

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

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BY

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# DECLARATION

I declare that the work in this dissertation entitled DEPURATION STUDIES ON KADUNA REFINERY WASTEWATER USING MODIFIED Cu-DOPED GOETHITE

CATALYST has been carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Hambali Umar HAMBALI Nameof StudentSignature Date

# CERTIFICATION

This dissertation titled ³'HSXUSDtudWieLs RonQKaduna Refinery Wastewater Using

Modified Cu-Doped Goethite Catalyst´ PHHWVu latiWonKs gHov ernUinHg Jthe award of Masters of Science Degree in Chemical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Professor I. A. Mohammed-Dabo Chairman, Supervisory Committee Signature Date

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| Professor Kabir Bala |  |  |
| Dean, School of Postgraduate Studies | Signature | Date |

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# ABSTRACT

Undoped and copper doped goethite catalysts weresynthesized and applied in Fenton depuration of Kaduna refinery wastewater. The percentage of copper in the doped catalysts are 0.2 wt% copper in Cu-doped (A), 1.6 wt% copper in Cu-doped (B) and 3.3 wt% copper in Cu-doped (C), respectively. Characterization of the catalysts were done using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Absorption Spectrophotometer (AAS) and Surface Area Analysis. An experimental design matrix was used to evaluate the individual and combined effects of the process variables. Response surface methodology (RSM) was applied with a central composite design (CCD), and modelswere developed. The optimal conditions are pH of 3, 360 minutes reaction time, catalyst loading of 55mg/L and hydrogen peroxide dosage of 1.1g/L.Astonishingly, appreciable depuration percentage was achieved at near neutral pH, 67.44% was achieved by the undoped goethite catalyst, 79%, 82.56% and 83.72% were achieved by the Cu- doped A, B and C goethite catalysts, respectively. The obtained models for the undoped and doped catalysts gave R-square (R2) values of 0.9471, 0.9794, 0.9371 and 0.9407, respectively which showed that the experimental data fitted the modelfairly well, depicting the viability and reliability of the model.It was observed that the Cu-dopedgoethite catalysts yielded improved depuration, confirming that the doped catalysts have great potential as an efficient tool for Fenton depuration of petroleum refinery wastewater.

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# LIST OF ABBREVIATIONS

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

# CHAPTER ONE INTRODUCTION

# Preamble

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

The conventional wastewatertreatment methods (primary and secondary) used for treating refineryeffluents include mechanical and physiochemical processes such as oil water separation, sedimentation, coagulation, and dissolved air flotation with further biological WUHDWPHQW *e* *t a*'*l*.L, 2\01D1).¶HXowGevGerH, bHioQlog ical processes are not efficient for treating wastewater with high toxicity and bio-refractory compounds (Saien and Nejati 2007). Therefore, it is imperative to introduce newer treatment technologies capable of effectively treating petroleum refinery wastewater. The newer technologies include advanced oxidation processes (AOP), filtration, nutrient removal and toxic elements or chemicals removal among others (Chunli, 2013).

Advanced oxidation processes are characterized by hydroxyl radicals 2g+en er ation, which can effectively destroy a wide range of toxic and bio-refractory compounds. Among these arethe homogenous and heterogeneous Fenton oxidation process which is an advanced oxidation process that utilizes the highly reactive 2+to destroy organic

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

Iron oxides play an important role in organic pollutants depuration as they represent strong sorption surfaces for pollutants and catalyze numerous redox transformations(Stiers and Schwertmann, 1985).Among the sixteen known iron oxides and hydroxides, goethite -Į

FeOOH), magnetite (Fe3O4 PDJK-HFeP2OL3) WanHd he maȖtite -ĮFe2O3) are the frequently used heterogeneous Fenton catalysts(Yang*et al*., 2009).Goethite is a synthetic or

naturally occurring iron oxide that consists of double chains of FeO (OH) octahedral

3 3

extending along the crystallographic Z-axis and is composed of about 80 to 90 percent Fe2O3 and approximately 10 percent water and forms hematite when dehydrated and upon hydration becomes limonite (Ohtani, 2011).

