PREPARATION AND APPLICATION OF α-FeOOH AND α-FeOOH-SiO_2-Al_2O_3 CATALYSTS FOR TANNERY EFFLUENT TREATMENT USING FENTON OXIDATION PROCESS

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DEPARTMENT OF CHEMICAL ENGINEERING
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DECLARATION

I Nasiru Yusuf declared that, this research dissertation entitled "Preparation and Application of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts for Tannery Effluent Treatment using Fenton Oxidation Process" has been carried out by me in the Department of Chemical Engineering, A.B.U, Zaria under the supervision of Dr. Abdulhamid Hamza, Dr. Diya'uddeen Basheer Hasan and Prof. Idris Muhammad Bugaje. The information derived from literatures has been duly acknowledged in the text and list of references provided. No part of this research dissertation was previously presented for another degree or diploma at this or any other institution.

Nasiru YUSUF _____ _____

Signature Date

CERTIFICATION

This dissertation entitled "PREPARATION AND APPLICATION OF α-FeOOH AND α-FeOOH-SiO_2-Al_2O_3CATALYSTS FOR TANNERY EFFLUENT TREATMENT USING FENTON OXIDATION PROCESS by NASIRU YUSUF meets the regulations governing the award of the degree of Masters of Science in Chemical Engineering of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research dissertation is dedicated to the Almighty Allah, my parent and entire brothers and sisters who worked tirelessly towards the success of my studies.

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All thanks are to Allah the most gracious and the most merciful. Peace and mercy of Allah be upon our noble Prophet Muhammad (S.A.W), his companions and entire family till the Day of Judgment. I am once again, extending my infinite thanks to the Almighty Allah for giving me the opportunity of seeing the starting and the completion of this research work.

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ABSTRACT

One of the problems facing leather industries is to come up with an efficient way of reducing the organic pollutant loads of their wastewaters. This research dissertation was aimed at the preparation and application of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts for tannery effluent treatment using Fenton oxidation process. Effluent at the point of discharge from Mamuda tannery industry, Sharada phase III, Kano state, Nigeria, was collected and characterized as highly polluted tannery effluent that needs to be treated before discharge in to the environment.The α-FeOOH catalyst was prepared through the use of precipitation method, doped with silica and aluminain the ratio 50:2:1 and calcined at 600^{o}C for 2 hours. The composite α-FeOOH-SiO_2-Al_2O_3 catalyst wascharacterized using XRD and SEM analyses. The SEM images revealed a cluster of crystal particles indicating an orthorhombic crystal shape of α-FeOOH catalyst and the crystal particles become bigger and agglomerated. Furthermore, design expert 6.0.7 versionsoftware of response surface methodology (RSM) was employed using central composite design (CCD) to optimize Fenton oxidation of tannery effluent. Quadratic models were developed for the response variable (COD reduction) and were found to be significant for applyingα-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts for tannery effluent treatment using Fenton oxidation process. The optimization of Fenton oxidation of tannery effluent was carried out using design expert 6.0.7 versionsoftware in order to achieve maximum COD reduction. The desired goal was set at target and at maximum and the optimum value of 68.57% COD reduction for applying α-FeOOH catalyst was predicted to be achieved by the design expert software at the optimal conditions of 30.00 mg/L catalyst loading, 900.00 mg/L peroxide dosage, 125.00mins reaction time and a pHof 3.00.While for applying α-FeOOH-SiO_2-Al_2O_3 catalyst, 82.43% COD reduction was predicted to be achieved at optimal conditions of 50.00mg/L catalyst loading, 400.00mg/L peroxide

dosage, 240.00mins reaction time and a pH of 7.00. Validation experiments were conducted based on the same optimal conditions stated in order to verify the accuracy and reliability of the optimized results predicted by the design expert software. The actual results of 65.93% and 79.29% COD reduction were obtained from validation experiments conducted for applying α-FeOOH andα-FeOOH-SiO_2-Al_2O_3 catalysts which are in close agreement with the optimized results predicted confirming the accuracy of the model.

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LIST OF ABBREVIATIONS

AOPs	Advance Oxidation Processes
XRD	X-ray Diffractometer
SEM	Scanning Electron Microscope
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
CCD	Central Composite Design
ANOVA	Analysis of Variance
EDCs	Endocrine Disrupting Compounds
BPA	Bisphenol A
CAS	Conventional Activated Sludge
MBR	Membrane Bio-Reactor
NESREA	National Environmental Standards and Regulation Enforcement Agency
FEPA	Federal Environmental Protection Agency
RSM	Response Surface Methodology
ICDD	International Centre for Diffraction Data
JCPDS	Joint Committee on Powdered Diffraction Standard

CHAPTER ONE

INTRODUCTION

1.1 Preamble

Tannery industries are sources of pollution due to manufacturing processes as well as type of technology employed in the conversion of hides and skins into leather (Halim, 2012). Tannery industries are also characterized as pollution complexes which generate recalcitrant effluent that varies with its character, quantity, nature of receiving media and dilution available from different procedures of tanning and finishing (Alexander *et al*., 2008). These procedures are identified by the kind of raw hides and skins employed and the required characteristics of finished products (Walter and Vennes, 2011). Tanning involves a combination of mechanical and chemical processes (Ahmad *et al*., 2013). The heart of these processes is the tanning operation itself in which organic and inorganic materials become chemically bounded to the protein structure of the hide and preserve it from deterioration. Tannery effluent discharged into water bodies alters the physical, chemical and biological characteristics of water and depletes the dissolved oxygen, increases alkalinity, suspended solids and sulphides which are injurious to human, animals as well as aquatic lives (Thompson *et al*., 2014). Hence, tannery effluent with high organic pollutant loads should be treated before discharge into the environment.

Various conventional processes such as; biological, coagulation, sedimentation, filtration and effluent recycling system are carried out to treat effluent from tannery industries. But most of these processes convert organic contaminants into secondary pollutants and the processes are characterized by high energy, time and reagents consumption (Klemes *et al*., 2007). Advanced oxidation processes were developed to overcome these setbacks by treating recalcitrant effluent through reaction with hydroxyl radicals which has the ability to oxidize non-biodegradable organic pollutants with minimal sludge generation

(Muthukumar, 2011).Fenton oxidation process is currently termed as one of the best among advanced oxidation processes because it produces strong hydroxyl radicals through reaction of ferrous iron with hydrogen peroxide for organic pollutants mineralization as represented by equations (1.1) and (1.2):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-} \quad (1.1)$$

$$Organic\ pollutants + H_2O_2 \rightarrow CO_2 + H_2O \quad (1.2)$$

Fenton oxidation process is useful for mineralization of non-biodegradable materials including aromatics, pesticides, petroleum constituents and volatile organic compounds (Rocha *et al*., 2012). Additionally, it degrades secondary pollutants and this is referred to as tertiary treatment. The organic pollutants are converted into mineralized inorganic compounds such as carbon dioxide and water as in equation (1.2). The treated effluent can then be properly discharged into open drains and rivers (Plata *et al*., 2009).

Mixed iron catalyst in the form of iron oxides including goethite (α-FeOOH), magnetite (Fe_3O_4), and hematite (α-Fe_2O_3) are used as heterogeneous catalyst for Fenton oxidation process (Chong *et al*., 2012). These solid catalysts present potential degradation of recalcitrant pollutants usually found in tannery effluent. Goethite with chemical formula of α-FeOOH is the most abundant iron oxide among iron bearing minerals due to its low cost, environmentally friendly, ability to operate within the acidic pH range, thermodynamic stability among others (Haber *et al*., 2015). It is an oxy-hydroxide mineral found mostly in natural environment as a weathering product of iron-bearing minerals. In many dried or tropical environment, goethite is usually found in association with hematite but apparently, hematite is dissolved resulting in the formation of goethite (Othman *et al*., 2010).

Therefore, this research dissertation focused on the preparation and application ofα-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts for tannery effluent treatment using Fenton

oxidation process.

1.2 Problem Statement

Tannery effluent has high contents of organic compounds, suspended and dissolved solids. Various conventional treatment methods such as; biological, coagulation, sedimentation, effluent recycling system and membrane separation only convert non bio-degradable organic contaminants into secondary pollutants. The introduction of homogeneous Fenton oxidation process for organic contaminants degradation has pH dependence (2.5- 4.0).

1.3 Justification

This research dissertation on the preparation and application of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts for tannery effluent treatment seeks to address the problem of degrading non bio-degradable organic pollutants and comparing the performance of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts by studying the reduction of organic pollutant loads in tannery effluent.

1.4 Aim and Objectives

The aim of this research dissertation is to prepare α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts and apply them for tannery effluent treatment using Fenton oxidation process.

The objectives are:

i. To characterize tannery effluent
ii. To prepare and characterize α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts using XRD and SEM analyses
iii. To study the reduction of organic pollutant loads in tannery effluent via catalytic Fenton oxidation process
iv. To optimize Fenton oxidation of tannery effluent using design expert software of response surface methodology.

1.5 Scope of Research

The scope of this research dissertation was limited at the characterization of tannery effluent, preparation and characterization of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts and application of the prepared catalysts for treatment of tannery effluent. Optimization of Fenton oxidation of tannery effluent using design expert software of response surface methodology.

CHAPTER TWO

LITERATURE REVIEW

2.1 TANNERY INDUSTRY DESCRIPTION

Leather tanning industry is one of the oldest industrial activities in Nigeria. This is because it predates colonial occupation as it had generated items for Trans-Saharan trade for the markets of Sudan and Maghreb. The so called fine Moroccan leather was actually made from the goat skins of Sokoto (Munta, 2011). In pre-colonial times, tanning and leather processing activities were carried out by peasants and artisans that can still be seen today. This artisanal sector has been practiced on a rural cottage basis operated along family lines for centuries using traditional tanning techniques. These methods consist of tanning pits and a local vegetable tanning material known as chest nut. This material is obtained from the pod of Acacia niloticato produce crust tanned leathers. These local tanneries are concentrated in the livestock producing areas of Northern Nigeria. Their numbers was put at 1000 in 1971, 924 in 1991 and 2000 in 1996 (Moura *et al.*, 2011). The leathers produced by these traditional tanneries are consumed locally (Rocha *et al.*, 2012). Currently, the local tanning industry in Nigeria consists of the traditional tanning and leather cottage industries and the large post-colonial mechanized tanneries whose leather was initially meant for export (Plata *et al.*, 2009). Tannery industries contribute significantly towards exports, employment generation and play an important role in Nigerian economy (Hameed *et al.*, 2012). Tannery effluent is ranked as the contents industrial effluents discharged to the environment (Savant *et al.*, 2013).The effluent discharged for 100 kg of hides and skins varies from 3000 litres to 3200 litres (Hayer *et al*., 2013). The effluent after processing raw hides and skins into finished leather is highly alkaline and decomposes organic matter, sulphide and organic nitrogen with high amount of other toxic chemicals. Pre-tanning process contributes 80-90 percent of toxic pollution in leather industries and generates noxious gases such as hydrogen sulphide as well as

solid wastes and chrome sludge (Eddy and Mike, 2014). The sources of leather are the hides and skins of animals. The skins of big animals including cattle, camels and horses are referred to as hides while those of the smaller animals like sheep, goats, snakes, crocodiles among others are known as skins (Galvez *et al*., 2015). Immediately after slaughtering the animal, the skin is removed and fleshed in order to ensure absence of any remaining meat tissue or fat. Freshly fleshed skins are transported in refrigerated trucks to tanneries for immediate processing into leather. If this is not possible, the fleshed skins are cured by immersion in agitated salty water (Brine) so as to avoid sudden degradation in the tissue (Bashford *et al*., 2014). After curing, the skins can be stored for several months without rotting and can be shipped to tanneries throughout the world.

2.2 PROCESS STAGES OF LEATHER PRODUCTION

The process stages of leather production are usually carried out in tanneries in order to convert hide and skins of animals into leather which is more durable and less susceptible to decomposition. Fleshing and sludge are the two major solid wastes emanating from tanning and treatment of tannery wastewater. It was reported that, about 140-200 kg of fleshing which are putrescible by nature are generated for every tonne of leather processed (Garrido *et al.,* 2010). It contains about 80-90% moisture, 6-12% dry volatile matter and 4-8% ash and minerals (Lee *et al.,* 2006). Large-scale leather processing activity in the country employing mechanical removal of fleshing has led to the generation of large quantity of fleshing which poses serious disposal problem. In general, the leather process stages in tanneries can be categorized into four main stages namely: Beam house operations, tanning, post-tanning and finishing (Bosnic *et al*., 2011). The environment is under increasing pressure from solid and liquid wastes emanating from the leather industry. These are inevitable by products of the leather manufacturing process and cause significant pollution unless treated in some way prior to discharge. In some

instances, liquid waste is discharged into sewage systems where it undergoes full-scale treatment before being returned to the environment via surface waters (Garrido *et al.*, 2010). In those cases, effluent treatment standards set by the authorities are governed by the scale of dilution with other effluents and domestic sewage treatment plant capabilities, and problems related to plant and equipment management or maintenance. Under these conditions, discharge limits are lower than those on discharge direct into surface waters. However, factors such as final sludge disposal and discharge limits for treated effluents also have to be taken into account. Where effluent is discharged directly into streams and rivers, it needs to be of higher quality as the environment is sensitive and highly susceptible to damage. The greater the volume of the effluent compared to the volume of surface water, the higher the quality of the effluent demanded by the environment (Farhana *et al.*, 2012).

2.2.1 Curing Process

Curing is employed by applying wet-salt on hide and skins of animals to prevent putrefaction of protein substance from bacterial growth before being transported to tanneries. It also helps to reduce excess water from the hides and skins using a difference in osmotic pressure. The moisture content of hides and skins is greatly reduced and the osmotic pressure is increased to a point that bacteria are unable to grow. Generally, curing substantially reduces the chance of spoilage by bacteria and preserves the skins at a very low temperature as it can be observed from plate 2.1.

Plate 2.1: Samples of hides and skins under curing process (Liang *et al.*, 2009).

2.2.2 Soaking and Unhairing Processes

Soaking is usually the first process that hides and skins undergo in tannery as the previous dehydrated raw material must be carefully rehydrated before it can be subjected to extended mechanical penetration and removal of curing agents, nonstructural proteins and fats. Soaking involves putting hides and skins into a clean water to remove dirty materials, blood and salt left over from curing and increase the moisture content so that the hides and skins can further be treated. Soaking allows hides and skins to re-absorb lots of water that most have taken place during transportation to tanneries. Unhairing is a process that deals with a chemical dissolution of hair in an alkaline medium of sodium. sulphide, and calcium hydroxide in order to open up fiber structures of hides and skins and allows penetration and action of tanning agents.

2.2.3 Liming and De-liming Processes

Liming is a treatment of hides and skins with milk of lime that involves the addition of sharpening agents like sodium sulphide, cyanides and amines among others. The objectives of this operation are mainly to:

i. Remove the hairs, nails and other unwanted organic matter.

ii. Remove some of the inter-fibrillary soluble proteins like mucins.

iii. Swell and split up the fibers to alkaline medium

iv. Removal of natural grease and fats to some extent

v. Bring the collagen in the hide to a proper condition for satisfactory tannage.

De-liming process is usually carried out to lower the pH of the collagen to a certain level using acid ammonium salt so that enzymes may act on it so as to soften, remove hair remnants and degrade proteins from hides and skins of animals as it can be observed from (Plate 2.2).

Plate 2.2: Hides and skins under liming and de-liming processes (Galvez *et al.*,2015).

2.2.4 Pickling Process

Pickling process involves decreasing the pH of collagen using sodium chloride salt and then sulphuric acid so as to facilitate the penetration of tanning agents into the substance and to prevent the hides and skins from mould growth. The salt penetrates the hides and skins twice as fast as the acid and checks the ill effect of the sudden drop of pH. The pH is very acidic when the chromium is introduced to ensure that the chromium complexes are small enough to fit between the fibers and residues of the collagen. Once the desired level of penetration of chromium into substance is achieved, the pH is raised again to facilitate the process.

2.2.5 Tanning and Re-tanning Processes

Tanning process is carried out in order to convert hides and skins of animals in to leather. During tanning, the hides and skins structures are stabilized in their open forms by replacing some of the collagen with complex ions of chromium. Depending on the compounds used the colour and texture of the leather changes. When hides and skins are transformed into leather, they have the ability to 'breathe' and withstand boiling water as well as becoming more flexible than an untreated dead skin. Chromium salts (particularly chromium sulphate) are the most widely used tanning substances today. Hides and skins tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermal resistance in comparison with hides treated with vegetable substances. Unfortunately, only a fraction of the chromium salts used in the tanning process react with the hides and skins. The rest of the salts remain in the tanning exhaust bath and are subsequently sent to a depuration plant where the chromium salts end up in the sludge. One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced as a by-product of wastewater treatment. At high concentrations chromium is toxic, mutagenic, carcinogenic

and teratogenic. Chromium exists in oxidation states of +2, +3 and +6 (Farhana *et al.*, 2012). The trivalent oxidation state is the most stable form of chromium and is essential to mammals in trace concentration and relatively immobile in the aquatic system due to its low water solubility. The hexavalent chromium is much more toxic to many plants, animals and bacteria inhabiting aquatic environments. Most micro-organisms are sensitive to Cr (VI) toxicity but some groups possess resistance mechanisms to tolerate high levels. A relationship was found between the total chromium content of soil and the presence of metal tolerant/resistant bacteria. In natural waters two stable oxidation states of Cr persist (III and VI), which have contrasting toxicities, motilities, and bioavailability. Cr (VI) is motile and highly toxic and soluble in water and it is a strong oxidizing agent that causes severe damage to cell membranes.Re-tanning is a process of using oils and vegetable extracts for further transformation of hides and skins into leather. Re-tanning changes the physical and chemical characteristics of leather produced. It also improves the quality of leather particularly the grain tightness and chrome uptake thereby reducing the input of chrome. The re-tanned leather is referred to as crust and it is often coloured depending on the requirement. The crust is now complete leather and can be finished to various formats by the spray of pigments and lacquers. Chemicals used in re-tanning include; dyes, formic and sulphuric acids, fatliqours and Syntans, aldehydes, resins.

2.2.5.1 Vegetable Tanning Process

Vegetable tanning employs the use of natural tannins available in liquid or powdered form obtained from different part of plants including woods, barks, fruits, fruit pods and leaves. The most common tannins are obtained from Chestnut wood. The vegetable tanning process begins with soaking hides and skins in lime to loosen the hair as demonstrated in plate 2.3. They are then removed from the lime solution and the hair is removed mechanically. The hides and skins are then soaked and rinsed and the fleshing operation is accomplished. After fleshing, the hides and skins are trimmed into a roughly rectangular

shape and then passed through a bate and pickle operation similar to that used in the chrome tanning process. The next operation is colouring which is often carried out by utilizing a weak tanning solution. Normally vegetable tanned leather is not highly coloured. After colouring, the hides are placed into vats containing the bark extract tanning solution and moved from a strong tanning solution to a slightly weaker one, then rinsed and partially dried (Lofrano, 2006).

Plates 2.3: Vegetable tanning process (Lee *et al*., 2006)

2.2.5.2 Chrome Tanning Process:

The general steps required for chrome tanning of hides and skins into leather include; soaking, fleshing, unhairing, liming, deliming, bating and pickling among others are similar to that of vegetable tanning. However, in chrome tanning, the additional processes of re-tanning, dyeing, fat liquoring and finishing are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins. Chrome tanning is based on the reaction between the hides, skins and a trivalent chromium salt. When the reaction is completed, the leather is said to be fully chrome

tanned as it can be seen from plate 2.4. Chrome tanning produces leather better suited for certain applications, particularly for the upper parts of boots and shoes and requires less processing time than traditional vegetable tanning (Anjana *et al*., 2008).

Plate 2.4: Samples of chrome tanned leather (Lee *et al*., 2006)

2.2.6 Neutralizing, Dyeing, Fat Liquoring, Drying and Finishing Operations

During the process of neutralization, the leather is treated with alkaline solution to neutralize and prevent it from deterioration. The leather produced is then dyed using different colours of interest which involves fixing varieties of compounds onto the chromium. The leather is then lubricated using oil and grease usually from animals or vegetable's origin in order to achieve product specific characteristics in a process known as fat liquoring. Drying is carried out to reduce the moisture content and to stabilize the chemical properties of the leather. Finishing operation enhances the beautiful appearance of the leather and provides the performance characteristics expected with respect to colour,

gloss, feel, flex and adhesion (Plate 2.5). Various leather process stages, chemicals and waste generated from tannery industries are presented in Table 2.1.

Plate 2.5: Samples of finished leather setting out and drying (Galvez *et al.*, 2015).

Table 2.1: Leather process stages, chemicals and waste generated from tannery industries

Leather process stages	Chemicals used	Waste generated
Curing and preservation	Sodium chloride salt, pentachlorophenol	Putriscible skin
Soaking and unhairing	Clean water, sodium sulphide, caustic soda	Wastewater and shaving hair
Liming and de-liming	Milk of lime, cyanides, amines, acid ammonium salt	Unwanted proteins
Pickling	Sodium chloride salt, sulphuric acid	Wastewater
Tanning and re-tanning	Chromium, fat liquor, aldehydes	Wastewater containing chromium and oily substances
Neutralizing, dyeing and fat liquoring	Alkali solution, dye stuffs, vegetable oil and grease	Coloured wastewater, waxes, fats and oil
Drying and finishing	Liquor emulsion, chrome pigment, water-proofing agents	Wastewater

Source: (Liang *et al.*, 2009)

2.3 ENVIRONMENTAL IMPACT OF TANNERY EFFLUENT

The environment is under increasing pressure from solid, liquid and gaseous wastes emanating from leather industries (Zeng *et al*., 2012). These are inevitable by-products of leather manufacturing process and cause significant pollution unless treated in some ways prior to discharge. In some instances, liquid waste is discharged into sewage systems (indirect discharge) where it undergoes full-scale treatment before being returned to the environment via surface waters (Borja and Bank, 2014). In those cases, effluent treatment standards set by the authorities are governed by the scale of dilution with other effluents and domestic sewage treatment plant capabilities and problems related to plant and equipment management and maintenance. Under these conditions, discharge limits are lower than those on discharge direct into surface waters (Najeem *et al*., 2011). That

notwithstanding, factors including final sludge disposal and discharge limits for treated effluents that might be imposed on the sewage treatment authority also have to be taken into account. Where effluent is discharged direct into streams and rivers, it needs to be of higher quality as the environment is sensitive and highly susceptible to damage (Hamdan *et al*., 2014). The greater the volume of the effluent compared to the volume of surface water, the higher the quality of the effluent demanded by the environment (Yang and Wang, 2014). Tannery effluents are mainly characterized by high salinity, organic loading and specific pollutants like chromium. The tannery effluent is found to contain higher concentrations of total dissolved solids, chromium, chloride, ammonia, nitrate and sulphates when the samples were collected from the outlets of the industry (Haber *et al*., 2015). Besides these, chemicals including zinc chloride, mercuric chloride and formaldehyde are used as disinfectants, sodium chloride in curing and as bleaching powder and sodium fluoride to prevent putrefaction, lime is used in liming, sodium sulphate, ammonium chloride, borax and hydrochloric acid in are used de-liming, sodium is used for degreasing and basic or acidic dyes is used in leather finishing (Moura *et al*., 2011). Hence, tannery waste is always characterized by its strong colour (reddish dull brown), high COD, BOD_5, pH, and dissolved solids. The other major chemical constituents of the waste from tanning industries are sulphide and chromium (Liang *et al*. 2013). These chemicals mixed with water are discharged from the tanneries and pollute the ground water permanently and make it unfit for drinking, irrigation and general consumption. Therefore, there comes an urgent need to determine the pollution levels in the wastewater from these industries. The environment is under increasing pressure from solid, liquid and gaseous wastes which are emitted by leather industries in the form of effluent, solid wastes and air emissions respectively (Molina and Lee, 2015).

