catalyst

The values of  $\beta$  and  $\theta$  for Cu-doped (B) Goethite catalyst were obtained from Figure B3.

$$\beta = 24.98^{\circ} - 24.84^{\circ} = 0.14^{\circ} \text{ (0.00244 radian)}$$

$$2\theta = 24.90^{\circ} \quad \theta = 12.45^{\circ} \text{ (0.21729 radian)}$$

$$D = \frac{0.94\lambda}{\beta \cos\theta} = \frac{0.94 * 0.1542}{0.00244 * \cos(0.21729)} = 59.33 \text{ nm}$$

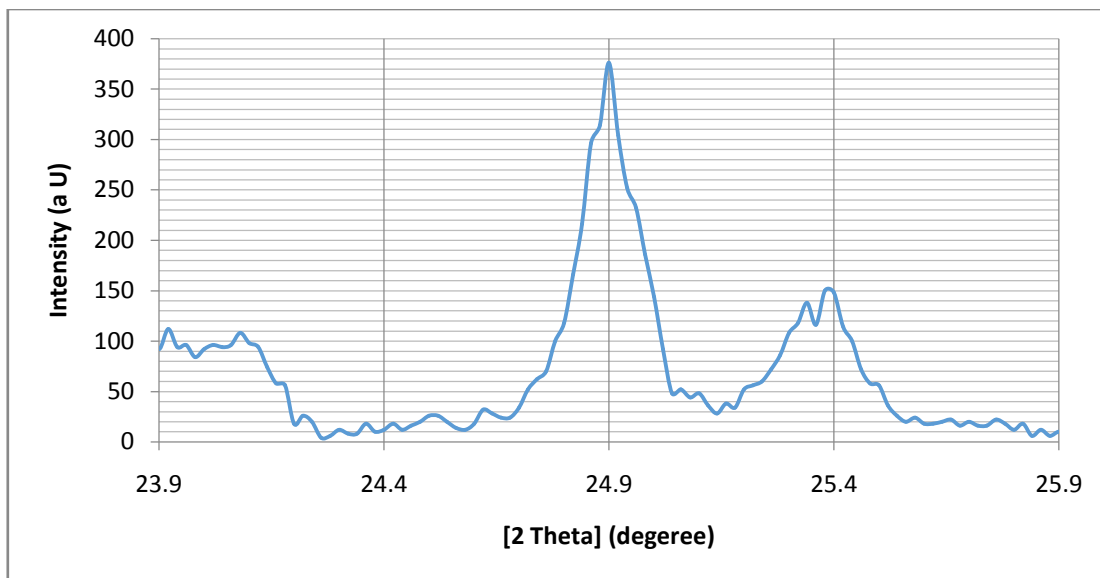


Figure B3: XRD showing the peaks for particle size of Cu-doped (B) Goethite catalyst

#### 4. Cu-doped (C) Goethite Catalyst

The values of  $\beta$  and  $\theta$  for Cu-doped (C) Goethite catalyst were obtained from Figure B4.

$$\beta = 24.18^{\circ} - 23.99^{\circ} = 0.19^{\circ} \text{ (0.00332 radian)}$$

$$2\theta = 24.10^{\circ} \Rightarrow \theta = 12.05^{\circ} \text{ (0.21031 radian)}$$

$$D = \frac{0.94\lambda}{\beta \cos \theta} = \frac{0.94 * 0.1542}{0.00332 * \cos(0.21031)} = 43.60 \text{ nm}$$

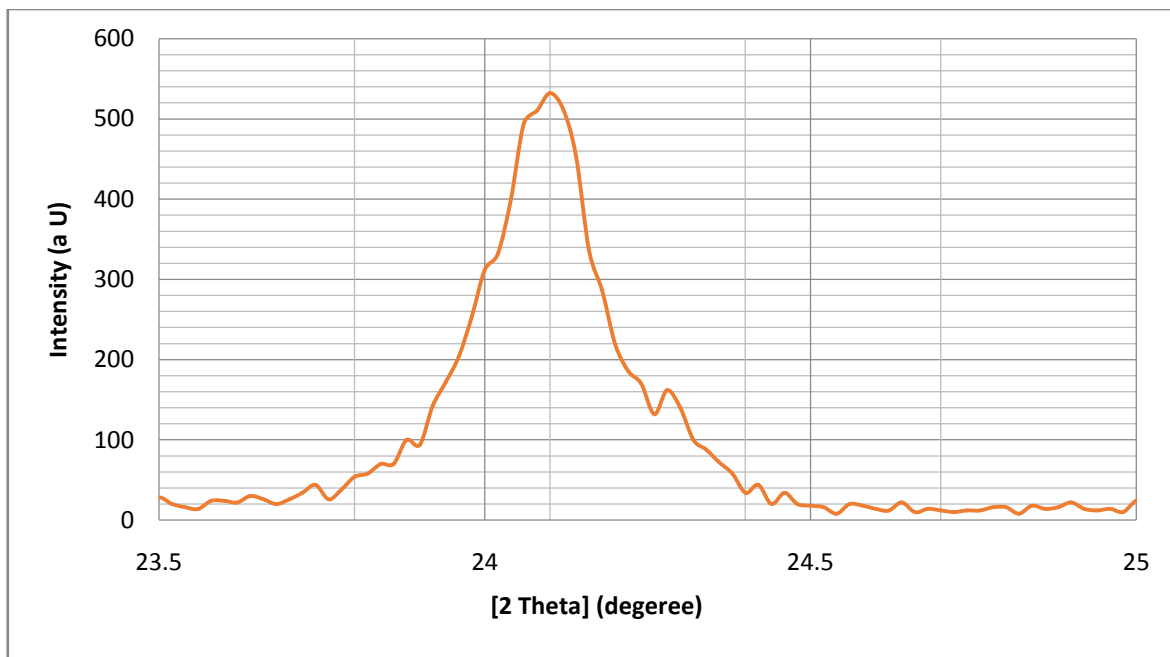


Figure B4: XRD showing the peaks for particle size of Cu-doped (C) Goethite catalyst