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

2+ 3+ 3+ 3+ 2+ 2+ 2+

of metals like Cu , Al , Mn , Cr , Ni , Zn , Pb may have notable effect on

thechemical and physical properties of goethite and hematite (Subrt *et al*., 2000).

In this work,goethiteand copper dopedgoethite catalysts were synthesized and used as heterogeneous Fenton catalysts.Effect of copper inclusion onthe surface of the goethite catalyst and its performance ondepuration of Kaduna refinery wastewater were evaluated.

# Problem Statement

* + 1. Voluminous petroleum refinery wastewatergenerated contain highly toxic and large amount of organic contaminants, and the current treatment techniques have many drawbacks such as inefficient treatment of wastewater with high toxicity among others.
    2. An attractive option is the homogenous Fenton process which yields substantial depuration rate. However, its pH adjustment requirements and large sludge generation are subject to many ongoing research efforts.
    3. Heterogeneous Fenton process which uses solid catalyst such as goethite, among others, has the potential to address the problems.
    4. Doped goethite catalyst is expected to improve Fenton process efficiency.

However, research works are scanty on its development and application.

# Aim and Objectives

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

The specific objectives are to:

* + 1. CharacterizeKaduna refinery wastewater.
    2. Synthesize and characterize goethite and copper doped goethite catalystsusing XRD, SEM and surface area analysis.
    3. Investigate the depuration of Kaduna refinery wastewater using thesynthesized goethite and copper doped goethite catalysts.
    4. Establish optimal conditions for the depuration ofKaduna refinery wastewater.
    5. Investigate the stability of the copper doped goethite catalyst.

# Scope of the Work

This work is limited to the following:

* + 1. To synthesize and characterize goethite and copper doped goethite catalyst.
    2. To depurate Kaduna refinery wastewater using the copper doped goethite catalyst.
    3. Stability analysis of the copper doped goethite catalyst.

# Research Justification

* + 1. Heterogeneous Fenton process isenvironment friendly and an efficient form of wastewater treatment that generates small amount of sludge.
    2. Little work has been done on goethite doped catalyst development and application.
    3. The amount of energy utilized in this technology is low, as the depuration process is carried out at atmospheric conditions.

# CHAPTER TWO LITERATURE REVIEW

# Petroleum Refinery Wastewater

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

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

Globally, crude oil demand is expected to rise to 107mbpd over the next two decades, and

ZLOO DFFRXQW IRU RI WKH ZRUOG¶V HQHUJ\

and biodiesel, are expected to account for 5.9 mbpd by 2030, and the contributions from renewable energy sources like wind and solar power are estimated to be 4±15% (Molina *et al.*, 2012). These data clearly indicate that petroleum refinery effluents will continually be

SURGXFHG DQG GLVFKDUJHG LQOrWtizR*et*  *al.*W, 2K00H8). HZowRevUerO, G¶V P

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

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

# Wastewater composition and effects

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

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

Table 2.1: Causes and Effects of Wastewater Pollution

# Causes Effects

Metals and organic

materials

Aesthetic inconveniences, toxic effect, death

and bio accumulation in the food chain

Bacterial infections Typhoid, cholera ,fever and bacillary dysentery diseases

Viral Infections Infectious hepatitis and poliomyelitis diseases

Protozoan infections Amoebic dysentery diseases

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

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

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

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

# Sources of refinery wastewater

Refinery wastewater originates from numerous sources and varies according to the quantity and degree of contamination (Pignatello*et al*., 1992). It contains oil which is the major contaminant in the wastewater being composed of a range of different hydrocarbons and other organic compounds present in the crude oil, and chemical substances produced by the refinery process such as sulphides, mercaptans, cyanides, ammonia, phenols, inorganic salts, and traces of some heavy metals (Lettinga*et al*.,1980).Table 2.2 shows the unit wise wastewater generation in petroleum refinery, with 350 m3/hr wastewater generated. The major wastewaters from petroleum refineriesare sour water from multiple processes, scrubber water from reformer catalyst regeneration, spent potassium hydroxide stream from alkylation, desalting wastewater, and caustic wash water from isomerization (Basheer *et el.,*2011). Furthermore, wastewater emanatesfromquench wastewater, rainwater run-off from paved areas in the processing unitsand cooling water leaking into the hydrocarbon stream of the heat exchanger (Mota*et al*.,2008).