2.3.1 Tannery Wastewater

Water is used as a carrier for chemicals to render the cleaning of raw hides and skins. Untreated tannery effluent discharged into streams, rivers and lakes has serious effects on human, animals and aquatic lives particularly upon consumption and has become one of the most critical environmental problems as it can be observed from plate 2.6. Environmental quality standards are also used to monitor the protection of aquatic lives based on fate, behaviour and aquatic toxicity. Much of this highly sensitive information is drawn from research data covering a variety of sources and species. Considerable data are often available to facilitate the decision-making process, in their absence; however, conclusions may include expert judgement. Environmental quality standards may be defined as the concentration of a substance which must not be exceeded if a specific use of the aquatic environment is to be maintained.

Plate 2.6: Effect of untreated tannery effluent to living things (Hameed *et al*., 2012)

Tannery wastewater results from a variety of processes that employ different chemicals and materials that are discharged into the atmosphere (Haber, 2015). This wastewater result in varying threats to the environment, particularly those containing surplus, spent or washed out chemicals. The complexity of tannery wastewater originates from a wide range of components such as; raw materials (skins) residues, excess dosage of reagents

including a high concentration of proteins, lipids and salts (sulphide, sulphate and chloride), tanning agents such as; natural and synthetic tanning (in the case of vegetable tanning), dyes and surfactants (Lee *et al*., 2006).

The choice of the treatment process is strictly related to the presence of significant fractions of slowly hydrolysable and inhibiting compounds requiring technologies such as Membrane Bioreactor (MBR), granular biomass, etc., which increase the sludge age and consequently the capacity to degrade substrates usually not biodegradable in conventional wastewater treatment plants. (Farhana *et al*., 2007). In leather tanning industrial areas, sulphide management represents a major problem. Biological sulphide oxidation to sulphur, represents a convenient solution to this problem. Elemental sulphur is easy to separate and the process is highly efficient in terms of energy consumption and effluent quality. However, it has been shown that the yield of the sulphide oxidation process depends on the features of the selected microbial community. As the oxidation process is performed by specialized bacteria, selection of an appropriate microbial community is fundamental for obtaining a good yield (Gupta, 2007). The wastewater of leather industry which is one of the most widespread industries having large amount of water consumption and very high pollution loads, may be characterized by several key parameters including toxic pollutants exhibiting toxicity.

Therefore the effluent of leather tanning industry must be handled carefully during both treatment plant design and operation. Standards within one and the same country can vary from one region to another (Abdul Malik, 2008). The Figures in the table 2.2 should be treated with caution; direct comparisons are possible (Bosnic *et al*., 2011). Leather processing requires large amount of chemicals like sodium chloride, chromium sulphate, calcium salts, ammonium salts, sodium sulphide, acids, alkalis, fat, liquor, and organic dyes. However, one of the major emerging environmental problems in the tanning

industry is the disposal of chromium contaminated sludge produced as a by-product of wastewater treatment. Tannery effluents severely affect the mitotic process and reduce seed germination in extensively cultivated pulse crops (Abdul Malik *et al*, 2007).

Table 2.2: Typical characteristics of tannery effluent

Parameter	**Units**	**Pollution load**	**NESREA limit**
COD	mg/L	4000	200
BOD_5	mg/L	2000	50
TSS	mg/L	500	25
TDS	mg/L	5000	2000
Cl^-	mg/L	1500	600
SO_4^{2-}	mg/L	1800	500
S^{-2}	mg/L	20	0.2
Oil and grease	mg/L	150	10
pH		9.0	6.5-7.5

Source: (Hameed *et al.*, 2012)

Normally water consumption of 50 litres/kg is recommended for tanneries but it was found that tanneries generally consume more water and in some cases it was found to be as high as 150 litres/kg (Patric *et al*., 2010). Tannery wastewater is highly polluted in terms of biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), suspended solids, total Kjeldhal Nitrogen, conductivity, Sulphate, Sulphide, and Chromium. The quantity of these pollutants in the wastewater is very high. Considerable quantity of sludge is also found in the wastewater. Wastewater of each tannery process consists of pollution of varying pH values. Discharge of these chemicals into wastewater is hazardous for the environment. Tannery wastewater is highly contaminated and the contamination observed is many times beyond the limits set by Environmental Quality Standards for all wastewater parameters. Chemical pollution entering rivers and streams can be classified according to the nature of its source (Munta and John, 2011).

2.3.2 Solid Tannery Wastes

The major solid wastes consist of dusted curing salt, wet trimmings, dry trimmings, wet shaving, buffing among others. These solids originated from all stages of leather making comprised of fine leather particles, residues from various chemical discharges and reagents from different waste liquors (Tolle *et al*., 2009). Large volumes are generated during beam house processes. During handling of raw skins, adhered dusted salt which is contaminated with blood, hair, dirt and certain type of bacteria is removed and dumped. Trimmings are cuttings of edges of raw skins. Fleshing is the flesh material of the limed skins generated during fleshing operation (Lofrano, 2010). Chrome wet shaving is produced when skins are shaved for proper thickness after chrome tanning. Except dusted salt, most of the solid wastes are sold in the local market to the poultry feed manufacturers due to the protein content of the solid wastes. (Anjana *et al*., 2008). The Chrome tanned waste contains Chromium in trivalent form but it was found that when the solid wastes are used in making poultry feed the Chromium is converted to hexavalent form which is carcinogenic. The mixing of this metal in poultry feed could produce serious human health problems. It is estimated that for a tannery producing on an average 10,000 kilograms of skins per day, a total of about 5,500 kilograms of solid waste would be produced per day (Kazmi *et al*., 2012).

The solids to be found in tannery effluent can be categorized as suspended solids component of an effluent defined as the quantity of insoluble matter contained in the wastewater. These insoluble materials cause a variety of problems when discharged from a site; essentially, they are made up of solids with two different characteristics; Solids with a rapid settling rate which include materials that can be seen in suspension when an effluent sample is shaken but settles when the sample is left to stand. The majority of these solids settle within 5 to 10 minutes, although some fine solids require more than an

hour to settle (Galvez *et al.,* 2015). These solids originated from all stages of leather making; they comprise fine leather particles, residues from various chemical discharges and reagents from different waste liquors. Large volumes are generated during beam house processes. If the waste waters are to be treated in sewage works or undergo traditional effluent treatment, the main problems that arise are due to the large volume of sludge that forms as the solids settled. Sludge often contains up to 97% water giving rise to huge quantities of light sludge. Even viscous sludge has a water content of around 93% and can easily block sumps, sludge pumps and pipes (Chong *et al.,* 2012). Sludge has to be removed, transported, dewatered, dried and deposited, thus placing an inordinate strain on plant, equipment and resources. If the waste water is to be discharged into surface water, the rate of flow will determine the distance the material is carried before settling on the stream or river bed. Even a thin layer of settled sludge can form a blanket that deprives sections of the river or lake bed of oxygen. Plant and aquatic life dies and decomposition sets in. Semi-colloidal solids Semi-colloidal solids are very fine solids that, for all practical purposes, will not settle out from an effluent sample, even after being left to stand for a considerable period of time. They can, however, be filtered from solutions. Together with the more readily settleable solids, they thus comprise the suspended solids of an effluent that can be measured analytically. Most of these solids are protein residues from the beam house operations mainly liming process; however, large quantities are also produced owing to poor uptake in vegetable tanning process and another source being poor uptake during re-tanning process. Semi-colloidal solids will not directly cause a sludge problem but can be broken down over an extended period by bacterial digestion and they produce solids which will eventually settle. Although suspended solids analysis is the method most commonly used to assess insoluble matter, analysis of the settleable solids content is sometimes required (Bosnic *et al.,* 2011).

The settleable solids content is determined by leaving the shaken sample to settle and then filtering a known volume of the semi-colloidal matter remaining in suspension. After drying and weighing, the quantity of semi-colloidal matter can be calculated. The difference between the suspended solids and this figure is the settleable solids content. Gross solids are larger than a sampling machine can handle, hence they are not measured. Their presence however, is clear to see and the dangers they pose are fully recognised. The solid waste components that give rise to this problem are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair debris and remnants of paper bags. They can be easily removed by means of coarse bar screens set in the wastewater flow. If however, they emerge from the factory, they settle out very rapidly. Major problems can develop, if these materials settle in the pipe work as they lead to blockages. The problems can be very serious when blockages occur in inaccessible pipe work. The cost of replacing a burned out motor or broken rotors is high. If discharged into gullies, ditches or water courses, the debris rapidly accumulates causing blockages and leading to stagnation (Borja, 2014).

2.3.3 Air Emissions by Tanneries

In tanneries, air emissions are produced from the stacks of boilers and generators and during the processing of leather. Emissions from the stacks are well within the limits and pose no serious environmental impact but hydrogen Sulphide and ammonia gases which are emitted during different processes are health hazard for the workers (Munter *et al*., 2009). Chemical reactions involving air pollutants can create acidic compounds that cause harm to vegetation and buildings. Sometimes, when an air pollutant, such as sulphuric acid combines with the water droplets that make up clouds, the water droplets become acidic, forming acid rain. When acid rain falls over an area, it can kill trees and harm animals, fish, and other wild lives. Air pollutants can be in the form of particulate matter

which can be very harmful to our health (William *et al*., 2010). The level of effect usually depends on the length of time of exposure as well the kind and concentration of chemicals and particles exposed to the atmosphere.Short-term effects include irritation to the eyes, nose, throat, and upper respiratory infections such as bronchitis and pneumonia. Others include headaches, nausea, and allergic reactions. Short-term air pollution can aggravate the medical conditions of individuals with asthma and emphysema. Long-term health effects include chronic respiratory disease, lung cancer, heart disease, and even damage to the brain, nerves, liver and kidneys. Continual exposure to air pollution affects the lungs of growing children and may aggravate or complicate medical conditions in the elderly people.

Air pollution from tanneries may cause problems of various kinds including:

i. Global warming, as a result of emissions of carbon dioxide
ii. Changes in the ozone-layer as a result of emissions of CH_4 and NO_2
iii. Acid rain, as a result of emissions of SO_2 and NH_3
iv. Destabilizes health conditions

2.4 TANNERY EFFLUENT TREATMENT METHODS

Many conventional processes have been applied to treat wastewater from tannery industries among which are: biological, coagulation, sedimentation and bio membrane reactor method. Tannery wastewater treatment is an essential process that reduces contamination and destruction of waterways, drinking water and natural water resources. (Abdul *et al*., 2010).

2.4.1 Biological Treatment

Biological treatment of wastewater is evaluated as a good treatment method for industrial effluent. Treatment of wastes with bacteria involves the stabilization of waste by decomposing them in to harmless inorganic solids either by aerobic or anaerobic process.

In aerobic process, oxygen which acts as an electron acceptor is required in either the dissolved molecular form or in the form of anions such as nitrate and sulphate (Ludvik, 2007). The end result is a decrease in the quantity of organic pollutants and an increase in the quantity of microorganisms, carbon dioxide, water, and other by-products of microbial metabolism. A steady 24 hours flow is desirable from the sedimentation tank. It is essential to maintain the aerobic flora which can be affected adversely by bactericides, and certain metal salts (Bosnic *et al*., 2009).The decomposition rate is more rapid than anaerobic process and it is not accompanied by unpleasant odours whereas in anaerobic process longer detention period is required and gives unpleasant odours as it involves passing the discharged effluent through a coarse filter media. This may consist of a tower packed 3m deep with broken stones 50 to 100mm in size (Haber, 2015). For input of 1000 hides per day, this tower could be as high as 15m diameter and usually fitted with rotating sprinkler arms feeding the effluent uniformly over the top of the bed. Proper packing is important to allow uniform drainage of the effluent over the surfaces of the broken stones to the base of the tower and facilitating ventilation with air in the opposite direction, the packaging considerations becomes most critical factor. The surfaces of the checker work of stones usually become coated with bacterial growth and aerobic micro-organisms which use the substances as food. Almost all organic substances can be used as food by one or more species of bacteria, fungi, ciliates, rotifers, or other microorganisms. Complex organic molecules are systematically broken down, or disassembled then reassembled as new cell protoplasm (Kayode *et al*., 2012).

2.4.2 Membrane Separation

In this method, membrane component that uses low pressure microfiltration or ultra-filtration membranes is utilized and this eliminates the need for clarification and tertiary filtration. The membranes are typically immersed in the aeration tank, however, some

applications utilize a separate membrane tank (Iborra, 2008). A key benefit of MBR system is that it effectively overcomes the limitations associated with poor settling of sludge in conventional activated sludge (CAS) processes. The technology permits bioreactor operation with considerably higher mixed liquor suspended solids (MLSS) concentration than CAS systems, which are limited by sludge settling. The process is typically operated at MLSS in the range of 8,000–12,000 mg/L, while CAS is operated in the range of 2,000–3,000 mg/L (Lofrano, 2010). The elevated biomass concentration in the MBR process allows for very effective removal of both soluble and particulate biodegradable materials at higher loading rates. Thus increased sludge retention times, usually exceeding 15 days, ensure complete nitrification even in extremely cold weather (Iborra and James, 2008). The cost of building and operating an MBR is often higher than conventional methods of sewage treatment. Membrane filters can be blinded with grease or abraded by suspended grit and lack a clarifier's flexibility to pass peak flows. The technology has become increasingly popular for reliably pretreated waste streams and has gained wider acceptance where infiltration and inflow have been controlled, however, and the life-cycle costs have been steadily decreasing. The small footprint of MBR systems and the high quality effluent produced makes them particularly useful for water reuse applications (Blackman, 2011).

2.4.3 Oxidation Ditches

Oxidation ditches is another alternative for treating discharged effluent from tannery industry, usually easier to construct, operate and have been preferred for effluents from vegetable tannages (Fakayode, 2010). The ditch may be 1 metre deep, 4 metres wide at the top and 2metres wide at the bottom. It may be built as an oval in plan to minimize land usage. The effluent is paddled round by four or five surface aerators which consist of steel brush-bladed paddles which entrain quantities of air as they rotate. The biochemical

action is similar to that of the activated sludge plant. Two or three times each day the rotors are stopped and the effluent is allowed to settle for 1 hour, when the clear liquor can be decanted off leaving the bulk of the activated sludge in the ditch. A proportion of this may have a life of many days in the ditch, giving a high degree of biological burn-up. The discharge from any of these secondary biochemical degradation systems should be suitable for discharge into most rivers, bore-holes or disused underground workings, (Zafaruddin, 2008).

2.4.4 Tannery Effluent Recycling

Tannery industries must look for the production alternatives minimizing the environmental impacts derived from their industrial activities mainly in the stages that have the greatest effect on the environment as in the case of tanning stages. The treatment and conditioning plant for effluent recycling to be used for purposeful industrial processes should be equipped with the following systems:

i. Wastewater channelling
ii. Storage and recirculation of the Wastewater
iii. Wastewater pre-treatment and pumping to the homogenization basin

2.4.4.1 Wastewater Channeling

In this type of effluent recycling, the baths from different process stages were drained by opening the drum valves and leaving the bath to drain to the ground in order to be subsequently gathered in collection boxes where the different effluents were mixed, thus, making their reuse impossible. In order to avoid this drawback, the drain system of tanning drums have been modified by installing some curved channels equipped with a flexible out let in order to separate the effluents of the tanning drums. The new channels are equipped with a flexible hose to be connected to different out lets according to the destination of the effluent tanning drum. Finally, the tanning effluent is led to a channel

where the system fine leather particles sediment is located (FEPA, 2009).

2.4.4.2 Storage and Recyclation of Wastewater

The clarified water free from fats and suspended solids, flows by gravity to the storage tanks which are inter connected in their bottom parts and where activated carbon air purification system have been installed in the vent holes. Besides, the system is equipped with level probes and a pH controller as well as a continuous conduct meter in order to control the quality of the recovered liquor. Finally, a manually operated pumping station takes the chromium liquor from the storage tanks to the drum's inlet. The recovered liquor does not directly go in to serving but it first go into an intermediate tank serving as "lung" where some products are added so that to readjust the bath conditions (Gupta, 2007).

2.5 ADVANCED OXIDATION PROCESSES

Advanced oxidation processes (AOPs) are set of chemical treatment procedures designed to degrade organic pollutants by oxidation through reaction with hydroxyl radicals (Farhana *et al.,* 2012). However, these chemical treatment procedures show great promise for application in many industrial processes (Othman *et al*., 2011). It is an emergent technology that may be employed for specific goals and utilize the strong oxidizing power of hydroxyl radicals to degrade and mineralize organic compounds in to carbon dioxide and water but notwithstanding, it has not been widely applied yet, because of the chemical processes behind it that are not completely understood (Javeed, 2009).

Advanced oxidation processes involve; Chemical oxidation processes using hydrogen peroxide, ozone, combined ozone and peroxide, hypochlorite, Fenton reagents, the use of ultra-violet light which enhances oxidation of UV/ozone, UV/peroxide and UV/air. Advanced oxidation processes are usually appropriate for effluent containing toxic and non-biodegradable pollutants. It possesses advantages over conventional methods including:

i. Fenton oxidant is commercially available and easy to handle environmentally

ii. Simultaneous degradation and mineralization of organic pollutants

iii. Absence of secondary pollution generation

iv. Ability to handle fluctuating flow rates and compositions

Advanced oxidation processes rely on in-situ production of highly reactive hydroxyl radicals, these reactive species are strong oxidants that can be applied in wastewater treatment and virtually oxidize any compound present in the wastewater matrix into smaller inorganic molecules (Doan *et al*., 2009). In general, when applied in proper conditions advanced oxidation processes reduce the concentration of contaminants and significantly bring COD percent reduction. Advanced oxidation processes are useful for treating biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in wastewater. In addition, advanced oxidation processes can be used to treat effluent of secondary treated wastewater which is then called tertiary treatment. The contaminants are converted into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization (Yang *et al*., 2010). A goal of the wastewater purification by means of Advanced oxidation processes is the reduction of the chemical contaminants and the toxicity that the treated wastewater may be reintroduced into receiving streams or at least, into a conventional sewage treatment.

Advanced oxidation processes have not been put into commercial use on a large scale (especially in developing countries) even up to today because of the relatively high costs. Nevertheless, its high oxidative capability and efficiency make AOPs a popular technique in tertiary treatment in which the recalcitrant organic and inorganic contaminants are to be eliminated. The increasing interest in water reuse and more stringent regulations regarding water pollution are currently accelerating the implementation of AOPs at a larger scale (William *et al*., 2008).

2.5.1 Chemical Principles of Advanced Oxidation Processes (AOPs)

Chemistry in AOPs could be divided into three parts (Farhana *et al*., 2012)

1. Formation of ·OH;
2. Initial attacks on target molecules by ·OH and their breakdown to fragments;
3. Subsequent attacks by ·OH until ultimate mineralization.

The mechanism of ·OH production depends on the sort of AOP technique that is used. For example, ozonation, UV/H_2O_2 and photo catalytic oxidation rely on different mechanisms of ·OH generation (Othman *et al*., 2011).

1. UV/H_2O_2

a. $H_2O_2 + UV \rightarrow 2{\cdot}OH$ (homolytic bond cleavage of the O-O bond of H_2O_2 leads to formation of 2·OH radicals)

2. Ozone Based AOP:

a. $O_3 + HO^- \rightarrow HO_2^- + O_2$(reaction between O_3 and a hydroxyl ion leads to the formation of H_2O_2 (in charged form)

b. $O_3 + HO_2^- \rightarrow HO_2^{\cdot} + O_3^-$(a second O_3 molecule reacts with the HO_2^- to produce the ozonide radical)

$O_3^- + H^+ \rightarrow HO_3{\cdot}$ (this radical gives to ·OH upon protonation)

c. $HO_3^{\cdot} \rightarrow {}^{\cdot}OH + O_2$

3. Photocatalytic oxidation with TiO_2:

d. $TiO_2 + UV \rightarrow e^- + h^+$(irradiation of the photocatalytic surface leads to an excited electron (e^-) and electron gap (h^+)

e. Ti(IV) + H_2O $\rightleftharpoons$ Ti (IV) + H_2O (water absorbs onto the catalyst surface)

f. Ti (IV) + H_2O + h^+ $\rightleftharpoons$Ti(IV) + ·OH + $H^+$the highly reactive electron gap will react with water.

2.5.2 Fenton Oxidation Process

Fenton oxidation process is one of the advanced oxidation processes in which ferrous iron reacts with hydrogen peroxide to generate hydroxyl radical as represented in the chemical equation (Farhana *et al*., 2012)

$Fe^{2+} + H_2O_2 \quad \rightarrow \quad Fe^{3+}HO\cdot + OH^-$ (2.1)

The hydroxyl radical reacts with organic pollutants according to four (4) types of reactions (Othman *et al*., 2011)

i. Addition Reaction: $\cdot OH + C_6H_6 \rightarrow (OH)C_6H_6$

ii. Hydrogen Abstraction Reaction: $\cdot OH + CH_3OH \rightarrow CH_2OH + H_2O$

iii. Electron Transfer Reaction: $\cdot OH + [Fe(CN)_6]^4 \rightarrow [Fe(CN)_6]^{3-} + OH^-$

iv. Radical Interaction Reaction: $\cdot OH + \cdot OH \rightarrow H_2O_2$

During Fenton reaction, all the parameters are adjusted to promote the first two (i and ii) types of reactions between the pollutants and the hydroxyl radicals. The hydroxyl radicals which are second to fluorine among common oxidants, could react rapidly and non-selectively with nearly all organic pollutants, indeed, the $OH^{\bullet}$ concentration determines the lifetime of many compounds in the environment and consequently, it has been called "mother nature's vacuum cleaner" (Ahmad *et al*., 2013). pH is one of the important factor to be taken into consideration for wastewater treatment using Fenton oxidation process since at acidic pH the direct attack by free radical ($\cdot OH$) is predominant and improve the efficiency of Fenton reaction while at neutral and basic pH there was a major contribution of the free radical pathway and the addition of hydrogen peroxide can promote or inhibit the reaction of free radicals. Considering the Fenton method which can be used as a preliminary step prior to biological wastewater treatment, one has to adjust pH twice, first to an acidic pH of 3 and then back to a neutral pH to perform the Fenton oxidation process. The biodegradability of the treated waste increased with increasing in hydrogen

peroxide. Electrochemical method oxidizes organic pollutants by means of electrode reactions (electrolysis). The electrodes are available in various shapes (bar, plate, porous and fiber) and are made of various materials. In wastewater, such oxidizable pollutants as organic compounds are oxidized at the anode surface and such reducible pollutants as most inorganic metals are reduced and deposited at the cathode surface. To bring about the required reaction, a certain electro-potential is applied to the anode and cathode. Electrochemical method is employed mainly for metal ion elimination among which the recovery of copper and lead, mercury (II) and zinc (II), cobalt (II) and cadmium. Another interesting application of electrochemical method is cyanide oxidation in wastewater. In most metal finishing and hydrometallurgical industrial wastewaters containing metal ions (such as gold, silver, chromium) and cyanides, the electrochemical method has an advantage in that simultaneously cyanide is decomposed (oxidized) at the anode and heavy metals are deposited (reduced) at the cathode without causing sludge generation. Neutralization reaction involves the addition of sodium hydroxide (NaOH) to the effluent stream so as to neutralize the solution (William *et al*., 2010). This titration or neutralization reaction can be represented by the chemical equation (2.2):

$HCl + NaOH \rightarrow NaCl + H_2O$(2.2)

From equation 2.2, hydrochloric acid (HCl) is neutralized with sodium hydroxide (NaOH) and yields ordinary table salt (NaCl) and neutral water. NaCl, being soluble in water, remains dissolved in solution and very little or no solids are generated. It is the task of the pH adjustment system to add just the right amount of caustic to achieve the end point of the neutralization that is desired. This is not quite simple because of the logarithmic nature of the pH titration curve presented in Figure 2.1. The titration curve shown in Figure 2.1 depicts graphically the neutralization process of HCl with NaOH as the neutralizing agent.

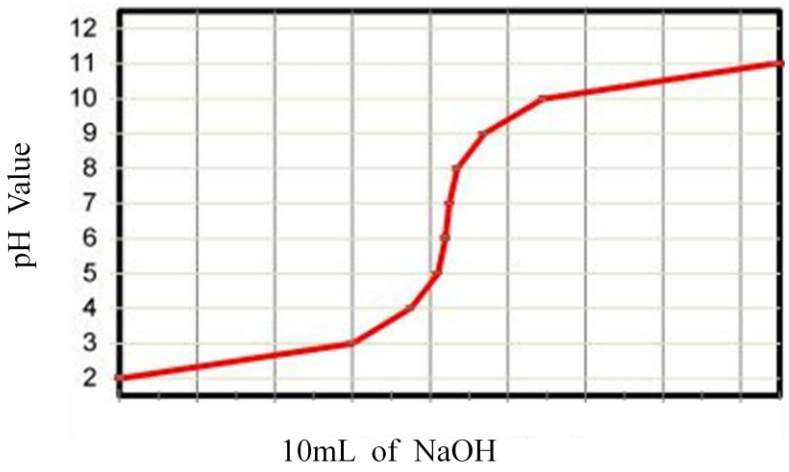

Figure 2.1: Plots of pH values of HCl vs NaOH

The curve indicates the actual titration results of pH Adjustment of HCl with a beginning pH of 2.0 and ending pH of 11.0. Dilute sodium hydroxide solution was used as neutralizing agent. A brief glance at the curve indicates that the process of pH neutralization is not particularly easy. 10 ml of NaOH was added to increase the pH from 2.0 to 3.0. An additional 1 ml was added to further raise the pH to 4.0 and another 0.1 ml added to raise the pH to 5.0. An increase of 1 pH unit requires 1/10th the amount of caustic required to achieve the previous increase. Descending from 7.0 to 0.0, each unit on the pH scale represents a tenfold increase in acidity. In simple terms, very large volumes of a neutralizing agent are required to achieve very small results at high and low pH values. At near neutral, small volumes must be added to achieve neutralization. This means that the pH adjustment system must be capable of delivering large volumes of reagent at extremely high levels of precision. The steep portion of the curve which is the area near neutral (pH 7.0) is the range that most industrial effluents must be held (Ahmad *et al*., 2013).

Coagulation is a method of physical process separation which removes dirt and other particles suspended in water. Alum and other chemicals are added to water to form tiny

sticky particles called "floc" which attract the dirt particles. The combined weight of the dirt and the alum (floc) become heavy enough to sink to the bottom during sedimentation (Bergendahl, 2009). The process is carried out in such away wastewater forms smaller particulates. These particulates with the same charge are suspended into a colloid (a mixture with properties between fine suspension and solution).

The repulsion process and the physical property of particles with the same charge (i.e., negative and negative) repelling each other stops the particulates from combining into a settled form. Coagulation method involves chemicals that assist water particulates in combining together. When particulates are aggregated, they can be more easily removed from the treated wastewater (Walther, 2011).

Fenton oxidation process has several advantages over conventional wastewater treatment methods, namely:

i. Fenton oxidation process degrades recalcitrant organic and inorganic pollutants including aromatics, pesticides, petroleum constituents and volatile organic compounds in wastewater
ii. It further treats secondary treated water (tertiary treatment) by converting the contaminants into stable inorganic compounds such as; water, carbon dioxide and salts (mineralization)
iii. Its high oxidative capability and efficiency make it a popular technique in tertiary treatment
iv. The implementation of Fenton oxidation process encourages the increasing interest in wastewater recycling system and reuse for irrigation purposes
v. Non-biodegradable organic pollutants are completely degraded rather than collecting or transferring them into secondary pollution

vi. Fenton oxidation process does not introduce any new hazardous substances into the treated water after treatment.

It should be understood that, Fenton oxidation process has also several drawbacks, namely:

i. Fenton oxidation process is cost effective due to continuous input of expensive chemical reagents required to maintain the operation of the process.
ii. Some techniques require pre-treatment of wastewater to ensure reliable performance which could be potentially costly and technically demanding. For instance, the presence of bicarbonate ions (HCO_3^-) can appreciably reduce the concentration of ·OH due to scavenging processes that yield H_2O and a much less reactive species (CO_3^-), as a result, bicarbonate must be wiped out from the system.
iii. It is not profitable to use Fenton oxidation process to handle a large amount of wastewater, instead, it should be deployed at the final stage after primary and secondary treatment have successfully removed large proportion of contaminants.

2.6 CATALYSIS

Catalysis is a phenomenon by which chemical reactions are accelerated by small quantities of foreign substances, called catalysts. Catalysis is also the chemical reaction br ought about by a catalyst. A catalyst is the chemical version of a "matchmaker" because it physically brings together two chemicals in such a way that their chance to react is maxi mized.However, catalysts can't make a match between chemicals if there's no "chemistry" (Borja, 2014). Instead, they make it possible for reactions to happen faster, fast enough to be used in environmental cleanup or to produce a chemical product.Catalysts take many f orms. Some are porous solids, such as the platinum, rhodium and palladium meshes that r

emove nitrogen oxide from automobile exhaust. Others are protein molecules, called enzy mes that are contained in microorganisms. Still others are naturally occurring solids, such as manganese or iron oxides. No matter what the catalyst's structure, though, it speeds up reactions without being changed itself.A catalyst is also a substance that increases the rate of chemical reaction towards equilibrium without being appreciably consumed in the process (Anjana *et al.,* 2014). A catalyst usually changes a reaction rate by promoting a different molecular path ("mechanism") for the reaction. For example, gaseous hydrogen and oxygen are virtually inert at room temperature, but react rapidly when exposed to platinum. A suitable catalyst can enhance the rate of a thermodynamically feasible reaction but cannot change the position of the thermodynamic equilibrium. Most catalysts are solids or liquids but they may also be gases (Bosnic, 2010). The principal theme in catalysis is the desire to control the rate of chemical reactions and the secondary theme is to understand the mechanism of the control. Catalysis is of crucial importance for the chemical industry, the number of catalysts applied in industry is very large and catalysts come in many different forms, from heterogeneous catalysts in the form of porous solids over homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes. The catalytic reaction is a cyclic process. According to a simplified model, the reactant or reactants form a complex with the catalyst, thereby opening a pathway for their transformation into the product. Afterwards, the catalyst is released and the next cycle can proceed. However, catalysts do not have infinite life. Products of side reactions or changes in the catalyst structure lead to catalyst deactivation. In practice, spent catalysts must be reactivated or replaced (Silva, 2010). In the presence of a catalyst, less free energy is required to reach the transition statebut the total free energy from reactants to products does not change. A catalyst may participate in multiple chemical transformations. The effect of a catalyst may vary due to the presence of other

substances known as inhibitors or poisons (which reduce the catalytic activity) or promoters (which increase the activity). The opposite of a catalyst, a substance that reduces the rate of a reaction, is an inhibitor. Catalyzed reactions have a lower activation energy (rate-limiting free energy of activation) than the corresponding uncatalyzed reaction, resulting in a higher reaction rate at the same temperature and for the same reactant concentrations (Cornelis, 2010). However, the detailed mechanics of catalysis is complex. Catalysts may affect the reaction environment favorably or bind to the reagents to polarize bonds, e.g. acid catalysts for reactions of carbonyl compounds or form specific intermediates that are not produced naturally, such as; osmate esters in osmium tetroxide catalyzed di-hydroxylation of alkenes or cause dissociation of reagents to reactive forms, such as chemisorbed hydrogen in catalytic hydrogenation. Kinetically, catalytic reactions are typical chemical reactions; i.e. the reaction rate depends on the frequency of contact of the reactants in the rate-determining step. Usually, the catalyst participates in this slowest step, and rates are limited by amount of catalyst and its activity (Plata *et al.*, 2009).

2.6.1 Homogeneous Catalysis

Homogeneous catalysis comprises the process in which a catalyst is in solution with at least one of the reactants. An example of homogeneous catalysis is the industrial process for manufacturing normal isobutyl aldehyde. It has propylene, carbon monoxide and hydrogen as the reactants and a liquid-phase cobalt complex as the catalyst. Reactions carried out in supercritical fluids have been found to accelerate the reaction on rate greatly. By manipulating the properties of the solvent in which the reaction is taking place, inter phase mass transfer limitations can be eliminated (Walther, 2011). Homogeneous catalysis is a catalytic reaction where the catalyst is in the same phase as the reactants. It applies to reactions in a gas and solid phase. The significance of homogeneous catalysis is growing r

apidly particularly in the area of pharmaceutical and polymer industry. Some of the impor tant industrial processes include: Oxidations of alkenes such as production of acetaldehyd e, propylene oxide and polymerization such as production of polyethylene, polypropylene or polyesters. A new major development in homogeneous catalysis is the application of or gano metallic complexes as catalysts. The use of organo metallic catalysts has revolutioni zed the homogeneous processes increasing economic viability. Another new area is bio-ca talysis involving enzymes catalysts. Enzyme catalysts are highly selective and active for p roduction of fine chemicals, pharmaceuticals etc. Enzyme catalysts are discussed in a sep arate section.In homogeneous catalysis, all the reactants and catalysts are present in a sing le fluidphase and usually in the liquid phase. Homogeneous catalysts are the simple molec ules orions such as HF, H_2SO_4, M^{+2} as well as complex molecules such as organometallic complexes, macro cyclic compounds and large enzyme molecules (Plata *et al.,* 2009).

Advantages of homogeneous catalysis

i. Homogeneous catalysts are more active and selective compared to heterogeneous catalysts
ii. In homogeneous catalysis, the catalysts are molecularly dispersed within the fluid
iii. Homogeneous catalyst has no pore diffusion limitations which lead to bulk phase mass transfer limitation
iv. Catalytic chemistry and mechanism for homogeneous catalysis are better studied and understood. Therefore, it is easier to control and manipulate the process parameters

Disadvantages of homogeneous catalysis

i. Homogeneous catalysts are stable only in relatively mild conditions which limit their applicability.

ii. Since the catalysts are molecularly dispersed in the phase as the reactant, products and solvents, the separation at the end of the process is difficult and expensive

iii. Difficulty in catalyst recovery

2.6.2 Heterogeneous Catalysis

Heterogeneous catalysis is a process that involves more than one phase, usually the catalyst is a solid and the reactants and products are in liquid or gaseous form. Much of the benzene produced in this country today is manufactured from the dehydrogenation of cyclo hexane (obtained from the distillation of crude petroleum) using platinum-on-alumina as the catalyst (Liang *et al*., 2009). Sometimes the reacting mixture is in both the liquid and gaseous forms, as in the hydro desulfurization of heavy petroleum fractions. These two types of catalysis, heterogeneous catalysis is the most common type. The simple and complete separation of the fluid product mixture from the solid catalyst makes heterogeneous catalysis economically attractive; especially because many catalysts are valuable and their re use is demanded. A heterogeneous catalytic reaction occurs at or very near the fluid-solid interface. The principles that govern heterogeneous catalytic reactions can be applied to both catalytic and non-catalytic fluid-solid reactions (Othman *et al*., 2012).

The two other types of heterogeneous reactions involve gas-liquid and gas-liquid-solid systems. Reactions between gases and liquids are usually mass-transfer limited. In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by physical attraction called adsorption while the reaction takes place. Adsorption may be relatively weak (physical adsorption) or may have a strength comparable to the strengths

of chemical bonds (chemisorptions). In either case adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called active sites. The function of the catalyst is to provide an energetically favorable pathway for the desired reaction, in which the activation barriers of all intermediate steps are low compared to the activation energy of the non catalyzed reaction. In heterogeneous catalysis, the diffusion of reagents to the surface and diffusion of products from the surface can be rate determining.

A nano material-based catalyst is an example of a heterogeneous catalyst. Analogous events associated with substrate binding and product dissociation apply to homogeneous catalysts. Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated or destroyed by secondary processes. In heterogeneous catalysis, typical secondary processes include coking where the catalyst becomes covered by polymeric side products. Additionally, heterogeneous catalysts can dissolve into the solution in a solid–liquid system or sublimate in a solid–gas system. Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. The total surface area of solid has an important effect on the reaction rate.The smaller the catalyst particle size, the larger the surface area for a given mass of particles. A heterogeneous catalyst has active sites which are the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active site may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two. Thus, not only most of the volume but also most of the surface of a heterogeneous catalyst may be catalytically inactive. For example, in the Haber process, finely divided iron of ammonia from nitrogen and hydrogen serve as a

catalyst for the synthesis. The reacting gases adsorb onto active sites on the iron particles. Once physically adsorbed, the reagents undergo chemisorptions that result in dissociation into adsorbed atomic species and new bonds between the resulting fragments form in part due to their close proximity. In this way, particularly strong triple bond in nitrogen is broken which would be extremely uncommon in the gas phase due to its high activation energy. Thus, the activation energy of the overall reaction is lowered and the rate of reaction increases.

Another place where a heterogeneous catalyst is applied is in the oxidation of sulphur dioxide on vanadium (V) oxide for the production of sulphuric acid. Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Supports prevent or reduce agglomeration and sintering of the small catalyst particles, exposing more surface area, thus, catalysts have a higher specific activity on a support. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly alumina, zeolites or various kinds of activated carbon. Specialized supports include silicon dioxide, titanium dioxide, calcium carbonate, and barium sulphate.

2.6.3 Methods of Catalyst Preparation

The catalytic properties of heterogeneous catalysts are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. It is easily understood that the preparation methods are also dependent on the choice of the base materials and experience shows that several methods of catalyst preparation can be considered. (Anjana *et al.*, 2014).

2.6.3.1 Precipitation

Precipitation technique is probably the simplest and most efficient chemical pathway to obtain iron oxide particles. It involves the following steps as: mixing, filtration washing, drying, forming and heating (Alexander *et al.*, 2008). The aim of these steps is to precipitate a solid from a liquid solution while each intermediate in the preparation chain can be considered the precursor of the following one. Precipitation gives rise to the basic precursor because it really creates the imprint or latent image of the final solid that subsequent operations will progressively reveal. Washing of the intermediate solids formed by precipitation is generally required to remove adsorbed ions such as Na^+ introduced during the precipitation method. The solvent may be eliminated by drying without chemical transformation (Bredhult et *al*., 2011).

Many different processes may be applied such as drying in an oven, fluidized bed drying, spray drying and freeze drying. The intermediate solids are usually subjected to heat treatment, sometimes called calcinations which result in chemical transformation of the intermediate solids. In addition of providing general details of the method (Concentration, temperature and pH), it is necessary to indicate specifically the order and rate of addition of one solution into the other, a description of the mixing procedure and the details of the ageing procedure, if any. The association of two or more active elements in the precipitate in a single or several phases may be achieved by co-precipitation (Galasso, 2009).

The main advantage of the precipitation process is that; a large amount of nano particles can be synthesized. However, the control of particle size distribution is limited because only kinetic factors are controlling the growth of the crystal. In the precipitation process, two stages are involved i.e. a short burst of nucleation occurs when the concentration of the species reaches critical super saturation and then there is a slow growth of the nuclei by diffusion of the solutes to the surface of the crystal. To produce mono disperse iron

oxide nano particles, these two stages should be separated; i.e. nucleation should be avoided during the period of growth (Cornelis, 2010). Size control of mono dispersed particles must normally be performed during the very short nucleation period because the final particle number is determined by the end of the nucleation and it does not change during particle growth. A wide variety of factors can be adjusted in the synthesis of iron oxide nano particles to control size, magnetic characteristics, or surface properties. The size and shape of the nano particles can be tailored with relative success by adjusting pH, ionic strength, temperature, nature of the salts (per chlorates, chlorides, sulfates, and nitrates), or the Fe(II) / Fe(III) concentration ratio (Rasheed, 2007).

2.6.3.2 Impregnation

This is the easier method of preparing a catalyst in which porous support such as; silica, alumina and activated carbon are contacted for a specified time with a solution containing the active elements (a suitable metallic compound). The support is then dried and the catalyst is activated as in the case of precipitated catalyst (Moura *et al*., 2011). When the active elements are contained in a volume of solution corresponding to the pore volume, the procedure is called dry or pore volume impregnation. The volume of the solution is empirically determined as corresponding to that beyond which the catalyst begins to look wet. One or several parallel processes such as; adsorption, ion exchange, selective reaction on or with the surface of the support may take place during impregnation. Sometimes the process of impregnation is carried out by percolation of the impregnating solution through a bed of support or by support dipping the support in the impregnation solution. Two or more active elements may be introduced either in a single step by co-impregnation or subsequently one after the other in successive impregnations. Drying and often calcinations take place between impregnations.

2.6.3.3 Chemical Deposition

Deposition involves the application of the catalytic components (for example; nickel, as nickel nitrate) on to a separately produced support (e.g. silica and alumina). Any treatment of the support before the deposition step must be precisely described (Klemes *et al*., 2007). Deposition may be achieved by impregnation i.e. by contacting the support for a specified time with a solution containing the active elements. Deposition involving the formation of a strong bond (e.g. a covalent bond) between the support and active element is usually described as grafting or anchoring. This is achieved through a chemical reaction between functional groups (e.g. hydroxyl groups) on the surface of the support and an appropriately selected inorganic or organo- metallic compound of the active element. The term "chemical vapour deposition" is used; when deposition takes place by adsorption or reaction from the gas phase. Sometimes, a special technique of precipitation-deposition is used, in which an active element (e.g. nickel) is deposited onto a carrier (e.g. silica) in suspension in the precipitating solution (e.g. nickel nitrate) by slow addition or in situ formation (e.g. of OH^- by hydrolysis of urea) of a precipitating agent (Kazmi, 2012).

2.6.3.4 Activation of the Precursor

The final step in the preparation of catalyst is the transformation of the precursor to the active phase (e.g. metal, sulfide) which is sometimes called activation. The activation may be a reduction (e.g. by H_2), reduction – sulfidation (e.g. by H_2 + H_2S), dehydroxylation (e.g. by removal of H_2O from zeolite) or oxidation (e.g. by O_2). The details of the activation process must be stated (e.g. partial pressure and purity of gas, method of heating and its rate, gas reacting flow rate, sample size, among others).

2.6.4 Physical Properties of Catalysts

2.6.4.1 Total Surface Area

Many catalysts are porous solids of high surface area and with such materials it is often

useful to distinguish between the external and internal surface. The external surface is usually regarded as the envelope surrounding discrete particles or agglomerates but is difficult to define precisely because solid surfaces are rarely smooth on an atomic scale. It can be taken to include all the prominences plus the surface of those cracks, pores and cavities which are wider than they are deep. The internal surface comprises the walls of the rest of the pores, cavities and cracks. In practice, the demarcation is likely to depend on the methods of assessment and the nature of the pore size distribution. The total surface area (A) equals the sum of the external and internal surface areas. The roughness of a solid surface may be characterized by a roughness factor, i.e. the ratio of the external surface to the chosen geometric surface. Gas adsorption methods are often used to determine the surface area and pore size distribution of catalysts. The Brunauer-Emmett-Teller (BET) adsorption method is the most widely used standard procedure (Bashford, 2014).

2.6.4.2 Pore Structure

Porosity is a concept related to texture and refers to the pore space in a material. It can be defined as the fraction of the bulk volume that is occupied by pore or void space. An open pore is a cavity or channel communicating with the surface of a particle, as opposed to a closed pore. Void is the space or interstices between particles. The pore systems of solids are of many different kinds. The individual pores may vary greatly both in size and in shape within a given solid and between one solid and another. A feature of special interest for many purposes is the width of the pores, e.g. the diameter of a cylindrical pore or the distance between the sides of a slit-shaped pore.

Pores can be classified according to their sizes:

i. Pores with widths exceeding about 50 nm are called macro pores;

ii. Pores with widths not exceeding 2 nm are called micro pores;

iii. Pores of intermediate size are called meso pores.

These limits are to some extent arbitrary, it is worth emphasizing that amongst solids as a whole a wide and continuous range of pore sizes is to be found, from macro pores through meso pores and micro pores to grain boundaries, cleavage planes and dislocations. The total pore volume, sometimes called specific pore volume when referred to unit mass, is the total internal volume per unit mass of catalyst. Some of this pore volume may be completely enclosed and thus inaccessible to molecules participating in a catalytic reaction. The total accessible pore volume is often derived from the amount of vapour adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorptive. The accessible pore volume may be different for molecules of different sizes. It may be useful to determine the dead space by means of a non sorbable gas (normally helium) in conjunction with the determination of the bulk volume of the catalyst by means of a non-wetting liquid (mercury) (Matson, *et al*., 2009).

The pore-size distribution is the distribution of pore volume with respect to pore size. It is an important factor controlling the diffusion of reactants and products in the porous catalyst and thus an essential property for its characterization. The computation of pore size distribution involves a number of assumptions and therefore, reporting of the data should always be accompanied by an indication of the method used for its determination. The pore geometry of the majority of catalysts consists of an interconnected three-dimensional network of inter particle spaces, pores or capillaries. Usually capillary segments of different shapes and sizes are distributed over the network in some irregular fashion, the detailed shapes of pores will depend on the size distribution of the primary particles and on their mode of packing. Platelets will tend to form wedge-shaped pores or slits. With spheres, the closeness of packing will depend on the average number of

neighbors.

2.6.4.3 Density

Density may be defined as the mass of a powder or particle divided by its volume excluding all pores and voids. In a strict physical sense, this density can be calculated only through X-ray or neutron diffraction analysis of single crystal samples (Matson, *et al*., 2009). The term apparent density has been used to refer to the mass divided by the volume including some portion of the pores and voids, and so values are always smaller than the true density. This term should not be used unless a clear description is given of what portion of the pores is included in the volume. So-called helium densities determined by helium expansion are apparent densities and not true densities since the measurement may exclude closed pores. Bulk density or packing density, includes all pores and voids (inter particle spaces in its calculation. It is determined by filling a graduated cylinder, with or without tapping. It follows that the value obtained is dependent upon the form of the catalyst (powder, tablets, extrudates) because of the different contribution of inter particle void space to the pore volume (Forbes, 2012). Tap density is the apparent density of a bed of particles in a container of stated dimensions when a given amount of powder is vibrated or tapped under controlled conditions. The use of the term bulk density should be encouraged, accompanied by the detailed description of the conditions of its determination. Catalyst manufacturers also define an effective solid density, determined by displacement of a given liquid (water, ethanol). Values obtained with different liquids may vary substantially, depending on the extent to which the molecules of the liquid are able to penetrate into the pores of the catalyst. The term piece density is sometimes used when the measurement is performed with a liquid which does not substantially penetrate into the pores.