# Refinery wastewater characterization

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

Table 2.2: Petroleum RefineryProcess Wastewater

|  |  |
| --- | --- |
| Units/ Processes in Refinery | Wastewater  flow rate (m3/hr) |
| Crude / Vacuum Distillation Unit | 171.04 |
| Catalytic Reforming Unit | 5.70 |
| Hydrocracker Unit | 16.22 |
| Naphtha/Diesel Hydrotreater Unit | 31.93 |
| Catalytic Cracking Unit | 15.20 |
| Hydrogen Generation Unit | 1.23 |
| Asphalt Plant/ Bitumen Blowing Unit | 13.07 |
| Product Blending | 87.44 |
| Sulfur Recovery Unit | 0.26 |
| Isomerization Unit | 3.26 |
| MEK Dewaxing Unit/ Solvent Unit | 0.01 |
| Aromatic Extraction Unit | 2.14 |
| Lube Oil/Specialty Processing Unit | 2.06 |
| Tank drawdown/ Washings | 0.76 |
| (Source: Srikumar and Papita, 2015) |  |

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

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

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

* + - 1. *Heavy metals*

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

* + - 1. *Phenols*

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

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

Table 2.3:Characteristics of Refinery Wastewater

|  |  |  |
| --- | --- | --- |
|  | **Minimum** | **Maximum** |
| Temperature (ºC) | 22 | 41 |
| pH | 6.2 | 10.6 |
| Conductivity (ms/cm) | 5.2 | 6.8 |
| BOD (mg/L) | 17 | 280 |
| COD (mg/L) | 140 | 3340 |
| Sulphides (mg/L) | 0 | 38 |
| Phenol (mg/l) | 11 | 14 |
| N-Hexane (mg/l) | 1.8 | 1.85 |
| Sulphate (mg/l) | 14.5 | 16 |
| Total dissolved solid (g/l) | 3.8 | 6.2 |
| Total suspended solid (g/l) | 0.03 | 0.04 |
| Hardness as CaCO3 (mg/L) | 139 | 510 |
| Alkalinity as CaCO3 (mg/L) | 77 | 356 |
| Oil (mg/L) | 23 | 200 |
| Phosphorus (mg/L) | 0 | 97 |
| Ammonia (mg/L) | 0 | 120 |
| Chlorides (mg/L) | 19 | 1080 |
| Sulphates (mg/L) | 0 | 182 |
| (Source: Mota *et al.,* 2008) |  |  |

# Parameter Limits

* + - 1. *Total dissolved solids*

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

# Wastewater Treatment Methods

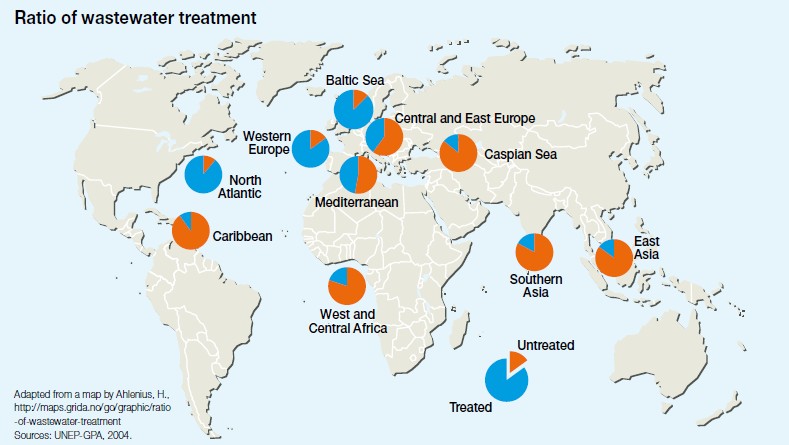
Almost all industrial processes produce contaminated water as a by-product. Treatment is then necessary before the water can be discharged to the environment or to a municipal wastewater treatment planttreatment.In many developing countries, more than 70 percent of industrial wastes are dumped untreated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

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

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

# Primary treatment method

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

The primary treatment steps involve:

1. Screening to remove large objects, such as stones that could plug lines orblock tank inlets.
2. Grit chamber to slow down the flow in orderto allow grit to fall out.
3. Sedimentation which is mostly achieved in a settling tank orclarifier, thesettleable solids settle out and are pumpedaway, while oils float to the top and are skimmed off.