2.6.4.4 Mechanical Strength

It is desirable for commercial catalysts to have a sufficient mechanical strength so that losses during handling and uses are minimized. Broken pieces and fines (fine powder) lost during handling or produced during commercial use can represent a significant expenses, especially for catalysts containing precious metals such as platinum and re- depending on the design of the commercial reactor, broken catalyst, or fines, can lodge in support screens or in containment screens causing a restriction in the flow of reactants and products through the reactor. Various laboratory tests have been designed to provide information concerning the ability of a catalyst to maintain its physical integrity (Pascal *et al*., 2005). Crush strength is defined as the resistance of formed catalysts to compressive forces. Measurements of crush strength are intended to provide an indication of the ability of the catalyst to maintain its physical integrity during handling and use. When crush strength is measured for single pieces it is called piece crush strength and when it is measured for a bulk sample, it is called bulk crush strength. Other terms which have been used for piece crush strength, but which are not recommended are static crush strength and single pellet crushing strength. Piece crush strength is commonly measured by placing individual catalyst pieces between two flat surfaces, applying a compressive load and measuring the force required to crush the piece. Best results are obtained for regular shapes such as beads and tablets. Crush strength measurement of extrudates is less straight forward and the results will vary greatly with particle geometry and with the details of the analytical procedures used. The procedure used should be described in detail. Some methods may be repeatable within a single laboratory but irreproducible between laboratories (Forbes, 2012). Bulk crush strength is commonly measured by placing a representative sample in a cylinder, applying a constant force with a piston, and measuring the amount of fines generated. Many different variants are possible and no

generally accepted method is yet available. The bulk crush strength is defined empirically and the results are expressed on an arbitrary scale. This measurement may be applied to all catalyst shapes. Attrition is defined as loss of catalyst during handling or use. Attrition can occur by loss of fines through abrasion, which is wearing, grinding, or rubbing of the particles with each other or with container walls. Attrition can also occur by loss of pieces due to breakages, which can be caused, by impact or collision of particles with container walls. Numerous tests have been designed to measure the resistance of catalyst particles to attrition. These tests vary considerably in complexity and severity. Their applicability depends on the particular type of catalyst being tested. A simple method to measure attrition is to place a representative sample of the catalyst in a closed container, vibrate or shake the container, and then measure the amount of fines generated. Another relatively mild method is to place a sample in a drum having a single baffle, rotate the drum for a fixed period of time, and then measure the amount of fines generated by sieving through a standard sieve (Salim, 2009). Larger particles of silica and alumina will hold very fine particles on their surface and these stay attached during sieving, but can be removed by agitation in water. More severe tests are applicable to catalysts used in moving bed reactors. Some tests use a high velocity stream of gas to cause attrition of the catalyst. In some tests, a small-scale plant which simulates the commercial plant is used. The amount of attrition measured in all these tests is very dependent on the exact procedure used. Reproducibility among laboratories is only likely to be possible if precise details of the method are given.

2.6.5 Characterization of Catalysts Response to Inhibitory Substances

The sensitivity of catalysts to inhibition (by poisoning, sintering or fouling agents) depends on the whole catalytic reaction system, nature of catalyst, degree of ageing (in particular, nature and degree of poisoning, modification of activity and selectivity by

inhibition and fouling), operating conditions (Zaki, *et al*., 2010). A catalyst may lose its activity or selectivity as a result of the following:

i. **Poisoning**: Poisoning consist of impurities present in the feed stream that reduces the catalytic activity and the rate of chemical reaction. The sensitivity to poisoning depends on the following:

   - ✓ Number of active centre in the catalyst: when it is small, the catalyst may be inhibited by a small amount of poison
   - ✓ Strength of adsorption of the poison on the active centres; the weaker is the adsorption of poison, the lesser is the sensitivity of the catalyst to poison;
   - ✓ Effectiveness of adsorbed poison for inhibiting the catalytic activity; the latter decreases sometimes on adsorption of small amounts of poison on active centres more than in proportion to the fraction of active centres covered by the poison.

ii. **Fouling (Coking)**: Fouling involves the formation of coke that reduces the catalytic activity of a catalyst. Fouling is bound by neither covalent nor other strong bonds to the active centre; the interaction is usually of the van der Waals, H-bond or sometimes ionic bond type. They form protective layers or block pores, thus, physically impeding access of reactants to the active centre. The fouling agents causing real problems are those which have a long standing effect and do not disappear spontaneously. Carbon deposits act partially or totally this way. Other examples are vanadium and nickel sulfide deposits in hydro treating catalysts. Fouling agents act in quantities equivalent to several layers spread over the catalyst surface or to pore volume; they may according to different cases, have a rapidly reversible, and only slowly reversible or an irreversible effect.

iii. **Sintering (Ageing)**: sintering involves the loss of catalytic activity due to the loss of active surface area resulting from prolonged exposure to high gas temperature and pressure without melting into the liquefaction point (Rocha *et al.,* 2012). Sintering occurs naturally in mineral deposits or as a manufacturing process used with metals, ceramics, plastics and other materials. The atoms in the materials diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece. A typical example of sintering can be observed when ice cubes in a glass of water adhere to each other which are driven by the temperature difference between the water and the ice. Sintering is effective when the process reduces the porosity and enhances properties such as; strength, electrical and conductivity.

2.7 IRON OXIDE MINERALS

Iron is the fourth most common element by mass in the Earth's crust and forms compounds in several oxidation states (Plata et *al*., 2009). Iron hydroxides which mostly occurred inherently and exclusively in the nano meter-size range, are ubiquitous in nature and readily synthesized. These facts add up to render many iron hydroxides suitable as catalysts. The catalytic efficiency of iron hydroxides is strongly affected by factors such as; iron oxidation state, surface area, isomorphic substitution of iron, pH and temperature (Davis, 2009). Moreover, the abundant availability of natural iron source from rocks and soils at minimal cost makes the potential use of heterogeneous catalyst attractive. Besides iron hydroxides that are inherently nano crystalline, iron oxide minerals including magnetite (Fe_3O_4), goethite (α-FeOOH), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), lepidocrocite (γ-FeOOH), pyrite $(FeS_2)_{15}$ have attracted great attention due to their outstanding catalytic properties, wide operating pH range and controllable iron leaching. Ferrihydrite, $Fe_5HO_8{\cdot}4H_2O$, feroxyhyte, δ′-FeOOH, magnetite (Fe_3O_4) are often used as catalyst because they have permanent magnetization and contain iron in both divalent and

trivalent states. Hematite, goethite and lepidocrocite have also been used as catalysts in their pure forms and as composites with carbon, alumina and zeolites among others. Iron ores consist of oxygen and iron atoms bonded together into molecules. To convert it to metallic iron it must be smelted or sent through a direct reduction process to remove the oxygen. Oxygen-iron bonds are strong and to remove the iron from the oxygen, a stronger elemental bond must be presented to attach to the oxygen.

Carbon is used because the strength of a carbon-oxygen bond is greater than that of the iron-oxygen bond at high temperatures. Thus, the iron ore must be powdered and mixed with coke to be burnt in the smelting process. However, it is not entirely as simple as that. Carbon monoxide is the primary ingredient of chemically stripping oxygen from iron. Thus, the iron and carbon smelting must be kept at an oxygen deficient (reducing) state to promote burning of carbon to produce carbon monoxide.

The inclusion of small amounts of some elements can have profound effects on the behavioral characteristics of a batch of iron or the operation of a smelter. These effects can be both good and bad, some catastrophically bad. Some chemicals are deliberately added such as flux which makes a blast furnace more efficient. Others are added because they make the iron more fluid, harder, or give it some other desirable quality. The choice of ore, fuel, and flux determine how the slag behaves and the operational characteristics of the iron produced. Ideally iron ore contains only iron and oxygen.

2.7.1 Iron Oxy Hydroxide (α-FeOOH)

Goethite (α-FeOOH) named after the German polymath and poet Johann Wolfgang von Goethe (1749–1832), is a common oxy hydroxide mineral which is found in natural environment and is formed as a weathering product of iron-bearing mineral (Plata *et al.,* 2009). This mineral is the most important and wide spread iron oxide in soils. It occurs in almost all soil type and climate regions (Garrido *et al.,* 2010). In many dry and tropical

environments, it is found in association with hematite (α-Fe_2O_3). Apparently, hematite is dissolved and under new environmental conditions results in the formation of goethite which is the most abundant, stable of all forms of iron-oxides in rocks, sediments, soil and its surface (Munter, *et al*., 2009). Goethite is an iron oxy hydroxide containing ferric iron. Goethite has chemical and physical properties as presented in Table 2.3, with hardness ranges from 5.0 to 5.5 on the Mohs scale and its specific gravity varies from 3.3 to 4.3 (Hanna *et al*., 2008). The mineral forms prismatic needle-like crystals ("needle iron ore"), but is more typically massive. Pure iron oxides such as goethite, hematite, magnetite etc, are utilized as catalyst for the oxidation of several organic pollutants. Goethite, as an iron oxy hydroxide (α-FeOOH), occurs as natural mineral and can be easily synthesized in the laboratory. It is one of the most thermodynamically stable iron oxide at room temperature and it has a lesser compact structure than hematite or magnetite as it can be observed from plate 2.7.

Plate 2.7: Presentation of natural goethite structure (Rocha *et al.,* 2012)

Goethite can generate proxy and hydroxy radicals as in equations (2.3) and (2.4).

$$Fe^{3+} + H_2O_2 \rightarrow HOO\cdot + H^+ + Fe^{2+} \quad (2.3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\cdot \quad (2.4)$$

In the first step iron (III) species is reduced to iron (II) by H_2O_2, generating peroxy radicals. Iron (II) species produced in the first step react with another portion of H_2O_2, producing hydroxy radical and hydroxyl anion (Munter *et al*., 2009). The combination of H_2O_2/Fe^{3+} producing Fe^{2+} species and hydro-peroxy radical (Equation 2.3) followed by the re-oxidation of Fe^{2+} species by H_2O_2 (Equation 2.4) is well known as a catalytic Fenton-like reaction. Therefore, pollutants can be oxidized by the combined action of hydroxy and hydro-peroxy radicals produced in both steps (Equations 2.3 and 2.4). Feroxyhyte and lepidocrocite are both polymorphs of the iron oxy hydroxide (α- FeOOH). Although they have the same chemical formula as goethite, their different crystalline structures make them distinct minerals. Its main modern use is as an iron ore being referred to as brown iron ore. It does have some use as a clay earth pigment Iron-rich lateritic soils that have developed over serpentine rocks in tropical climates are mined for their iron content as well as other metals. Fine goethite specimens are rare and therefore are valued collectibles. Banded or iridescent varieties are cut and polished into cabochons for jewelry making (Moura *et al.,* 2011).

Table 2.3: Chemical and physical properties of Goethite (α-FeOOH)

Properties	**Goethite (α-FeOOH)**
Category	Oxide minerals
Chemical formula	α-FeOOH
Color	Yellowish, reddish to dark brown
Crystal system	Orthorhombic
Fracture	Uneven to splintery
Mohs scale hardness	5-5.5
Luster	Adamantine to dull
Streak	Brownish yellow to orange yellow
Specific gravity	3.3-4.3
Refractive index	Opaque to sub-translucent
Fusibility	Fusible at 5-5.5
Cleavage	Perfect in one direction

Source: (Galvez et *al.*, 2015)

Like most other iron oxides, goethite is able to have affinity with anions and cations such as Cl^-, SO_4^{-2}, Al^{3+}, Zn^{2+}, and Cu^{2+}. This affinity is pH dependent because the surface charging is pH dependent. Based on the properties of goethite in (Table 2.3). Goethite can play significant role in the biogeochemical activities such as absorption of heavy metals, transformation of organic chemicals, cycling of micronutrients and uptake of toxic or non toxic elements from environment.

2.8 Previous related works

The previous works reported from literatures of published journals that are related to the present research work are presented in Table 2.4 in which Hanne *et al*., (2012), worked on investigating efficiency of α-FeOOH catalyst in the degradation of organic pollutants present in tannery wastewater, 36.54% COD reduction was achieved at a reaction time of 320 minutes at a pH of 6.5. The lower %COD reduction obtained may be due to the

catalyst instability above acidic medium of tannery wastewater.Liang *et al*., (2013), carried out research on the oxidation of dimethyl sulphoxide using α-FeOOH catalyst in the presence of hydrogen peroxide, 70.40% COD reduction was achieved at 445 minutes reaction time at a pH of 6.0. Despite the 70.40% COD reduction achieved, the process is time consuming. Hameed *et al*., (2014), worked on the preparation and application of α-FeOOH-SiO_2 catalyst in tannery effluent treatment using photo-Fenton oxidation process. Despite their achievement of 58.56% COD reduction at 290 minutes reaction time and a pH of 7.0, the Photo-Fenton oxidation process used needed the use of ultra-violet light source for irradiation.

Table 2.4: Related previous works

AUTHOR	TITLE	FINDING	REMARK
Hanne *et al*., 2012	Investigating efficiency of goethite in degradation of organic pollutants In tannery wastewater	36.54% COD reduction , pH 6.5 and 320minutes reaction time	Lower COD reduction due to catalyst instability
Liang *et al*., 2013	Oxidation of DMSO on goethite catalyst using peroxide	60.40% COD reduction at pH 6.0, 445 mins reaction time	High reaction time due to decrease in catalyst performance
Hameed *et al*., 2014	preparation and Application of α-FeOOH-SiO_2 catalyst for photo Fenton treatment of tannery effluent	58.56% COD reduction after 290 mins reaction time at pH 7.0	ultra-violet light source needed
Usman *et al*., 2014	Degradation of organic pollutants in wastewater using goethite catalyst.	30.26% COD reduction, 90 mins reaction time at pH 7.0	Poor COD reduction, instability of goethite catalyst at neutral pH
Diya'uddeen *et al*., 2015	Limitations of Fenton oxidation operational parameters	75.30% COD reduction, pH 3.0 and 40% sludge reduction	Iron Sludge generation at pH 3.0
Moura *et al*., 2015	Oxidation of organic pollutants on goethite catalyst	45.41% COD reduction, 180 mins reaction time at pH 7.0	Properties of goethite should be improved

CHAPTER THREE

MATERIALS, EQUIPMENT AND METHODS

3.1 MATERIALS

Some of the materials used for this research dissertation are:

1. Iron nitrate nona hydrate (98% purity) (Analar grade) M&B Ltd, England
2. Sulphuric acid (concentration: 98%) (Analar grade) M&B Ltd, England
3. Silica (96% purity) (PTDF LAB. Chem. Engineering Department, ABU, Zaria)
4. Alumina (92% purity) (PTDF LAB. Chem. Engineering Department, ABU, Zaria)
5. Sodium hydroxide (98% purity) (Analar grade) BDH, England
6. Hydrogen peroxide (30% wt/v)
7. Double distilled water

Some of the apparatus used for the research are:

1. Conical flask (250 and 500 mL) Pyrex
2. Beaker (250 and 500 mL) Pyrex.
3. Measuring cylinder (500 and 1000 mL)
4. Spatula
5. Filter paper
6. Magnetic stirrer
7. Funnel
8. Water bath.
9. Glass rod stirrer
10. Crucibles.
11. Thermometer (0-360^{o}C)

3.2 EQUIPMENT

Table 3.1: List of some equipment used for the research

Name	Model	Manufacturer
Scanning Electron Microscope	Pro-X	Phenom-World Co., Holland
X-ray Diffractometer	D/max-2550 PC	Shimadzu, Japan
Laboratory pH meter	APHA 2310	Mettler Toledo, Switzerland
Oven (0-260^{o}C)	TM OV-240	Gallenkamp, England
Analytical Balance (0-180g)	AB 204	Mettler Toledo, Switzerland
Exposed Element Furnace	TIKIR 11/12	Heraeus, Holland

3.3 METHODS

3.3.1 Method of Catalyst Preparation

The α-FeOOH sample was prepared in laboratory through precipitation method in which 60g of Fe $(NO_3)_3.9H_2O$ was dissolved in 100 mL of double distilled water. The solution was then heated with continous stirring at 55 ^{o}C for 2 hrs. 60 mL of NaOH (2.5 mol/L) was added to the solution and stirred for 30 minutes. The resulting thick suspension was aged for two days to ensure proper crystal development and then washed several times with double distilled water to remove impurities. The obtained sample was then oven dried at 90 ^{o}C for 18 hrs in a thermostatic oven. A mixed iron sample was finally obtained by crushing the solid sample. The crushed mixed iron sample was doped with silica-alumina obtained from PTDF laboratory, Chemical Engineering, ABU, Zaria in the ratio 50:2:1 (Baoling *et al*., 2015). A mixed iron composite sample was obtained and calcined at 600 ^{o}C for 2 hours.

Equations (3.1) and (3.2) are the reaction equations for the preparation of α-FeOOH sample where α is the crystal symbol of the FeOOH sample:

$$Fe(NO_3)_3.9H_2O + 3NaOH \rightarrow Fe(OH)_3 + NaNO_3 + 9H_2O \quad (3.1)$$

$$Fe(OH)_3 \rightarrow FeOOH + H_2O \quad (3.2)$$

3.3.2 Calcination Process

30 g of the prepared mixed iron composite sample was placed in a crucible and calcined at 600 ^oC for 2 hours using an expose element furnace (30 – 3000 ^oC), Naberthem GMBH Germany, at Chemical Engineering Department, ABU, Zaria, Nigeria.

3.3.3 Catalyst Characterization

3.3.3.1 X-ray Diffraction Analysis

The α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 composite were characterized by X-ray diffraction technique using PANanalytical England Philips diffractometer operated at 40 kV with 100-mA flux using X-ray source of cukα_1 radiation with a wavelength of 1.5406Å in the bragg angle region from 20^o to 80^o on 2θ scale.

3.3.3.2 Scanning Electron Microscopic Analysis

The microstructures and morphologies of the α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts were observed through the use of Scanning Electron Microscope, PHENON PRO-X machine model at Chemical Engineering Department, ABU, Zaria, Nigeria.

3.3.4 Modelling and Optimization of Tannery Effluent Treatment

3.3.4.1 Response Surface Methodology

Response surface methodology is a statistical method used for optimization of chemical reactions, industrial processes as well as generating experimental design matrix in order to assess the relationship between dependent and independent variables. It also employs a low-order polynomial equation in a predetermined region of the independent variables, analyzed and locates the optimum values of independent variables for obtaining the optimal response. Process optimization is faster for generating experimental research

results than using conventional and time consuming one factor at a time approach. However, in this research dissertation, central composite design (CCD) was used for the optimization of tannery effluent treatment using Fenton oxidation process. A four factorial, five level CCD consisting of 30 experimental runs was performed. Catalyst loading, peroxide dosage, reaction time and pH were considered as the independent variables while COD reduction percent was considered as the dependent variable. Experimental design matrix was analyzed using Design-Expert 6.0.7 software version and fitted a second-order polynomial equation.

Table 3.2 shows the experimental ranges of process parameters including factor: A,B,C and D that represent the four (4) independent variables as; catalyst loading (mg/L), peroxide dosage (mg/L), reaction time (minute) and pH with their respective low and high actual values as the experimental ranges obtained from previous literature reports. The experimental ranges were used as input values in Design-Expert 6.0.7 software version to generate experimental design matrix using central composite design (CCD) in order to assess the relationship between dependent and independent variables for optimization of tannery effluent treatment using Fenton oxidation process.

Table 3.2: Experimental ranges of process parameters

Factor Coded	Independent Variables	Low Actual	High Actual
A	Catalyst loading (mg/L)	10.00	50.00
B	Peroxide dosage (mg/L)	400.00	1400.00
C	Time (mins)	10.00	240.00
D	pH	3.00	11.00

3.3.5 Method of Sample Collection

Tannery effluent sample was obtained at the point of discharge from Mamuda tannery industry, Sharada Phase III, Kano State, Nigeria. The sample effluent was stored in a 5 litres gallon and 10 mL concentrated sulphuric acid was introduced into the effluent sample in order to create acidic medium. The 5 litres gallon containing the effluent sample was put in a black polyethylene bag and placed in a cooler and sealed in order to create an amber condition as stated in the standard method for examination of tannery wastewater (Borja, 2014).

3.3.6 pH Measurement

The activated electrode of pH metre was standardized with a known pH buffer solution of 4.5, 7 and 9.5 respectively. The electrode was then rinsed with distilled water and dipped into a beaker containing the sample effluent and a pH value was recorded.

3.3.7 Chemical Oxygen Demand

0.4 g mercuric sulphate was placed in a reflux flask and 20mL of the effluent sample was added and mixed. 10 mL of a standard potassium dichromate was added together with 3-4 glass beads to ensure proper mixing. 30 mL concentrated sulphuric acid containing silver sulphate was carefully added and the solution was refluxed for 1 hour after which it was cooled and the condenser was washed using distilled water. The excess dichromate together with standard ferrous ammonium sulphate was titrated using 2-3 drops of ferrous indicator. The oxidation of potassium dichromate produces green chromic compound and the higher the organic pollutants oxidized the deeper the green colour and the higher the chemical oxygen demand.

Calculations:

$$COD\ \left(\frac{mg}{L}\right) = (a-b) * c * \frac{800}{mL\ of\ sample} \quad (3.3)$$

Where:

a = titration for blank

b = titration for sample

c = normality of ferrous ammonium sulphate

3.3.8 Biological Oxygen Demand

The effluent sample was pipette into BOD_5 bottles containing dilution water. The amount of dissolved oxygen was determined and recorded. The sample bottles were incubated for five days at room temperature to prevent photosynthesis to take place. At the end of the five days, the final dissolved oxygen was determined and recorded. The BOD_5 of the sample was determined by subtracting the initial dissolved oxygen from the final.

The formular calculating BOD_5 (mg/L) is given as:

$$BOD_5\left(\frac{mg}{L}\right) = \frac{A}{B} * (C - D) + D \quad (3.4)$$

Where:

A = Total volume after dilution (mL)

B = Volume of diluted sample (mL)

C = Oxygen consumption of diluted sample after 5 days (mg/L)

D = Oxygen consumption of dilution water after 5 days (mg/L)

3.3.9 Fenton Oxidation Process

All oxidation experiments were carried out batch wise at ambient temperature (25 ^oC) in 100 mL reaction solution. The initial solution pH was adjusted using 1M NaOH and H_2SO_4 respectively. Fenton reagents were dosed under steady magnetic stirring to avoid concentration gradient. Required amount of α-FeOOH-SiO_2-Al_2O_3 catalyst obtained from the design matrix were added in a varied amount and the solution was allowed to mix up for a while in order to ensure homogeneity. The reactions were initiated by addition of hydrogen peroxide dosage to a pH adjusted solution. Inside the batch reactor, there was an

interaction reaction between α-FeOOH-SiO_2-Al_2O_3 catalyst and hydrogen peroxide and hydroxyl radical was generated which is responsible for organic pollutants degradation. At the end of the oxidation treatment, treated tannery effluent samples were withdrawn from the batch reactor at a given reaction time intervals, filtered through 0.22 μm filter paper and analyzed for chemical oxygen demand.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 CATALYSTS CHARACTERIZATION

4.1.1 XRD Analysis

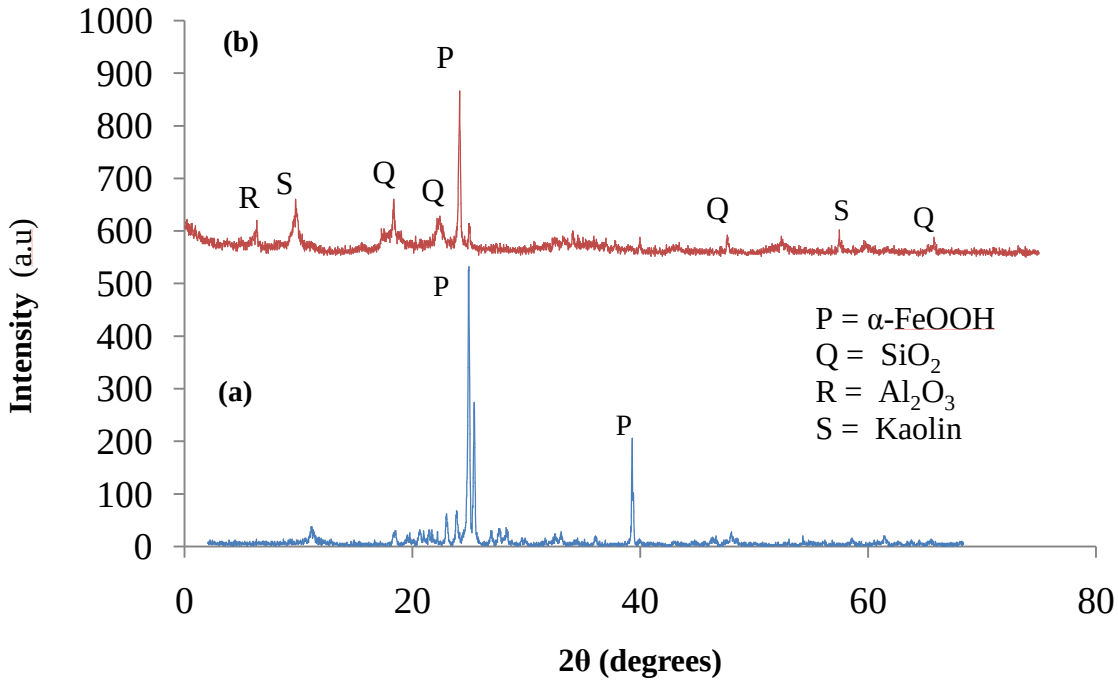

Figure 4.1: XRD patterns of **(a)** α-FeOOH **(b)** α-FeOOH-SiO_2-Al_2O_3

The XRD patterns of the powdered samples for α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 are shown in Figure 4.1. The sharp diffraction peaks observed in the XRD pattern of α-FeOOH catalyst at Bragg angles of 25.58^o and 39.26^o indicate its crystalline structure. The results are in good agreement with the JCPDS file for goethite (with JCPDS reference no. 29-0713) in the International Centre for Diffraction Data (ICDD) data base.

The sharp peak observed from Figure 4.1b at a bragg angle of 25.54^o indicates the crystalline structure of α-FeOOH and the increase in the intensity counts observed may be due to the presence of silica and alumina (Liang *et al*., 2013).

4.1.2 SEM Analysis

The morphology of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 were studied using scanning electron microscope (SEM). From plate 4.1a, one could easily observe a cluster of crystal particles indicating an orthorhombic crystal shape of α-FeOOH catalyst (Othman *et al*., 2010). It was also observed that, the crystal particles have a uniform arrangement which is in conformity with one of the properties of goethite catalyst (Galvez *et al.,* 2015). The SEM image of plate 4.1b indicates that, the crystal particles become bigger and agglomerated. It was also observed that, the non-uniform dispersion of the crystal particles indicate the increase in crystal growth as a result of doping (Hameed *et al*., 2014).

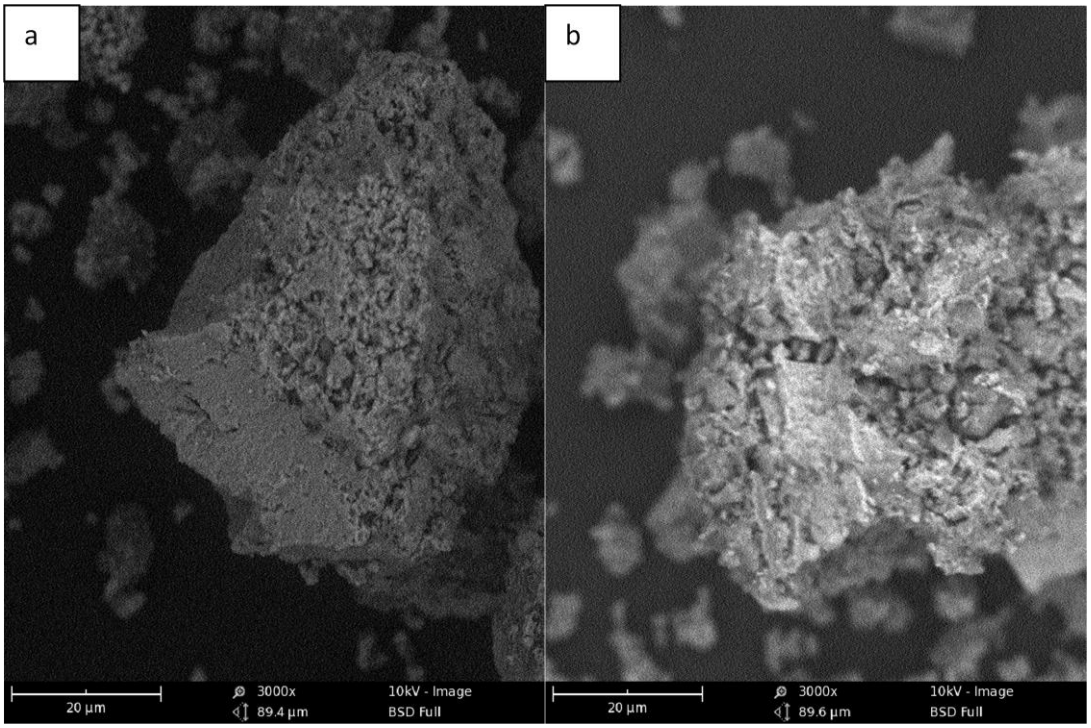

Plate 4.1: SEM images of **(a)** α-FeOOH **(b)** α-FeOOH-SiO_2-Al_2O_3

4.2 CHARACTERIZATION OF TANNERY EFFLUENT

Table 4.1 shows properties of the raw Mamuda tannery effluent used in this research dissertation. The properties of the raw effluent were measured in order to determine the level of its pollution implication by comparing with the National Environmental Standards and Regulation Enforcement Agency (NESREA) limits for tannery wastewater discharge. Therefore, the comparison clearly indicates that, Mamuda tannery effluent is highly polluted and needs to be treated before discharge into the environment.

Table 4.1: Results for the measured properties of the raw Mamuda tannery effluent

Parameter	Value	NESREA Limits
COD (mg/L)	1400.00	200.00
BOD (mg/L)	350.00	50.00
pH	9.00	6.5- 7.5

4.3 OPTIMIZATION OF FENTON OXIDATION OF TANNERY EFFLUENT USING DESIGN EXPERT SOFTWARE

4.3.1 Optimization of Fenton Oxidation of Tannery Effluent by applying α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts

The α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts were applied for tannery effluent treatment under different conditions in accordance with the experimental design matrix generated using design expert 6.0.7 software of response surface methodology. The experimental and predicted results on COD reduction are presented in Table 4.2 based on the performance degradation of organic pollutants in tannery effluent via catalytic Fenton oxidation process. The %COD reduction result observed by applying α-FeOOH catalyst clearly indicates that, the COD reduction is more pronounced within the acidic medium compared to the neutral and alkaline medium of the tannery effluent and the lower COD reduction observed within the neutral and alkaline medium of the tannery effluent may be due to the instability of α-FeOOH catalyst above acidic medium (Hanne *et al*., 2012). For the case of applying α-FeOOH-SiO_2-Al_2O_3 catalyst, it can be clearly seen that, there is a good improvement of %COD reduction result in the acidic, neutral and alkaline medium of the tannery effluent. The COD reduction was promoted for the case of applying α-FeOOH-SiO_2-Al_2O_3 catalyst due to the presence of silica and alumina as dopants which consequently made the α-FeOOH catalyst more stable above acidic medium of the tannery effluent (Hameed *et al*., 2014).

Therefore, the performance degradation of organic pollutants in tannery effluent by applying α-FeOOH-SiO_2-Al_2O_3 catalyst in acidic, neutral and alkaline medium of the tannery effluent is more pronounced compared to α-FeOOH catalyst as presented in Table 4.2.

Table 4.2: Experimental design matrix and results for COD reduction

					α-FeOOH catalyst		**α-FeOOH-SiO_2-A**
Run	**A**	**B**	**C**	**D**	**Exp'tal %COD reduction**	**Predicted %COD reduction**	**Exp'tal %COD reduction**
1	30.00	900.00	105.00	7.00	31.80	31.49	54.50
2	30.00	900.00	125.00	3.00	59.21	58.46	58.71
3	30.00	900.00	125.00	7.00	28.57	29.58	61.86
4	30.00	900.00	125.00	7.00	25.57	27.13	50.21
5	50.00	1400.00	10.00	11.00	18.50	19.23	54.36
6	30.00	900.00	125.00	7.00	31.36	30.71	69.10
7	30.00	900.00	125.00	3.00	65.93	64.54	55.43
8	50.00	1400.00	240.00	11.00	15.14	14.07	60.57
9	10.00	400.00	10.00	11.00	18.43	18.65	52.71
10	10.00	1400.00	10.00	3.00	50.14	50.32	60.14
11	50.00	400.00	240.00	7.00	22.14	22.30	79.29
12	10.00	400.00	240.00	11.00	21.50	20.85	55.71
13	30.00	900.00	125.00	7.00	31.57	32.41	57.62
14	30.00	900.00	125.00	3.00	68.57	68.10	71.33
15	30.00	900.00	125.00	7.00	40.71	40.47	59.64
16	50.00	400.00	10.00	3.00	55.30	55.22	69.43
17	10.00	1400.00	240.00	3.00	58.14	57.42	57.14
18	10.00	400.00	10.00	3.00	54.60	53.28	70.71
19	50.00	400.00	240.00	3.00	60.64	59.08	67.29
20	10.00	900.00	125.00	7.00	39.29	39.08	65.36
21	50.00	1400.00	240.00	3.00	61.71	62.61	53.57
22	50.00	400.00	240.00	7.00	23.57	22.61	82.43
23	10.00	1400.00	240.00	11.00	33.43	34.56	52.86
24	30.00	900.00	125.00	7.00	45.86	44.56	66.43
25	30.00	900.00	105.00	7.00	35.43	34.56	68.21
26	30.00	900.00	125.00	3.00	57.14	58.08	70.71
27	10.00	1400.00	10.00	11.00	29.64	28.08	55.57
28	10.00	400.00	240.00	3.00	58.71	56.08	64.29
29	50.00	900.00	125.00	7.00	38.21	39.08	56.79
30	50.00	1400.00	10.00	3.00	65.71	64.56	67.86

A = catalyst loading (mg/L), **B** = peroxide dosage (mg/L), **C** = reaction time (minute) and **D** = pH respectively

Equation (4.1) was employed in order to describe the interaction between the dependent and independent variables:

$$y = \beta_0 + \sum \beta x_i + \sum \beta_{ii}\, x_i^2 + \sum \beta ij x_i\, x_j + \varepsilon \qquad (4.1)$$

Where y is the response (i.e COD reduction), β_o is the constant coefficient, β_i, β_{ii} and

$\beta_{ij}$are the coefficient linear, quadratic and interaction effect, x_i and x_j are the factors and ε is the random error respectively (Galvez *et al*., 2015). The COD reduction is the dependent variable of the process which was approximated using central composite design (CCD) and represented by the final regression model expressed by second-order polynomial equations (4.2) and (4.3).

$$y = 39.08 + 8.43A - 1.59B + 5.03C + 5.77A^2 - 178.22B^2 + 145.72C^2 + 25.48D^2 - 2.85AB + 1.80AC + 6.50BC + 0.72BD - 0.64CD \quad (4.2)$$

$$y = 66.37 + 5.52A - 4.01B + 5.13C + 3.40D - 2.59A^2 + 397.93B^2 - 411.50C^2 + 4.53D^2 + 3.83AC + 2.08AD - 0.62BC - 0.88CD \quad (4.3)$$

Equations (4.2) and (4.3) present the models of COD reduction for the application of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts in tannery effluent treatment using Fenton oxidation process. The analyses of variance (ANOVA) conducted for COD reduction using α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts are presented in Tables 4.3 and 4.4, respectively. The ANOVA in Table 4.3 indicates that, the three independent variables: catalyst loading, peroxide dosage and reaction time represented by A, B and C are significant while for Table 4.4 as it can be observed, all the four independent variables: catalyst loading, peroxide dosage, reaction time and pH represented by A, B, C and D are significant and played an important role in the degradation of organic pollutants present in the tannery effluent through the use of Fenton oxidation process. The model F-values of 323.18 and 172.95 imply that the models are significant for COD reduction and there is only 0.01% chance that a "Model F-Value" this large could occur due to noise. The mean square values were obtained by dividing the sum of squares by the corresponding degrees of freedom. P-value usually determines the significant of a model by observing p-value to be less than 0.05 but a p-value greater than 0.1 indicates insignificant of a model. Therefore, p-values of 0.0001 obtained from Tables 4.3 and 4.4, indicate the significant of

the models. A high value of R^2 close to 1, ensures a satisfactory adjustment of the quadratic model to the experimental data. The values of the coefficient of determination R^2 were obtained to be 0.9956 and 0.9919 for Fenton oxidation process using α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts all of which are greater than 0.80. According to Rocha *et al*., (2012), the coefficient of determination R^2 should be atleast 0.80 for a good model fit. In this case, the R^2 values obtained from Tables 4.3 and 4.4 indicate that only 0.0044% - 0.0081% of the total variation is not explained by the models. The values of the adjusted R^2 of 0.9926 and 0.9861 for Fenton oxidation process using α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts are also high, indicating the strong significant of the models (Hameed *et al*., 2012).

Table 4.3: ANOVA results of quadratic model for Fenton oxidation process using α-FeOOH catalyst

Source	Sum of squares	Degree of Freedom	Mean square value	F-Value	P-Value
Model	4973.32	12	414.44	323.18	<0.0001
A	1278.49	1	1278.49	996.97	<0.0001
B	40.58	1	40.58	31.64	<0.0001
C	404.21	1	404.21	315.20	<0.0001
A^2	49.91	1	49.91	38.92	<0.0001
B^2	42.76	1	42.76	33.34	<0.0001
C^2	29.06	1	29.06	22.66	0.0002
D^2	1558.25	1	1558.25	1215.13	<0.0001
AB	130.42	1	130.42	101.70	<0.0001
AC	51.77	1	51.77	40.37	<0.0001
BC	676.78	1	676.78	527.75	<0.0001
BD	8.21	1	8.21	6.40	0.0216
CD	6.60	1	6.60	5.15	0.0365
Residual	21.80	17	1.28		
Lack of fit	13.60	8	1.70	1.87	0.1856
Pure error	8.20	9	0.91		
Total	4995.12	29			

$\mathbf{R^2}$ = 0.9956 $\mathbf{R^2_{adj}}$ = 0.9926

Table 4.4: ANOVA results of quadratic model for Fenton oxidation process using α-FeOOH-SiO_2-Al_2O_3 catalyst

Source	**Sum of squares**	**Degree of freedom**	**Mean square value**	**F-Value**	**P-Value**
Model	2755.12	1	229.59	172.95	<0.0001
A	548.14	1	548.14	412.90	<0.0001
B	256.72	1	256.72	193.38	<0.0001
C	420.97	1	420.97	317.11	<0.0001
D	184.89	1	184.89	139.28	<0.0001
A^2	10.05	1	10.05	7.57	0.0136
B^2	213.15	1	213.15	160.56	<0.0001
C^2	231.71	1	231.71	174.54	<0.0001
D^2	42.89	1	42.89	32.31	<0.0001
AC	235.24	1	235.24	177.20	<0.0001
AD	69.51	1	69.51	52.36	<0.0001
BC	6.06	1	6.06	4.57	0.0474
CD	12.48	1	12.48	9.40	0.0070
Residual	22.57	17	1.33		
Lack of fit	15.13	8	1.89	2.29	0.1194
Pure error	7.43	9	0.83		
Total	2777.69	29			

$\mathbf{R^2}$ = 0.9919 $\mathbf{R^2_{adj}}$ = 0.9861

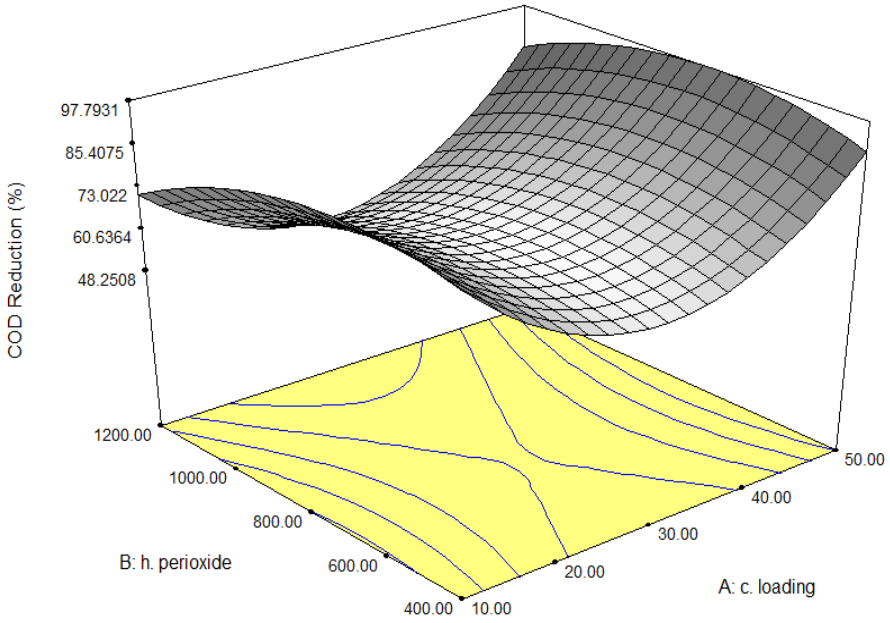

Figure 4.2: 3D response surface plot for COD reduction at reactiom time = 125 minutes and pH of 3

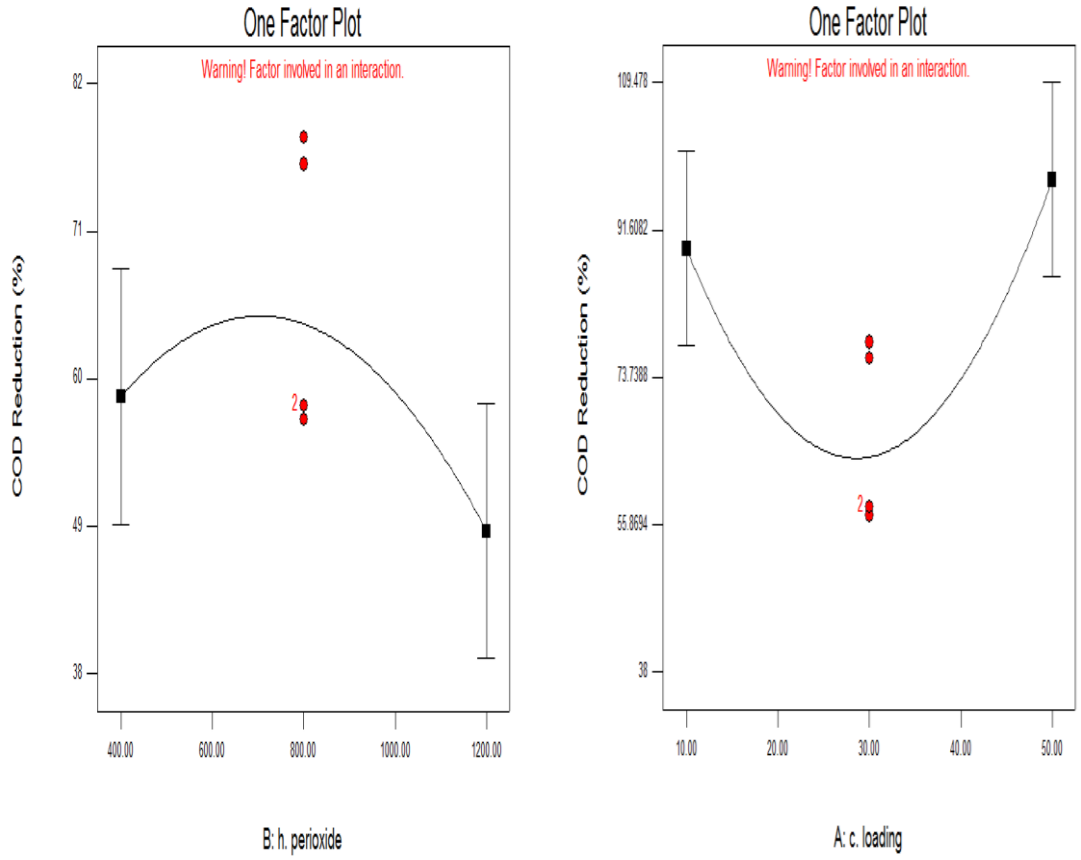

Figure 4.3: One factor plots of COD reduction vs peroxide dosage and catalyst loading

Figures 4.2 and 4.3 illustrate the 3D response surface and one factor plots for COD reduction as a function of peroxide dosage and catalyst loading. As it can be observed from Figure 4.3, the effect of peroxide dosage on COD reduction increases as the effect of catalyst loading decreases. The effect of peroxide dosage also decreases upon reaching its maximum of 800.00 mg/L with an increase of catalyst loading at 30.00 mg/L. This clearly indicates that, the COD reduction is directly related to the concentration of hydroxyl radicals produced and any further increase of catalyst loading will make the scavenging effect of hydroxyl radicals generated by hydrogen peroxide to occur which could produce hydroperoxy radicals (Liang *et al*., 2013). However, the hydroperoxy radicals produced do not contribute any oxidation of the organic pollutants present in the tannery effluent and therefore, resulting in a poor COD reduction (Hameed *et al.*, 2014).