# Secondary treatment methods

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

* + - 1. *Biological treatmentmethod*

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

* + - 1. *Biodegradation of organic compounds*

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

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

* + - 1. *Aerobic biodegradation process*

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

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

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

* + - 1. *Activated sludge reactor*

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

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

* + - 1. *Membrane bioreactor*

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

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

* + - 1. *Anaerobic biodegradation process*

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

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

* + - * 1. The insoluble organic pollutant brakes down into soluble substance, making them available for other bacteria.
        2. The acidogenic bacteria convert the sugars and amino acid into carbon dioxide, hydrogen, ammonia and organic acid;
        3. The organic acids convert into acetic acid, ammonia, hydrogen and carbon dioxide;
        4. The methanogens convert the acetic acid into hydrogen, carbon dioxide and methane, a kind of gaseous fuel.

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

* + - * 1. *Upflow anaerobic sludge blanket reactor*

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

Table 2.4: Advantages and Disadvantages of Membrane Methods

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Process** | **Target pollutants** | **Separation efficiency** | **Advantages** | **Disadvantages** |
| Biological | -COD | -96% | Generally for | -Higher membrane |
| Reactor | -Activated Sludge | - - - | membrane methods: | fouling |
| Membrane |  |  | -Lower energy | -High fixed costs |
|  | | | consumption |  |
| -Separation with no |  |
| need to use material |  |

Ultrafiltration

Microfiltration

-COD

* TOC
* Polymers

-Benzene, Toluene and Xylene

-Heavy metals (copper, etc.)

* Solids

-Petroleum compounds

* Suspended materials
* Q & G
* Suspended solids

- 90%

- 98%

- - - -

- 54%

- 95%

- 73%

- 54

* Very good
* >5 mg/ l
* >1 mg/l

-Performing separation at ambient temperature

-Low weight and size of separation equipment

-Simple installation and operation

-Minimum need for control, inspection and maintenance

-Ease of access and possible use of separate phases

Generally for membrane methods:

-Membranes becoming dirty and decreased flow rate

-Sensitivity to operating parameters and feed characteristics

-Requiring constant cleaning and parts replacement

Nanofiltration

* COD
* TOC
* Oil

- 90%

- 98%

* Remained

< 1%

Reverse osmosis

* Separation of all compounds
* Water
* Ions (K+, Na+, Mg2+, Ca2+)

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

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



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

* + - * 1. *Anaerobic biofilter*

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

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

Anaerobic biofilter system has numerous advantages such as:

The filler provides a large surface area for the growth of the microorganisms, and the filler also increases hydraulic retention time of the wastewater;

The system provides a large surface area for the interaction between the wastewater and film.

The fact that microorganisms grow on the filler reduces the run of the degraders.

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

# Advanced Oxidation Processes

Nowadays, due to the increasing presence of molecules, refractory to the microorganisms inthe wastewater streams, the conventional treatment methods (Primary and Secondary methods) cannot be used for complete treatment of the effluent. Therefore, it is imperative to introduce newer treatment technologies to convert effluents into less harmful or lower chain compounds (Chunli, 2013). The newer technologies include microscreening, precipitation, adsorption, ion exchange, resverse osmosis, electrodialysis,chlorination and ozonation and others as shown in Figure2.3. Advanced oxidation processes (AOP) is also known as tertiary treatment method, and is any level of treatment beyond

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

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

Generally, AOP is one of the newer treatment processes which utilize chemical oxidant (H2O2, O3, K2MnO4, K2FeO4 and others) to oxidize pollutant to slightly toxic, harmless substances or transform it into manageable form. Similarly, AOP constitute the use of oxidizing agents such as ozone and hydrogen peroxide, exhibit lower rates of degradation.