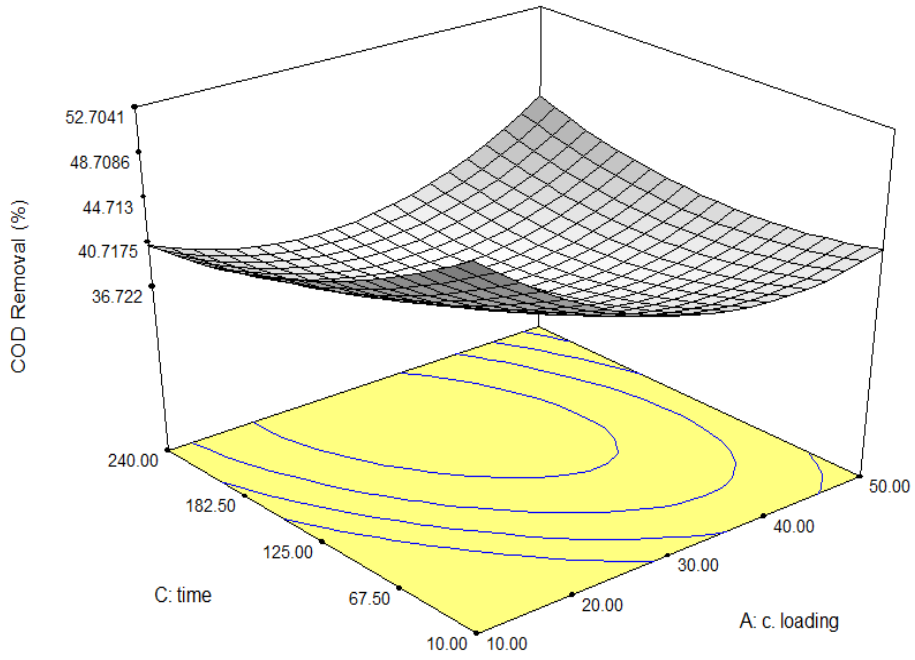

Figure 4.4: 3D response surface plot for COD reduction at H_2O_2 = 800.00 mg/L and pH of 7

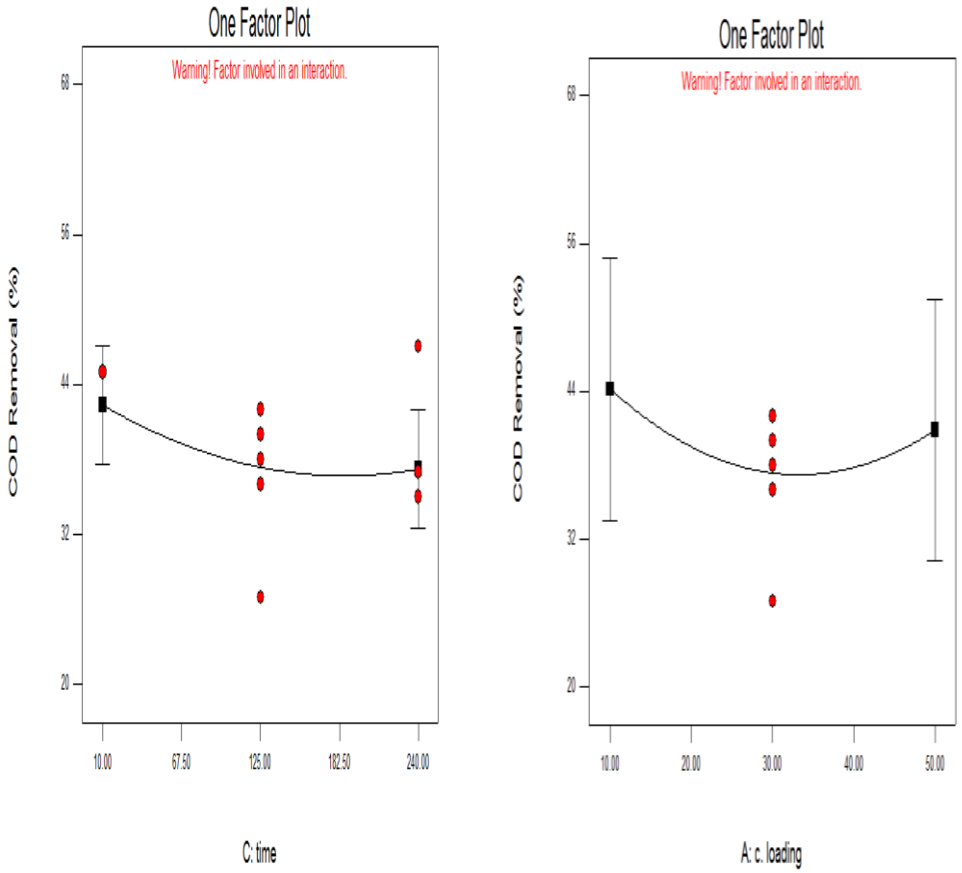

Figure 4.5: One factor plots of COD reduction vs. reaction time and catalyst loading

Figures 4.4 and 4.5 are 3D response surface and one factor plots of reaction time and catalyst loading, respectively. As it can be seen from Figure 4.5, the effect of catalyst loading on COD reduction decreases with a decrease in the effect of reaction time and there is an increase of catalyst loading from 30.00 mg/L to 50.00 mg/L with a slight increase in the effect of reaction time. This indicates that, the reaction interaction of the catalyst loading with respect to the increase in reaction time is more pronounced in relation with the COD reduction (Moura *et al*., 2015).

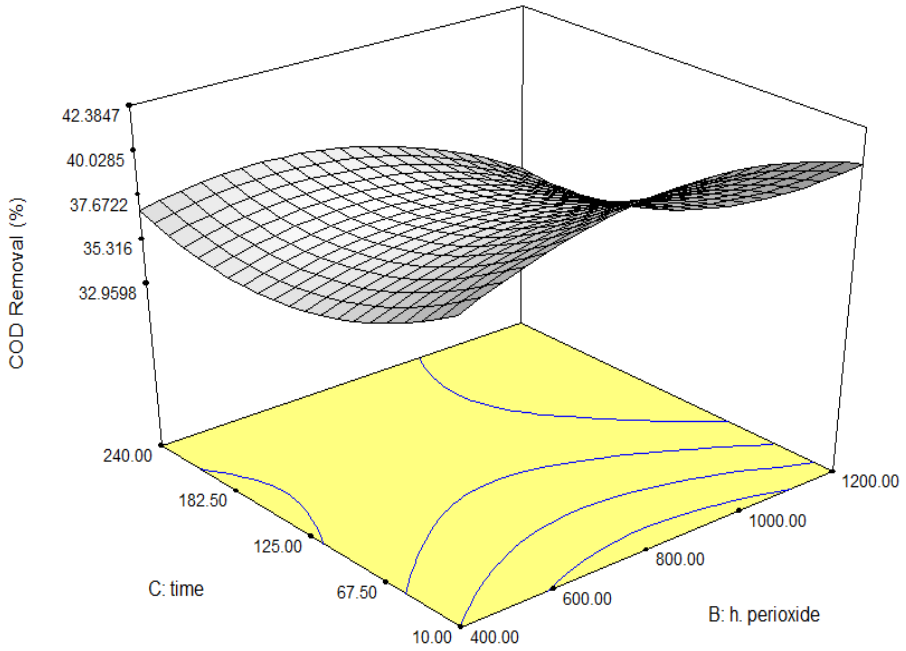

Figure 4.6: 3D response surface for COD reduction at 30.00 mg/L catalyst loading and pH of 11

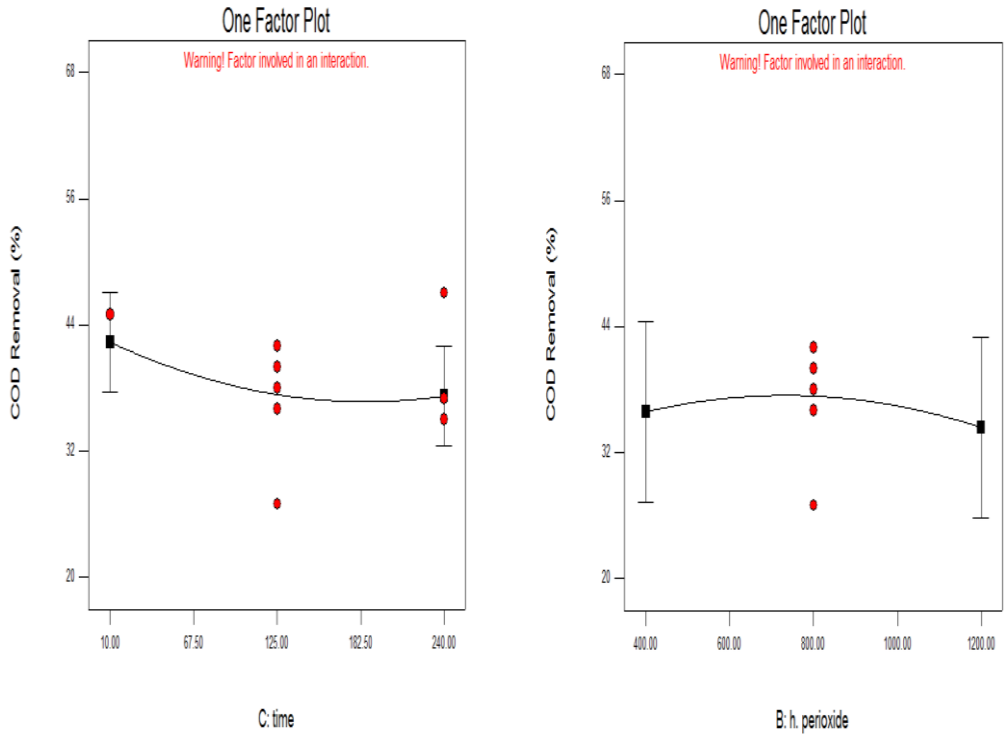

Figure 4.7: One factor plots of COD reduction vs. reaction time and peroxide dosage

From Figures 4.6 and 4.7, the effect of peroxide dosage on COD reduction increases with

a decrease in the effect of reaction time until the peroxide dosage reaches its maximum of 800.00 mg/L where the effect started decreasing up to 1200.00 mg/L with respect to the decrease in the effect of reaction time. This clearly indicates that, the hydroxyl radicals produced by the decomposition of hydrogen peroxide is not directly related to the increase or decrease in the reaction time (Bashford *et al.*, 2014). Consequently, organic pollutants degradation takes place immediately irrespective of the effect of reaction time.

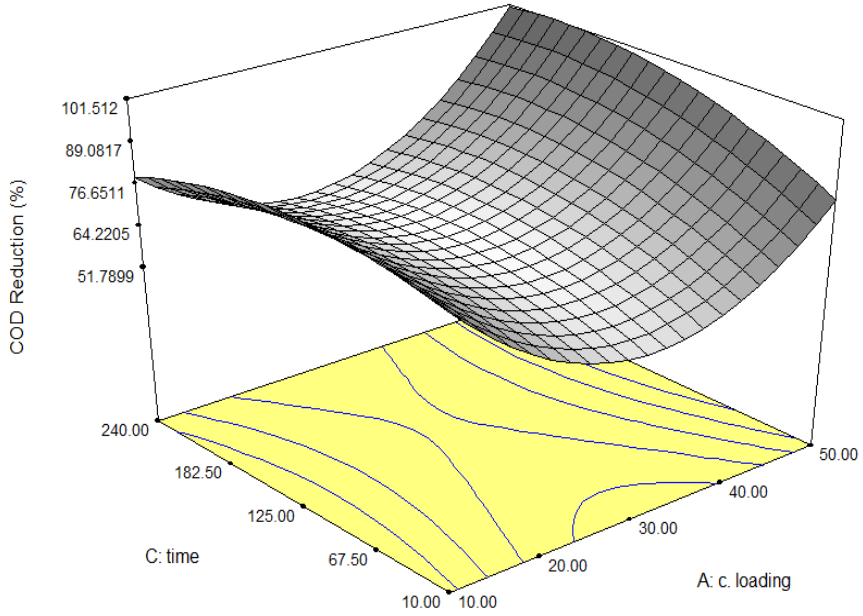

Figure 4.8: 3D response surface plot for COD reduction at H_2O_2 dosage = 800.00 mg/L and pH of 3

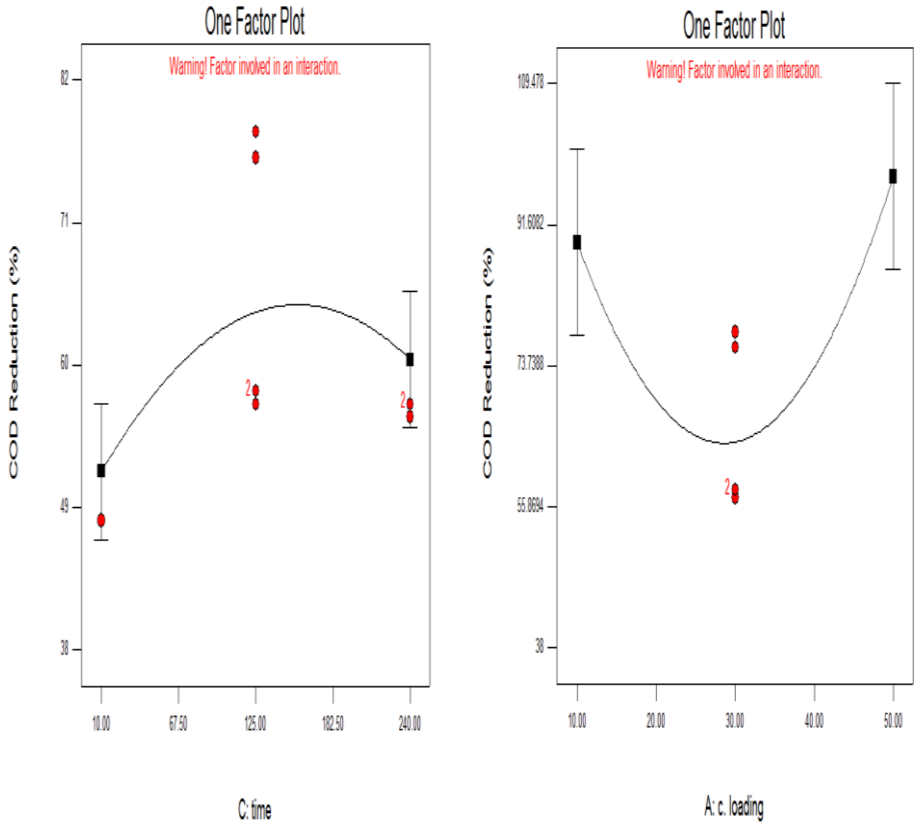

Figure 4.9: One factor plots of COD reduction vs. reaction time and catalyst loading

Figures 4.8 and 4.9 illustrate the effect of reaction time and catalyst loading with respect to the COD reduction. As it can be observed from Figure 4.9, the effect of reaction time increases with a decrease in the effect of catalyst loading and therefore, a sharp increase in the effect of catalyst loading was observed from 30.00 mg/L to 50.00 mg/L with a slight decrease in the effect of reaction time. This clearly indicates that, the reaction time has little or no influence on the catalyst loading. (Hanne *et al*., 2012). It was also observed that, the COD reduction by Fenton oxidation process increases in relation with the amount of hydroxyl radicals produced (Usman *et al*., 2014). Therefore by implication, any decrease in the amount of hydroxyl radicals produced may hinder the degradation process resulting in a decrease in COD reduction.

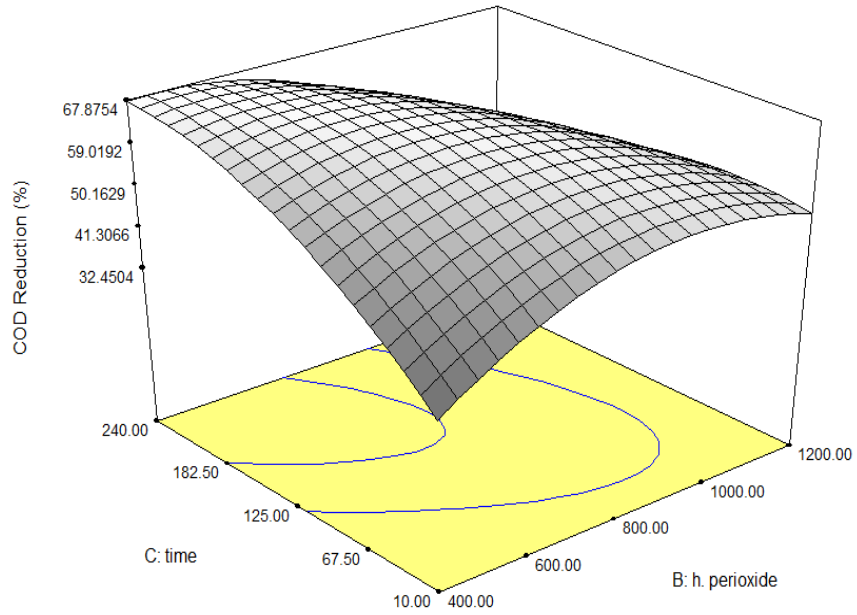

Figure 4.10: 3D response surface for COD reduction at 30.00 mg/L catalyst loading and pH of 7

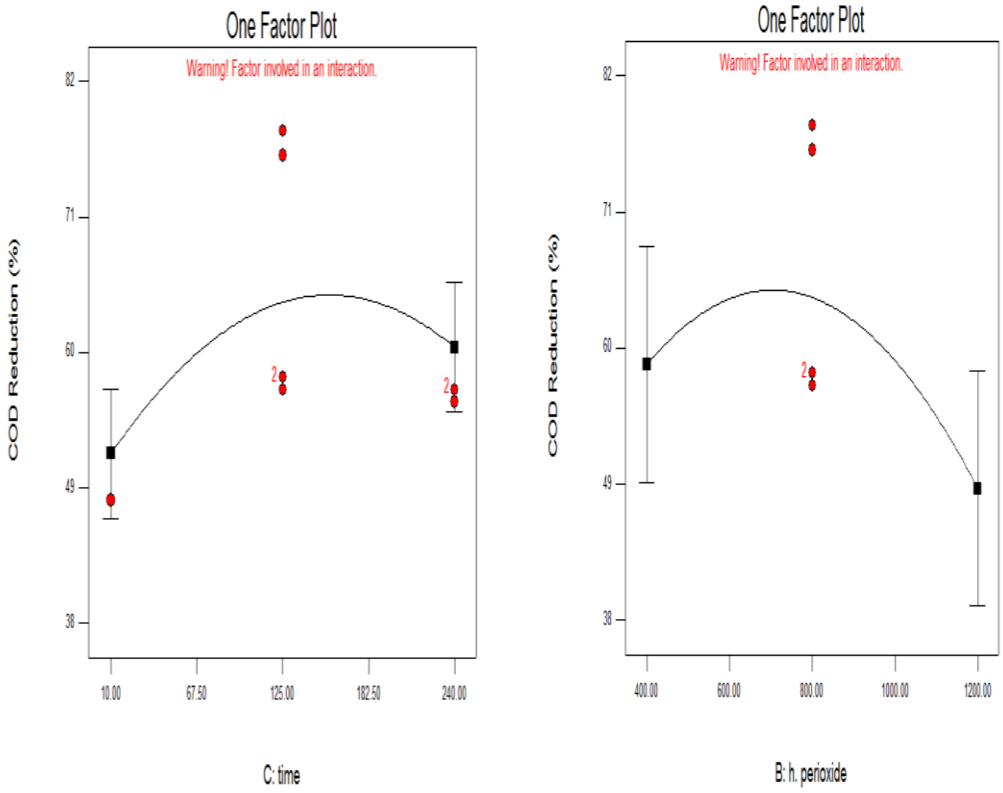

Figure 4.11: One factor plots of COD reduction vs. reaction time and peroxide

Figures 4.10 and 4.11 present the 3D response surface and one factor plots for COD

reduction as a function of reaction time and peroxide dosage. As it can be observed from Figure 4.11, there is an increase in the effect of reaction time as the effect of peroxide dosage increases but as the effect of reaction time increases further, a sharp decrease in the effect of peroxide dosage was observed which may be due to the scavenging effect of hydroxyl radicals by hydrogen peroxide (Galvez *et al.*, 2015). The increase in the effect of reaction time and peroxide dosage on COD reduction occurred as a result of having a good homogeneous interaction reaction of peroxide dosage generating hydroxyl radicals for organic pollutant degradation (Baoling *et al*., 2015).

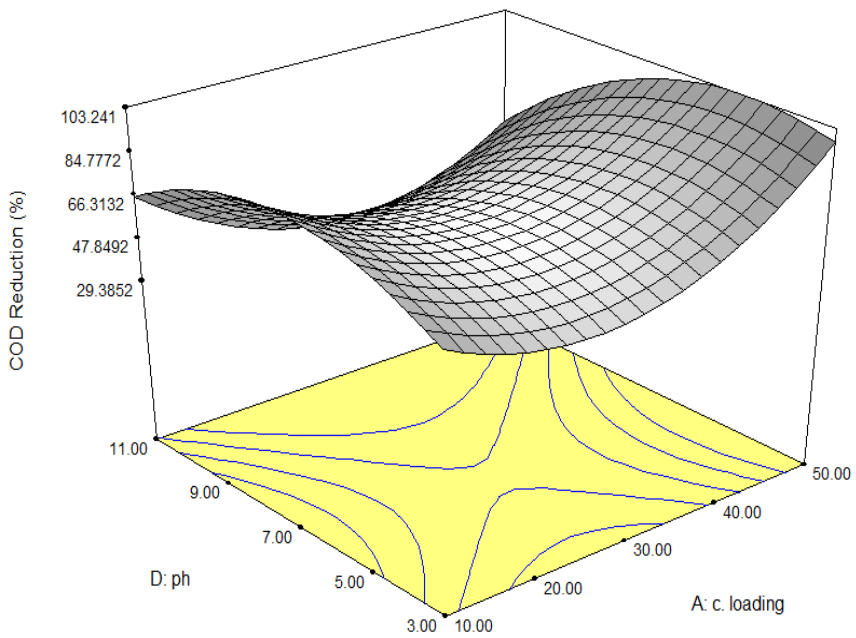

Figure 4.12: 3D response surface for COD reduction at H_2O_2 dosage = 800.00 mg/L and reaction time = 125 minutes

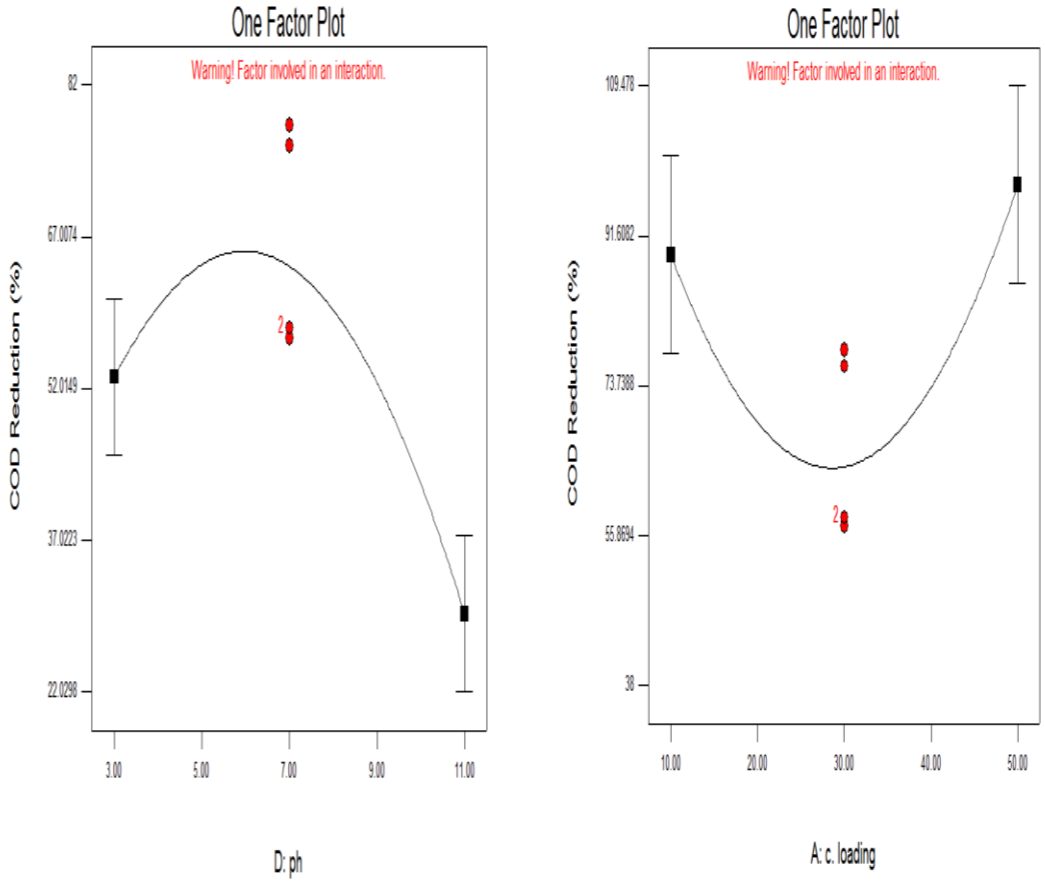

Figure 4.13: One factor plots of COD reduction vs. pH and catalyst loading

Figures 4.12 and 4.13 illustrate the 3D response surface and one factor plots for COD reduction as a function of pH and catalyst loading. Figure 4.13 clearly indicates that, the effect of pH increases on COD reduction with a decrease in the effect of catalyst loading as the solution pH can influence the degradation of organic compounds (Moura *et al.,* 2011). As the effect of pH reaches its parabolic shape, it decreases with an increase in the effect of catalyst loading. This clearly interprets that, as the amount of catalyst loading further increases there may be a scavenging effect which may hinder the rate of the reaction (Bashford *et al.,* 2014).

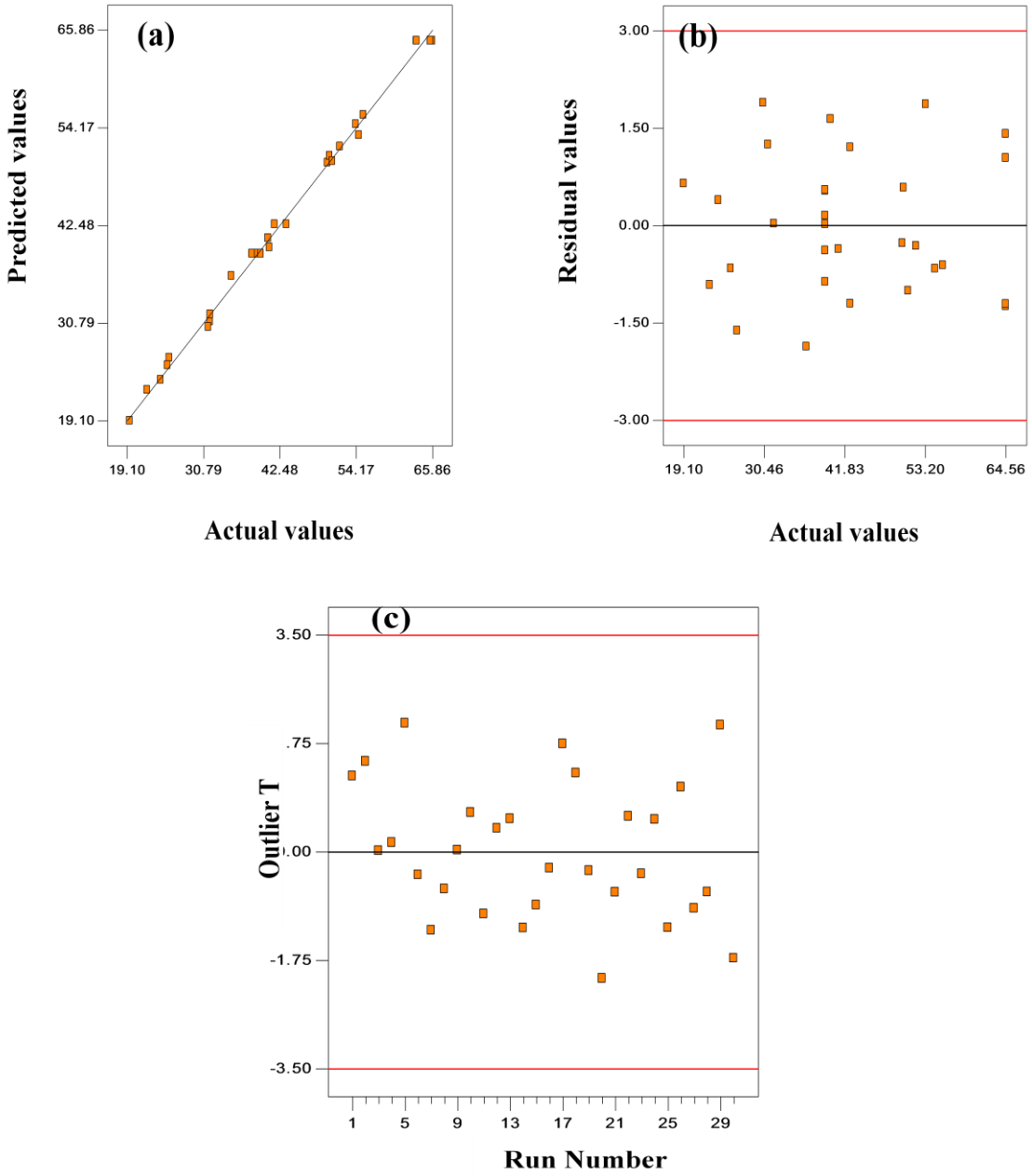

Figure 4.14: Diagnostic plots of **(a)** Predicted vs. actual values **(b)** Residual vs actual values and **(c)** Outlier T vs run number for Fenton oxidation of tannery effluent using α-FeOOH catalyst.

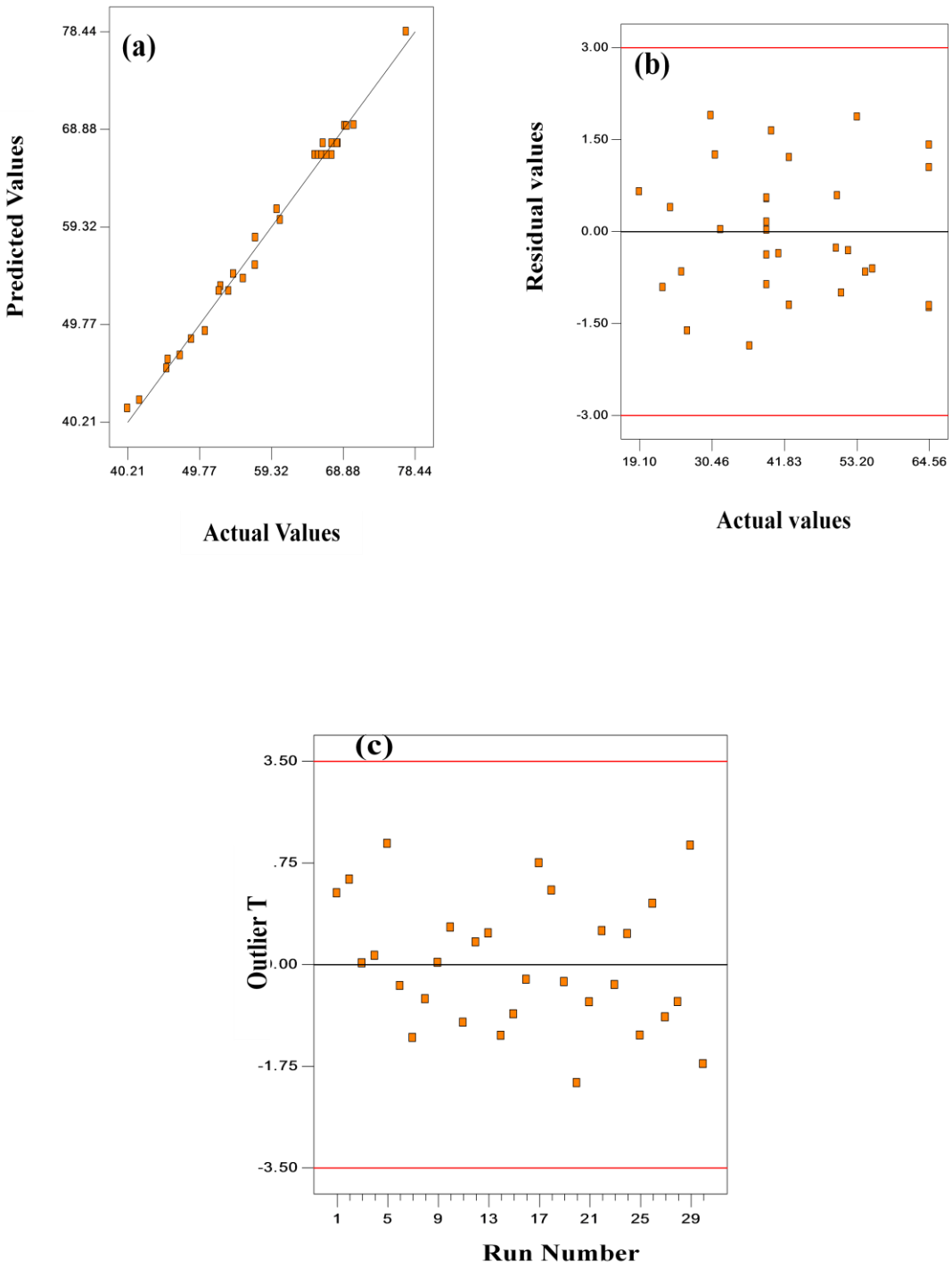

Figure 4.15: Diagnostic plots of **(a)** Predicted vs. actual values **(b)** Residual vs actual values and **(c)** Outlier T vs run number for Fenton oxidation of tannery effluent using α-FeOOH-SiO_2-Al_2O_3 catalyst.

The adequacy of a model can be assessed using diagnostic plots as in Figures 4.14 and 4.15 respectively. Figures 4.14a and 4.15a are diagnostic plots of predicted values vs

actual values showing good correlations between the two data confirming the adequacy of the model to predict COD reduction and the data points are well distributed relatively close to the straight line. Thus, the model can be used to navigate the design space and the plots indicate close agreement between the real data and the data obtained from the models.

Figures 4.14b and 4.15b are plots of residual vs. actual values in which a normal probability plots indicate whether the residuals follow a normal distribution in the sense that, the points appeared in a straight line because some scattering are expected even with normal data (Anjana *et al*., 2008). Thus, it can be understood that, the data are normally distributed. Furthermore, Figures 4.14c and 4.15c show diagnostic plots of the outlier T vs run number values indicating the approximation of the fitted model to the response surface is fairly good with no data recording error (Ahmad *et al*., 2013).

4.3.2 Optimization of operational conditions for Fenton oxidation of tannery effluent treatment

The optimization results for Fenton oxidation of tannery effluent was carried out using design expert 6.0.7 software of response surface methodology to determine the optimum points for the operational conditions in order to achieve maximum COD reduction. The desired goal for the operational conditions was set at target for both α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts in order to reduce the reaction time and the amount of reagents consumption. The desired goal was set at maximum in order to achieve the highest COD reduction and other parameters were set within experimental range. Hence, the optimal COD reduction for using α-FeOOH catalyst was predicted by the design expert software to be achieved at the optimal conditions of 30.00 mg/L catalyst loading, 900.00 mg/L peroxide dosage, 125.00 min reaction time and a pH of 3.00. This is predicted to an optimum value of 68.57% COD reduction.

For the case of α-FeOOH-SiO_2-Al_2O_3 catalyst, 82.43% COD reduction was predicted by the design expert software to be achieved at the optimal conditions of 50.00 mg/L catalyst loading, 400.00 mg/L peroxide dosage, 240.00 min reaction time and a pH of 7.00 as it can be observed from Table 4.5.In order to confirm the model's accuracy and reliability of the optimized results in Table 4.5, validation experiments were conducted using the same optimal conditions stated. From Table 4.6, it can be clearly observed that, the actual COD reduction of 65.93% and 79.29% obtained are in close agreement with the predicted optimized results of 68.57% and 82.43% confirming the accuracy of the models developed.

Table 4.5: Optimized results for tannery effluent treatment using Fenton oxidation process

Catalyst	**Catalyst loading (mg/L)**	**H_2O_2 dosage (mg/L)**	**Time (min)**	**pH**	**Predicted %COD Reduction**
α-FeOOH Catalyst	30.00	900.00	125.00	3.00	68.57
α-FeOOH-SiO_2-Al_2O_3 Catalyst	50.00	400.00	240.00	7.00	82.43

Table 4.6: Validation experiment results for tannery effluent treatment using Fenton oxidation process

Catalyst	Catalyst loading (mg/L)	H_2O_2 dosage (mg/L)	Time (min)	pH	Exp'tal %COD Reduction
α-FeOOH Catalyst	30.00	900.00	125.00	3.00	65.93
α-FeOOH-SiO_2-Al_2O_3 Catalyst	50.00	400.00	240.00	7.00	79.29

4.3.3 Comparison of Present Research Dissertation with Related Literature Reports

The related literature reports are compared with the present research dissertation in Table 4.7 where most of the previous works do not achieve more than 70% COD reduction. Hanne *et al*., (2012) worked on the investigating efficiency of goethite catalyst in the degradation of organic pollutants in tannery effluent and achieved 36.54% COD reduction at a reaction time of 320 minutes and a pH of 6.5. Liang *et al*., (2013), degraded dimethyl sulphoxide by applying goethite catalyst in the presence of hydrogen peroxide and obtained 70.40% COD reduction at a reaction time of 445 minutes and a pH of 6. Furthermore, the work of Hameed *et al*., (2014), succeeded in achieving 58.56% COD reduction at a reaction time of 290 minutes and a pH of 7 by applying α-FeOOH-SiO_2 catalyst for tannery effluent treatment using photo-Fenton oxidation process. Despite their achievement of 58.56% COD reduction but the Photo-Fenton oxidation process involves the use of ultra-violet light source for irradiation.

However, comparing with the present research dissertation in which 65.93% and 79.29% COD reduction were achieved at pH of 3 and 7 and reaction time 125 and 240 minutes by

applying α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts makes the Fenton oxidation process to be recommended than the photo-Fenton oxidation process since the Fenton oxidation process do not require the use of ultra-violet light source due to the irradiation hazards involved.

Table 4.7: Comparison of present research dissertation with related literature reports

REFERENCE	TITLE	FINDINGS	REMARKS
Hanne *et al*., 2012	Investigating efficiency of goethite in degradation of organic pollutants in tannery effluent	36.54% COD reduction pH 6.5 and 320 mins reaction time	Lower COD reduction due to catalyst instability
Hameed *et al*., 2014	Preparation and application of α-FeOOH-SiO_2 catalyst for tannery effluent treatment using Photo Fenton oxidation process	58.56% COD reduction after 290 mins reaction time at pH 7	Ultra-violet light source needed
Present work	Preparation and application of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts for tannery effluent treatment using Fenton oxidation process	65.93% and 79.29% COD reduction at pH 3 and 7, reaction time 125 and 240 minutes	Improved goethite catalyst used

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSIONS

The following conclusions could be drawn from the research dissertation carried out:

1. The measured COD, BOD_5 and pH results for characterization of the raw Mamuda tannery effluent are: 1400.00 mg/L, 350.00 mg/L and 9.00 indicating high organic pollutant loads of the effluent.
2. The XRD patterns for α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 reveals crystalline structure of the catalysts.
3. The SEM images of α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts indicate an orthorhombic crystal shape and it also indicate the non-dispersion of the catalytic materials probably due to preparatory problems.
4. Quadratic models were developed and the data fitted the response surface well with the R^2 values of = 0.9956 and 0.9919 for using α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts in tannery effluent treatment using Fenton oxidation process.
5. Validation experiments were conducted and COD reduction of 65.93% and 79.29% were obtained experimentally by applying α-FeOOH and α-FeOOH-SiO_2-Al_2O_3 catalysts. These values are very close to the optimized COD reduction results of 68.57% and 82.43% predicted by the design expert software.

5.2 RECOMMENDATIONS

1. Further research should be conducted to design a pilot plant for Fenton oxidation process through the application of α-FeOOH-SiO_2-Al_2O_3 catalyst for industrial effluent treatment.
2. Further study should be carried out best on the mechanism of Fenton oxidation process.

REFERENCES

Abdul Malik, F.M and Mohammed, M.A. (2008). Impact of long-term application of treated tannery effluent; Development of agriculture, Faculty of agricultural sciences, Algarh Muslim University, New Delhi, India. pp. 254-262.

Anjana, J.K., Bird, A.J., Jenkins, J.W and King F. (2008). Feasibility study on the application of advanced oxidation process for decentralized wastewater treatment, *Journal of environmental Engineering*, 6(3): 202-213.

Ahmad, S.M., Reuda, E.H., and Pawlik, M.A. (2013). Environmental and Microbiological problems arising fromrecalcitrant organic pollutants. *Journal of Biological Sciences*, 18(4): 90-102.

Abdul, S.F., Emmett, P.H., Baldrian, P.G. (2010). Photo-decomposition of iron (III) hydroxo and sulfato complexes in aqueous solution, Journal *of Environmental Engineering*, 8(5): 167-197.

Alexander, M., Aredes, K.O., and Klein (2008). Removal of methylene blue from aqueous solution with magnetite loaded multi-wall carbon nano-tubes: Kinetic, isotherm and mechanism analysis, Hamdan press, Ankara, Ghana, pp. 282-290.

Abdul Malik, J.O., Mahmoud, K.M., and John, Bali, P. (2007). Degradation of phenol in aqueous solution by Fenton oxidation process. *Journal of Chemical Engineering*, 12(4): 133-148.

Bashford, N., Selver, S., and Rasheed, B.H. (2014). Photo catalytic degradation of the insecticide diazinon in the presence of prepared nano crystalline ZnO powders under irradiation of UV-C light. *Journal of Environmental Engineering*, 5(8): 101-118.

Boria, Z. and Khataee, A.R. (2014). Photocatalytic degradation of the herbicide erioglaucine in the presence of nanosized titanium dioxide: Comparison and modelling of reaction kinetics. *Journal of Environmental Science and Health*, 4(2): 73–90.

Bosnic, O., Kurtoglu Z.O., and Kayode, M.H. (2011). Effect of doping on the photo catalytic, electronic and mechanical properties of sol-gel titanium dioxide films. Hall of India private Ltd, New Delhi, India, pp 147-155.

Bosnic, M. E., Longenbach T., Reddington T., Gogotsi Y. (2009). Effect of Calcination Temperature and Environment on Photocatalytic and Mechanical Properties of Ultrathin Sol-Gel Titanium Dioxide Films. *Journal of Alloys and Compounds*, 128(6): 127-135.

Bosnic, D.M. and Dionysiou, M.T. (2010). Chemical destruction of MTBE using Fenton's reagent: effect of ferrous iron/hydrogen peroxide ratio. *Journal of Water Science Technology*, 14(6): 165–171.

Blackman, T.D. and Richardson. (2011). Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent, *Journal of Water Resources*, 39(4): 107–118.

Bergendahl, M.D., and Gurol., S.M. (2009). Hydrogen peroxide/iron oxide-induced catalytic oxidation of organic compounds. *Journal of Advanced Oxidation Technology*, 7(2): 147–154.

Borowecki, S.K., and Giri, M.N. (2010). Synthesis and characterization of magnetite

nano particles using waste iron ore for adsorptive removal of dyes from aqueous solution, George and Michael, Chicago, USA, pp. 230-240.

Bredhult, J., Jang, Emmanuel P.K., and Boriki G. (2011). Polymer-encapsulated iron oxide nano particles as highly efficient Fenton catalysts. *Journal of Polymer Science,* 10(2): 178–182.

Baoling, Y., Yuan, J., Xiaoting, B.O and Liang, F.M. (20015). Preparation of α-FeOOH-SiO_2-Al_2O_3 catalyst from an iron-containing waste and surface-catalytic oxidation of methylene blue at neutral pH value in the presence of H_2O_2. *Journal of Chemical Engineering*, 6(5) 112-118.

Burukhin F.M., and Bahamon, D. F. (2008). New iron immobilized natural bentonite plate used as photo-Fenton catalyst for organic pollutant degradation, Grace Group Ltd, Ankara, Ghana, pp. 1185–1189.

Borja, K. And Bank P.O. (2014). Preparation and characterization of tin-doped α-FeOOH (goethite). *Journal of Chemical Engineering*, 10(5): 164-170.

Cornelis P.K. and Perry G. (2010). Assessment of tannery effluent management and characterization. Addis Ababa University, School of Post-Graduate studies, Department of Chemical Engineering, Addis Ababa, pp. 342-352.

Chong, S.M., Tolle G., and Roony, F. (2012).The scope of decreasing pollution load in leather processing, United Nation industrial development organization, 03(05): 31-37. ISSN: 2231- 3354.

Doan, J.A., Kemausuor, M.K., and Bashford B. (2009). Impact assessment of industrial effluent on water quality of receiving Alaro River, Ibadan, Nigeria, pp. 167-175.

Davis, H.G., (2009). Physical processes affecting contaminant fate and transport in oil and water. Academic Press (Elsevier Science, USA), San Diego, California, USA, pp. 53-54.

Diya'uddeen, B.H., Abdul-Aziz, A.R., and Wan Mohd, A.W. (2015). Limitations of Fenton oxidation operational parameters. *International Journal of Chemical Reactor Engineering*, 10(3): 64-95.

Eddy, F.O., and Mike, B.A (2014). Photo assisted degradation of anionic and cationic dyes over iron (III)-loaded resin in the presence of hydrogen peroxide, Academic press, London, England, pp. 121–127.

Farhana, J.O., Ayati G.T., and Monzerezi KA. (2007). Degradation of methylene blue in tannery effluent using hydrogen peroxide as an oxidant in Fenton oxidation process. *Journal of Environmental Management*, 64(04): 51-67.

FEPA, Final report on leather tanning.(2009). Emission factor documentation for AP-42 section 9.15.

Fakayode, B.O. (2010). Effect of reaction conditions on the oxidation efficiency in Fenton oxidation process, Department of Chemical Engineering, Bingham University, USA, pp. 17-60.

Farhana, D.I., Shoemaker, B.O., and Chaudharry, R.A. (2012). Fentons oxidation of various based tanning materials. *Journal of Desalination*, 50(6): 411-423.

Forbes, D.O. (2012). American Public Health Potential for treatment of hazardous organic chemical with biological process, Hammock press, California, USA, pp. 15-64.

Gupta, K.O. (2007). Effect of initial solution pH on the degradation of orange II using clay-based Fe nano composites as heterogeneous photo-Fenton catalyst, Water Resources Department, Oxford University, USA, pp. 641–646.