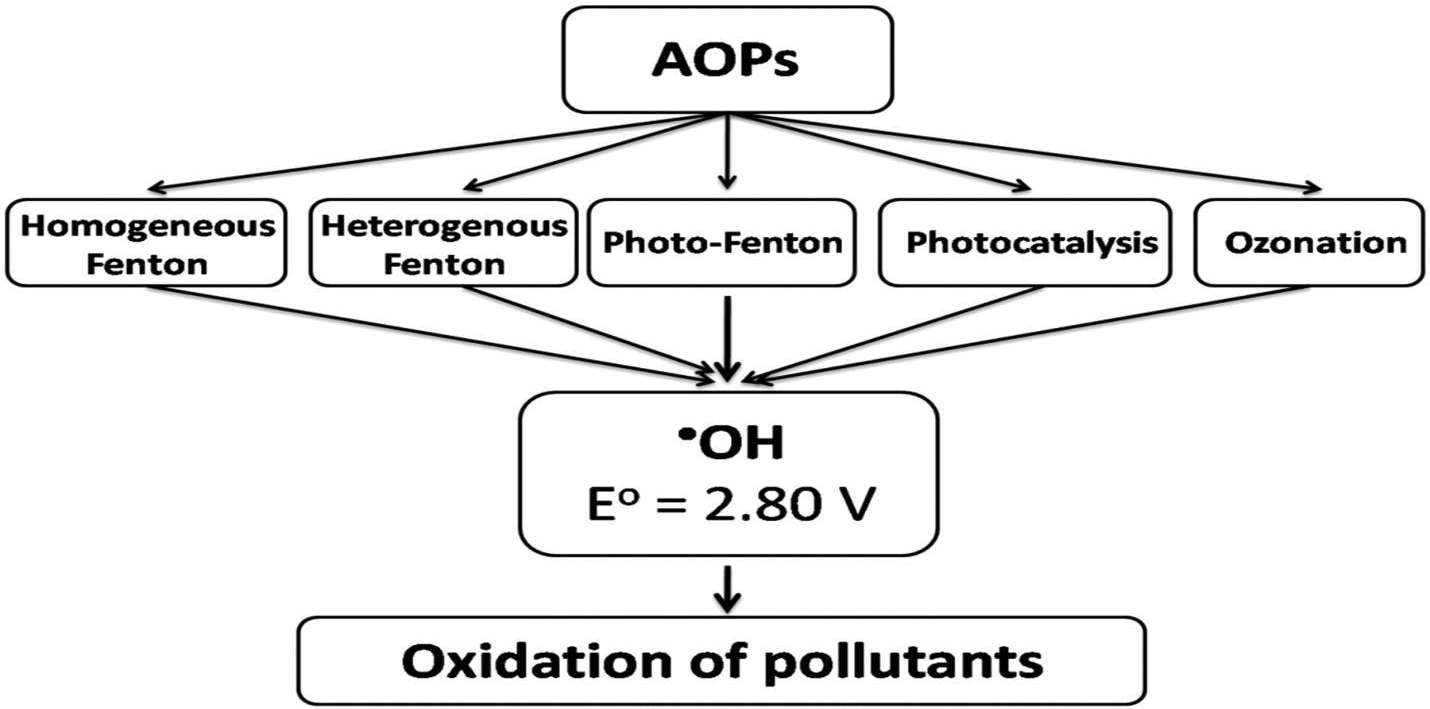


Figure 2.3: Advanced oxidation process (Source:Glaze and Chapin,1987)

Table 2.5: Description of Some AOP Technologies

AOP Brief

Description

System

Components

Advantages Disadvantages

H2O2/ UV

The .OH radical route is the predominant removal mechanism.

-UV Lamp

-H2O2storage and injection system

-Reaction chamber

-In line mixer

-Temperature controller

-Pumps and piping

-Monitoring and control system

-No potentials for bromate formation

* Can be used for full scale water treatment

-No off gases treatment required

-Not limited by mass transfer

-Turbidity can interfere with UV light penetration

-Less stiochiometrically efficient at generation .OH

-Interfering components (eg nitrate) can absorb UV light

H2O2/O3 The .OH formed

can oxidize most dissolved organic matters to form byproducts

O3/UV -The .OH are

generated with UV light is applied to ozonated water.