Garrido, N.K., Ojediran, B.O., Sam, M., Anjana and Forbe H. (2010). Characterization of leather industry's waste. *Journal of Environmental Studies*, 16(4): 86-97.

Galvez, S.A., Johnson, B.H., Buljan, S.M., and Varshneya, M.I. (2015). Assessment of physico- chemical parameters of effluents of three factories of bareilly district and their possible effects on grazing animals and cereals. *Journal of Environmental Biology*, 19(3): 21-27.

Galasso, P.K. (2009). Wastewater treatment in constructed wetlands: systems designs, removal processes and treatment performance. Constructed Wetlands for Quality Improvement. Hamdan Press, Boca Raton, Florida, USA, pp. 9-22.

Hameed, B.H., Tabet, M., Saidi, Pichat and Khalaf. (2012). Fe-pillared clay as a Fenton type of heterogeneous catalyst for organic pollutant degradation. *Journal of Chemical Engineering*, 36(9): 104-115.

Hayer, T.L., Dantas, V.P., Mendonca, Jose, Rodrigues and Moreira. (2013). Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe_2O_3/carbon, Journal *of Chemical Engineering*, 02(4): 41-47.

Haber, P.G., Wang, Y. D., Zhang, X.S., and Moura. (2015). Controlled synthesis, magnetic and sensing properties of hematite nano-rods and micro-capsules. *Journal of Environmental Engineering*, 20(10): 132-140.

Halim, L.O., Song, S., Zhang and Bosnic. (2012). Formation of α-Fe_2O_3/FeOOH nano structures with various morphologies by a hydrothermal route and their photo catalytic properties, Hoffman Ltd, London, England, pp. 217–220.

Hanna, S.H. Tian, Y.T., Alexander, Forbes D.P., Bali and Doan. (2008). Degradation of Acid Orange II at neutral pH using $Fe_2(MoO_4)_3$ as a heterogeneous Fenton-like catalyst. *Journal of Chemical Engineering*, 169 (20): 31–37.

Henry, B.A., Eddy, T., Jackson, L and Robinson. (2011). Wastewater Engineering, McGraw Hill Publications. Third Edition, Tata McGraw-Hill Publishing Company Ltd, New Delhi, India, pp. 16-30.

Hamdan, F.M., Moura, P., Fabris, K. And Jiang, Z. (2014). Synthesis and thermal treatment of cu-doped goethite: Oxidation of quinoline through heterogeneous Fenton process. *Journal of Alloys and Compounds*, 108(10): 269-276.

Hameed, M., Usman B.O., and James, O. (2014). Preparation and application of α-FeOOH-SiO_2 catalyst for tannery effluent treatment using photo Fenton oxidation process. *Journal of Environmental Management*, 5(3): 143-149.

Hanne, J.A., Forbes, P., and Johnson, M.I. (2012). Investigating efficiency of goethite in the degradation of organic pollutants. *Journal of Cleaner Production*, 17(4): 109-115.

Iborra, J. and James, F. (2008).Dye removal from textile dye wastewaters using recycled alum sludge. *Journal of Water Research*, vol. 35(7): 147-152.

Javeed, S.M., Yang, H. D., Lafrano, Gupta, W., Adriano and Mike. (2007). Decolorization of methylene blue by heterogeneous Fenton reaction using α-FeOOH catalyst at neutral pH. *Journal of Environmental Management*. 03(04): 51- 60. ISSN: 224-3375.

Klemes, O.H., Salman, B.S., and John K. (2007). The contribution of vanadium and titanium on improving methylene blue decolourization through heterogeneous UV-Fenton reaction catalyzed by their co-doped magnetite, University Press Ltd, Oxford, USA, pp. 567-590.

Kazmi, B., Vermin, G.O., and Morrison. L.I. (2012). Characterization of tannery effluent and pollution control. *Journal of Hazardous Materials*, 15(4): 34-43.

Kayode, N., Balham, and James, H.A. (2012). Wastewater treatment problems in the operation of woven and knit fabric industry, *Journal of Biochemical Engineering*, 07(12): 75-82.

Liang, J.O., Huang, G.Y., Bashford, Dennis, T. and Duan. (2009). Visible-light sensitive cobalt-doped $BiVO_4$ (Co-$BiVO_4$) photo-catalytic composites for the degradation of methylene blue dye in dilute aqueous solutions. *Journal of Hazardous Materials*, 14(6): 54-69.

Ludvik, M.O. (2007). Removal of sewage effluent- the use of a full-scale ozone plant, Water Science and Technology (Doctoral dissertation), Bingham University, USA, pp. 275-284.

Lofrano, Z.A. (2010). Effect of toxic substances in anaerobic treatment of tannery wastewater, Bio-process, Bio-system Engineering. Longman Group Ltd, Ankara, Ghana, pp. 67-75.

Lee, J.I., Kazmi, A., Miyata, S.O., and Garrido, B.O. (2006). Silica-supported iron oxidecatalyst capable of activating hydrogen peroxide at neutral pH values. *International Journal of Research and Reviews in Applied Sciences,* 07(13): 199-223.

Liang, B., James, L.I., and Dickerson, N. (2013). Oxidation of Dimethyl sulphoxide on goethite catalyst using hydrogen peroxide. *Journal of Hazardous Materials,* 5(2): 121-127.

Muthukumar, M.I. (2011). Heterogeneous photo catalysis transition metal ions in photo catalytic systems.*Journal of Chemical Engineering,*23(8): 89-114.

Moura, Y., Lokhande, R.S. Johnson, M. and Vaidya, S. (2011). Physiochemical studies of industrial effluents from the mid area of Kalyan-Dombivali. *Journal of Ecotoxicology and Environmental Monitoring,* 14(3): 199-202.

Molina, N. and Lee, O. (2015). Source and characteristics of diary wastes from a medium sized effluent on microorganisms, plant growth and their microbial change. *Journal of Microbiological Organisms,* 3(9): 76-86.

Munta, B.O. and John, G. (2011). Assessment of physico chemical parameters of effluents of three factories of Bareilly district and their possible effects on grazing animals and cereals. *Chemical Engineering Journal*, 19(3): 271-274.

Moura S., Billy, M.H., Joseph, K. and Molina, D.P. (2015). Oxidation of organic pollutants using goethite catalyst. *Journal of Hazardous Materials,* 12(4): 25-30.

Munter, M., Morris, L., Boyad, T. and Mike, N. (2009). Wastewater treatment in constructed wetlands: systems designs, removal processes and treatment performance.Hamden Press, Boca Raton, Florida, USA, pp. 19-32.

Matson, S., Johnson, K., James, N. and Mike, G. (2009).Removal of sulphide in anaerobically treated tannery wastewater by wet air oxidation, *Journal of environmental science and health,* 31(7): 79-98.

Najeem, P.K., Joe, S., Suzuki, T. and Molina, R. (2011). Feasibility study on the application of advanced oxidation processes for decentralised wastewater treatment. *Journal of Cleaner Production*. 35(5): 30-40.

Othman, B.O., Miyauchi, M., Nakajima A. (2010). Photo catalysis and Photo induced Hydro philicity of Various Metal Oxide Thin Films. *Journal of Hazardous Materials,*14(6)**:** 110-116.

Plata, M., Nakabayashi S., and Honda K.M. (2009). Catalytic properties of goethite prepared in the presence of UV-light on oxidation reactions in industrial wastewater. *Journal of Chemical Engineering,* 12(6): 105-112.

Pascal, M.O., Nolan N. T, and Pillai S. C. (2005). Assessment of physico chemical parameters of effluents of three factories of bareilly district and their possible effects on grazing animals and cereals. *Journal of Environmental Engineering*, 19(3): 71-84.

Patric, M.I, Adekunle, P.K., and Meloni, K.A. (2010). Biodegradation of crude petroleum and petroleum products by fungi isolated from two oils. *Journal of Biological Sciences,* 26 (l2): 37-42.

Rocha, H., Pankaj, Chowdhury and Klemes, N. (2012). Immobilization of active and stable goethite coated-films by a dip-coating process and its application for photo-Fenton process. *Journal of Chemical Engineering*, 2(4): 142-150.

Rasheed, M. N. and El-Amin A. A. (2007). Tannery wastewater treatment using goethite catalyst. *International Journal of Physical Sciences*, 8(4): 162-168.

Silva, B.O., (2010). A method for preparing silica-containing iron (III) oxide adsorbents forarsenic removal. *Journal of Water Resources*, 7(3): 43–48.

Salim, A.J., Blanch, J.S., Quinton, C.E., andLenehan, A. (2009). The crystal chemistry of Albearing goethites: an infrared spectroscopic study, 72(9): 143–156.

Savant, Y.A., Ritmann B.E., and Johnson D.E. (2013). American Public Health Potential for treatment of hazardous organic chemicals with biological process, pp. 15-64.

Thompson, H.A., Sukumaran, M., and Rama Murthy, B.O. (2014). Biodiversity of Microbes in Tannery Effluent. *Journal of Ecotoxicology and Environmental Monitoring*, 18 (4): 313–318.

Tolle, J., Lee, R., Krishma, B., Fredick, G.and Robinson, S. (2009). Biological treatment of tannery wastewater in the presence of chromium, Journal *of Environmental Management*, 71(4): 345-349.

Usman, J.O., Eddy, U. and Perry, H.A. (2014). Degradation of organic pollutants in tannery wastewater. *Journal of Chemical Engineering*, 7(4): 18-24.

Walter, P.J. and Vennes. (2011). Iron oxide surface–catalyzed oxidation of ferrous iron by mono chloramine: implications of oxide type and carbonate on reactivity, *Journal of Environmental Science Technology*, 6 (3): 120–129.

William, P.K., Cheng, S.W., and Zacchi, S.M. (2010). Simultaneous removal of organic and inorganic pollutants in tannery wastewater using electro coagulation technique.*Chemical Engineering Journal*, 5(2): 13-19.

William, J., Kazmi, O., Bashford, K. and Henry, F.A. (2008).Biological treatment of tannery wastewater in the presence of chromium, *Journal of Environmental Management*, 71(4): 345- 349.

Yang, Y. Liang, G. Wang, I. and Lee, M. (2010).Kinetics Studies on Biological Treatment of Tannery Wastewater Using Mixed Culture. *International Journal of Chemical and Biological Engineering*, 3(2): 105-109.

Yang, M.I. and Wang D.H. (2014). Comparison of zinc oxide nano particles and its nano crystalline particles on the photocatalytic degradation of methylene blue. *Journal of Chemical Engineering, 51(3): 77-87.*

Zeng, A., Jiang, L., Baldrian, P.O. and Warneck, J. (2012). Removal of methylene blue from aqueous solution with magnetite loaded multi-wall carbon nano tube: Kinetic,

isotherm and mechanism analysis. *Journal of Hazardous Materials*, 9(6): 82-90.

Zafaruddin, M.K. (2008). American Public Health Potential for treatment of hazardous organic chemical with biological process. Longman Group Ltd, California, USA, pp. 15-64.

Zaki, Y.B., Ajayi, M.A., and Anderson H. (2010). Effective means of bio-filtration of heavy metals contaminated water bodies using aquatic weed Eichhorniacrassipes. *Journal of Environmental Monitoring and Assessment*, 9(3): 53-66.

APPENDICES

APPENDIX-A

Table-Ai: Experimental COD values

RUN	COD (mg/L)
1	955
2	571
3	1000
4	1042
5	1141
6	961
7	477
8	1188
9	1142
10	698
11	1090
12	1099
13	958
14	440
15	830
16	626
17	586
18	636
19	551
20	850
21	536
22	1070
23	932
24	758
25	904
26	600
27	985
28	578
29	865
30	480

Calculations for %COD Reduction of Tannery Effluent Treatment using α-FeOOH Catalyst

Blank Sample: Initial analysed COD value = 1400mg/L

$$COD reduction\ (\%) = \frac{Initial COD value - Final COD value}{Initial COD value} * \frac{100}{1}$$

$$Run\ 1 = \frac{1400\ -\ 955}{1400} * \frac{100\%}{1} = 31.80\%$$

$$Run\ 2 = \frac{1400\ -\ 571}{1400} * \frac{100\%}{1} = 59.21\%$$

$$Run\ 3 = \frac{1400 - 1000}{1400} * \frac{100\%}{1} = 28.57\%$$

$$Run\ 4 = \frac{1400 - 1042}{1400} * \frac{100\%}{1} = 25.57\%$$

$$Run\ 5 = \frac{1400 - 1141}{1400} * \frac{100\%}{1} = 18.50\%$$

$$Run\ 6 = \frac{1400 - 961}{1400} * \frac{100\%}{1} = 31.36\%$$

$$Run\ 7 = \frac{1400 - 477}{1400} * \frac{100\%}{1} = 65.93\%$$

$$Run\ 8 = \frac{1400 - 1188}{1400} * \frac{100\%}{1} = 15.14\%$$

$$Run\ 9 = \frac{1400 - 1142}{1400} * \frac{100\%}{1} = 18.43\%$$

$$Run\ 10 = \frac{1400 - 698}{1400} * \frac{100\%}{1} = 50.14\%$$

$$Run\ 11 = \frac{1400 - 1090}{1400} * \frac{100\%}{1} = 22.14\%$$

$$Run\ 12 = \frac{1400 - 1099}{1400} * \frac{100\%}{1} = 21.50\%$$

$$Run\ 13 = \frac{1400 - 958}{1400} * \frac{100\%}{1} = 31.57\%$$

$$Run\ 14 = \frac{1400 - 440}{1400} * \frac{100\%}{1} = 68.57\%$$

$$Run\ 15 = \frac{1400 - 830}{1400} * \frac{100\%}{1} = 40.71\%$$

$$Run\ 16 = \frac{1400 - 626}{1400} * \frac{100\%}{1} = 55.30\%$$

$$Run\ 17 = \frac{1400 - 586}{1400} * \frac{100\%}{1} = 58.14\%$$

$$Run\ 18 = \frac{1400 - 636}{1400} * \frac{100\%}{1} = 54.60\%$$

$$Run\ 19 = \frac{1400 - 551}{1400} * \frac{100\%}{1} = 60.64\%$$

$$Run\ 20 = \frac{1400 - 850}{1400} * \frac{100\%}{1} = 39.29\%$$

$$Run\ 21 = \frac{1400 - 536}{1400} * \frac{100\%}{1} = 61.71\%$$

$$Run\ 22 = \frac{1400 - 1070}{1400} * \frac{100\%}{1} = 23.57\%$$

$$Run\ 23 = \frac{1400 - 932}{1400} * \frac{100\%}{1} = 33.43\%$$

$$Run\ 24 = \frac{1400 - 758}{1400} * \frac{100\%}{1} = 45.86\%$$

$$Run\ 25 = \frac{1400 - 904}{1400} * \frac{100\%}{1} = 35.43\%C$$

$$Run\ 26 = \frac{1400 - 600}{1400} * \frac{100\%}{1} = 57.14\%$$

$$Run\ 27 = \frac{1400 - 985}{1400} * \frac{100\%}{1} = 29.64\%$$

$$Run\ 28 = \frac{1400 - 578}{1400} * \frac{100\%}{1} = 58.71\%$$

$$Run\ 29 = \frac{1400 - 865}{1400} * \frac{100\%}{1} = 38.21\%$$

$$Run\ 30 = \frac{1400 - 480}{1400} * \frac{100\%}{1} = 65.71\%$$

Table- Aii: ANOVA Result for Response Surface Linear Model

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F-Value**	**P-value**
Model	2054.46	1	513.61	4.37	0.0082
A	1278.49	1	1278.49	10.87	0.0029
B	40.58	1	40.58	0.34	0.5622
C	400.24	1	400.24	3.40	0.0770
D	333.23	1	333.23	2.83	0.1048
Residual	2940.66	25	117.63		
Lack of Fit	2932.47	16	183.28	201.21	< 0.0001
Pure Error	8.20	9	0.91		
Cor Total	4995.12	29			

R-Squared = 0.4113 Adj. R-Squared = 0.3171

Table Aiii: ANOVA result for Response Surface Mean Model

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F-Value**	**P-value**
Model	0.000	0			
Residual	4995.12	29	172.25		
Lack of Fit	4986.93	20	249.35	273.74	< 0.0001
Pure Error	8.20	9	0.91		
Cor Total	4995.12	29			

R-Squared = 0.0000 Adj. R-Squared = 0.0000

Table- Aiv: ANOVA result for Response Surface 2FI Model

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F-Value**	**P-value**
Model	2929.74	10	292.97	2.70	0.0302
A	1278.49	1	1278.49	11.76	0.0028
B	40.58	1	40.58	0.37	0.5485
C	400.24	1	400.24	3.68	0.0702
D	333.23	1	333.23	3.07	0.0961
AB	130.42	1	130.42	1.20	0.2871
AC	51.77	1	51.77	0.48	0.4985
AD	1.50	1	1.50	0.014	0.9077
BC	676.78	1	676.78	6.23	0.0220
BD	8.21	1	8.21	0.076	0.7864
CD	6.60	1	6.60	0.061	0.8079
Residual	2065.39	19	108.70		
Lack of Fit	2057.19	10	205.72	225.84	< 0.0001
Pure Error	8.20	9	0.91		
Cor Total	4995.12	29			

R-Squared = 0.5865 Adj R-Squared = 0.3689

APPENDIX-B

Table-Bi: Experimental COD values

RUN	COD (mg/L)
1	637
2	578
3	534
4	697
5	639
6	433
7	624
8	552
9	662
10	558
11	290
12	620
13	593
14	400
15	565
16	428
17	600
18	410
19	458
20	485
21	650
22	246
23	660
24	470
25	445
26	410
27	622
28	500
29	605
30	450

Calculations for %COD Reduction of Tannery Effluent Treatment using α-FeOOH-SiO_2-Al_2O_3 Catalyst

Blank Sample: COD value = 1400mg/L

$$CODreduction$$

$$= \frac{InitialCODvalue - FinalCODvalue}{InitialCODvalue} * \frac{100\%}{1}$$

$$Run\ 1 = \frac{1400\ -\ 637}{1400} * \frac{100\%}{1} = 54.50\%$$

$$Run\ 2 = \frac{1400\ -\ 578}{1400} * \frac{100\%}{1} = 58.71\%$$

$$Run\ 3 = \frac{1400 - 534}{1400} * \frac{100\%}{1} = 61.86\%$$

$$Run\ 4 = \frac{1400 - 697}{1400} * \frac{100\%}{1} = 50.21\%$$

$$Run\ 5 = \frac{1400 - 639}{1400} * \frac{100\%}{1} = 54.36\%$$

$$Run\ 6 = \frac{1400 - 433}{1400} * \frac{100\%}{1} = 69.10\%$$

$$Run\ 7 = \frac{1400 - 624}{1400} * \frac{100\%}{1} 55.43\%$$

$$Run\ 8 = \frac{1400 - 552}{1400} * \frac{100\%}{1} = 60.57\%$$

$$Run\ 9 = \frac{1400 - 662}{1400} * \frac{100\%}{1} = 52.71\%$$

$$Run\ 10 = \frac{1400 - 558}{1400} * \frac{100\%}{1} = 60.14\%$$

$$Run\ 11 = \frac{1400 - 290}{1400} * \frac{100\%}{1} = 79.29\%$$

$$Run\ 12 = \frac{1400 - 620}{1400} * \frac{100\%}{1} = 55.71\%$$

$$Run\ 13 = \frac{1400 - 593}{1400} * \frac{100\%}{1} = 57.64\%$$

$$Run\ 14 = \frac{1400 - 400}{1400} * \frac{100\%}{1} = 71.43\%$$

$$Run\ 15 = \frac{1400 - 565}{1400} * \frac{100\%}{1} = 59.64\%$$

$$Run\ 16 = \frac{1400 - 428}{1400} * \frac{100\%}{1} = 69.43\%$$

$$Run\ 17 = \frac{1400 - 600}{1400} * \frac{100\%}{1} = 57.14\%$$

$$Run\ 18 = \frac{1400 - 410}{1400} * \frac{100\%}{1} = 70.71\%$$

$$Run\ 19 = \frac{1400 - 458}{1400} * \frac{100\%}{1} = 67.29\%$$

$$Run\ 20 = \frac{1400 - 485}{1400} * \frac{100\%}{1} = 65.36\%$$

$$Run\ 21 = \frac{1400 - 650}{1400} * \frac{100\%}{1} = 53.57\%$$

$$Run\ 22 = \frac{1400 - 246}{1400} * \frac{100\%}{1} = 82.43\%$$

$$Run\ 23 = \frac{1400 - 660}{1400} * \frac{100\%}{1} = 52.86\%$$

$$Run\ 24 = \frac{1400 - 470}{1400} * \frac{100\%}{1} = 66.43\%$$

$$Run\ 25 = \frac{1400 - 445}{1400} * \frac{100\%}{1} = 68.21\%C$$

$$Run\ 26 = \frac{1400 - 410}{1400} * \frac{100\%}{1} = 70.71\%$$

$$Run\ 27 = \frac{1400 - 622}{1400} * \frac{100\%}{1} = 55.57\%$$

$$Run\ 28 = \frac{1400 - 500}{1400} * \frac{100\%}{1} = 64.29\%$$

$$Run\ 29 = \frac{1400 - 605}{1400} * \frac{100\%}{1} = 56.79\%$$

$$Run\ \ 30 = \frac{1400 - 450}{1400} * \frac{100\%}{1} = 67.86\%$$

Table Bii: ANOVA result for Response Surface Linear Model

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F-Value**	**P-value**
Model	1270.81	4	317.70	5.27	0.0032
A	548.14	1	548.14	9.09	0.0058
B	256.72	1	256.72	4.26	0.0496
C	442.44	1	442.44	7.34	0.0120
D	24.05	1	24.05	0.40	0.5334
Residual	1506.88	25	60.28		
Lack of Fit	1499.45	16	93.72	113.44	< 0.0001
Pure Error	7.43	9	0.83		
Cor Total	2777.69	29			

R-Squared = 0.4575 Adj R-Squared = 0.3707

Table-Biii: ANOVA result for Response Surface Mean Model

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F-Value**	**P-value**
Model	0.000	0			
Residual	2777.69	29	95.78		
Lack of Fit	2770.26	20	138.51	167.67	< 0.0001
Pure Error	7.43	9	0.83		
Cor Total	2777.69	29			

R-Squared = 0.0000 Adj R-Squared = 0.0000

Table-Biv: ANOVA result for Response Surface 2FI Model

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F-Value**	**P-value**
Model	1597.55	10	159.75	2.57	0.0367
A	548.14	1	548.14	8.82	0.0079
B	256.72	1	256.72	0.37	0.0563
C	442.44	1	442.44	7.12	0.0152
D	24.05	1	24.05	0.39	0.5412
AB	1.68	1	1.68	0.027	0.8710
AC	235.24	1	235.24	3.79	0.0666
AD	69.51	1	69.51	1.12	0.3034
BC	6.06	1	6.06	0.098	0.7581
BD	1.76	1	1.76	0.028	0.8680
CD	12.48	1	12.48	0.20	0.6591
Residual	1180.14	19	62.11		
Lack of Fit	1172.71	10	117.27	141.96	< 0.0001
Pure Error	7.43	9	0.83		
Cor Total	2777.69	29			

R-Squared = 0.5751 Adj. R-Squared = 0.3515