-Destruction of organic compounds .OH reactions occupied with direct photolysis and oxidation by molecular ozone

(Source: Hoigne, 1998).

* H2O2injection and storage systems.

-O3generators and diffuses

-Contactor and mixing vessels

-O3 off gas catalytic decomposer

-Pumps and piping

-Monitoring and control system

-UV Lamp

-H2O2storage and injection system

-Reaction chamber

-In line mixer

-Temperature controller

-Pumps and piping

-Monitoring and control system

-Supplemental disinfectant

* More effective than UV or H2O2 alone

-Established technology for remediation applications

-Supplemental disinfectant

* More effective than UV or O3 alone

-More efficient at generating .OH than H2O2/UV process for equal oxidant concentrations

* May require treatment for excess H2O2due to potential for microbial growth
* May require ozone off gases treatment
* Energy and cost intensive
* potential for bromate formation

-Turbidity can interfere with UV light penetration

* May require ozone off gases treatment
* Interfering components (eg nitrate) can absorb UV light

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

# Adsorption treatment methods

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

# Activated carbon treatment method

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

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

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

# Zeolites

Zeolites are minerals or synthetic resins that have ion exchange capabilities (Thomas, 2001).There are several types of zeolites such as MCM-22, ZSM-5, ZSM-22, BETA, and

Y. Studies showed that synthetic zeolites have higher adsorption capacity than the natural

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

# Natural materials

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

# Photocatalysis

Photocatalysis is a promising and very attractive wastewater treatment method. However, the process is achievedusing titanium dioxide (TiO2) for water splitting after UV irradiation, it has been shown that this can encompass a wide range of reactions, especially the oxidation of organic compounds. Therefore, several studies on photo degradation of substances such as halogenated hydrocarbons, aromatics, nitrogenated heterocyclic, hydrogen sulfide, surfactants and herbicides, and toxic metallic ions, among others has clearly shown that the majority of organic pollutants present in waters can be mineralized or at least partially destroyed. The photocatalytic activity is dependent on the surface and

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

Several variety of semiconductor powders such as oxides and sulfides, acting as photocatalysts have successfullybeen utilized. However, TiO2has mostly been considered due to its high photocatalytic activity having a maximum quantum yields, its resistance to photo corrosion, its biological immunity and low cost. Basically, there are two types of reactors,namely reactors with TiO2suspended in the reaction medium and reactors with TiO2 fixed on a carrier material (Li *et al*., 2009). A very promising method for solving problems concerning the separation of the photocatalyst from the reaction medium is the application of photocatalytic membrane reactors (PMRs), having other advantages such as the realization of a continuous process and the control of a residence time of molecules in the reactor (Mozia, 2010). Therefore, the self-assembly of TiO2 nanoparticles was established through coordinance bonds with (.OH) functional groups on the membrane surface, improving reversible deposition, hydrophilicity and flow and diminishing the irreversible fouling (Mansourpanah *et al*., 2009). TiO2functionalized membranes may be obtained by different methods, but the sol gel process is used because it has numerous exceptional features such as purity, homogeneity, controlover the microstructure, ease of processing, low temperature and low cost (Alphonse *et al*., 2010).

# Fenton Oxidation

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

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

The standard reduction potentials (1.77V) of hydrogen peroxide imply that it is a strong oxidant in both acidic and basic solutions. It can oxidize many kinds of organic contaminants in wastewater directly. However, the classical Fenton oxidation process has the advantages of being nonselective and effective in the treatment of severalwastewaters. Furthermore, it is a cost effective treatment methodby using hydroxyl radicals and easy to handle reagents, and treats wastewater with COD of more than 500mg/l.The disadvantages in using the Fenton reagent include the production of a substantial amount of Fe(OH)3 precipitate,need for pH adjustment before and after oxidation and residual catalyst in the treated effluent which requires further purification (Di Iaconi *et al*., 2010).

# History of Fenton oxidation

H.J.H. Fenton discovered in 1894 that hydrogen peroxide (H2O2) could be more reactive by the use of Fe (II) salts to oxidize tartaric acid. Subsequently, iron catalyzedH2O2 activation became known as FenWRQ¶V RR[esLeaGrchDwWaLs lRateQr do ne considering different metals to investigate their potentials in terms of power to generatehydroxyl radical (OH.)and theirelectron transfer propertieswhich eventually improve the use ofH2O2. Pignatello *et al*., (2006) made athorough review on history of Fenton oxidation covering the century of its existence. Laboratory investigations were the final phase of the trend in Fenton oxidation which promoted interest in the process as the strength and frugal

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

# Fenton process

Fenton oxidation basic principle has been extensively studied and elaborated by several researchers (Umar *et al.*, 2010),the summary of trends of the process is listed in Table 2.6. Basically, the process is an oxidative cycle shown in Figure 2.4 with amultipurpose oxidant (H2O2)inducedvia catalytic decomposition of H2O2 by ion (Fe2+) as shown in 2.5,and ion (Fe3+)are also produced. The cycle is completed by the reduction of ferric iron by H2O2 and the subsequent generation of per hydroxyl radicals and ferrous iron (Lucas *et al.*, 2007).

The series of the Fenton reactions are as follows:

(2.1)



 (2.2)



 (2.3)



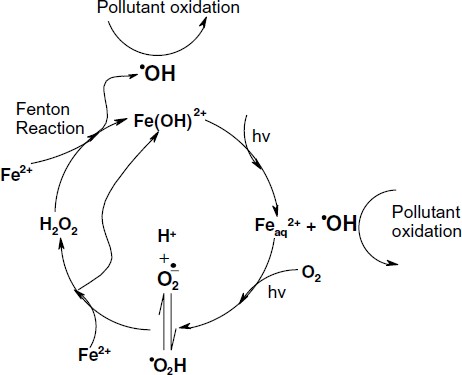


Figure 2.4: Schematic diagram of photo-assisted Fenton oxidation (Rodraguez *et al*., 2005).

Table 2.6:Summary of the Trends in Fenton Oxidation Evolution

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Researcher(s)** | **Findings/Highlights** |  |  |  |  |  | **Year** |
| Fenton | Correspondence to | the | journal | editor | of | Chemical | 1876 |

Newsdescribing a violet colour emanating fromthe reaction between H2O2, tartaric acid, an Fe(II)salt and a base as a test for tartaric acid

Fenton Identifying the violet colour as arising from a complex formed between iron and the oxidation product of tartaric acid

Fenton Pioneered the Fenton oxidation by the discovery that Fe(II) salts could activate H2O2and potentially oxidize tartaric acid in a characteristic way, providing a new and valuable oxidizing agent

1881

1894

Haber and Weiss

Barb and coworkers

Proposed that the active oxidant generated by the Fenton reaction LV 2+

Proposed the chain reaction mechanism in the Fenton oxidation aV ³FODVVLFDOa´fte r RsevUer al ³yeIarsUofHinHve stiUgaDtioGn on organic compounds

1934

1949-

1951

Eisenhauer Application of Fenton oxidation in small-scale industry 1964

Walling and co-workers

Buxton and co-workers

Several Workers

Novel work on the free radical pathway of the Fenton oxidation. The reported results were central to the understanding and subsequent Proliferation of research in varied branches of the Fenton oxidation.

'RFXPHQWHG RYHU OH r eacUtioDnsWwHit h organic and inorganic compounds in aqueous solution

The beginning of extensive research on the applications of Fenton oxidation for waste treatment in academic laboratories

1975

1988

1990

-

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

Mineralization of the RHcomponent of the wastewater induces free organics as

transient intermediates,and are subsequently oxidized to produce more stable products by hydroxyl radicals, hydrogen peroxide,oxygen and ions ( Fe3+,Fe2+) as shown in

equations ( 2.4-2.8) (Umar *et al* ., 2010).

(2.4)



(2.5)



(2.6)



(2.7)



 (2.8)



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

Generally, i n the presence of UV radiations (photo-Fenton process), an additional number

of HO. Radicalsare produced both through direct H2O2 photolysis and through UV radiations interaction withthe iron species in aqueous solutions (Eq. 2.9-2.11) (Pignatello, 1992)

(2.9)



