CHAPTER ONE

INTRODUCTION

1.1 GENERAL OVERVIEW

Treatment of wastewaters is becoming more important due to diminishing fresh water resources, increasing wastewater disposal costs, and stricter wastewater discharge regulations that have lowered permissible contaminant levels in wastewater streams. In many countries, tannery industry is one of the major contributors to national economy and provides employment opportunities to people. Tanning involves a complex combination of mechanical and chemical processes. The preservation and processing of raw hides and skins for tanning process cause severe environmental pollution (Sarkar, 1981).

The World production of leather is 22700.5 mft²/y (FAO, 2008). The characteristics of tannery effluent vary considerably from tannery to tannery depending upon the size of the tannery, chemicals used for specific process, amount of water used, etc. Wastewater from a typical tannery contains large concentration of biochemical oxygen demand (BOD), chemical oxygen demand (COD), Chromium ions, sodium sulphide and suspended solids. Leather is mostly produced by chrome tanning compared to vegetable tanning because chrome tanning is more suited for certain applications, particularly for upper parts of boots and shoes, and requires less processing time than vegetable tanning. Conventional chrome tanning results in wastewater containing as high as 5-3000 mg/l of chromium. Chromium has acute and chronic toxicity to humans (Aravindhan et al., 2004). Chromium toxicity is dependent on its oxidation state. Chromium (vi) compounds are more soluble than chromium (iii) and much more toxic (mutagenic and carcinogenic) to microorganisms, plants and animals (Freiberg et al, 1980).
The excess of chromium (iii) is also proven to be potential soil, surface water, ground water and air contaminant under specific condition (Rao et al., 1999).

Wastewater treatment methods are broadly classified into physical, chemical and biological (Metcalf and Eddy, 1999). Some of the treatment methods for tannery wastewater include sedimentation, electrofloatation, filtration and membrane filtration; chemical precipitation, coagulation, adsorption, ion exchange. Since some components of organic tannery wastewater are resistant to conventional chemical and biological methods of treatment (Schrank et al., 2004), there is the need for the development of an alternative methods of treating tannery effluent.

This work focuses on photocatalysis as an alternative method for treating raw effluent obtained from the Nigeria Institute of Leather and Science Technology (NILEST) Zaria. The method has been applied to reduce Cr (VI), COD and BOD₅ contents of raw tannery effluent using visible light from a 500W halogen lamp. The photocatalysts (ZnO-ZnFe₂O₄ composite and ZnFe₂O₄ composite on activated carbon support) used were synthesized and characterized using XRD, XRF and modified BET techniques. The efficiency of the photocatalytic treatment has been compared with that of adsorption on activated carbon. The obtained kinetic data for photocatalysis has been fitted to Langmuir-Hinshelwood kinetic model.

1.2 AIM AND OBJECTIVES

The aim of this work was to use ZnO-ZnFe₂O₄ and ZnO-ZnFe₂O₄/activated carbon composite photocatalysts for the treatment of tannery effluent.
Specific objectives are;

I. To synthesize ZnO-ZnFe$_2$O$_4$ composite photocatalyst and ZnO-ZnFe$_2$O$_4$ composite photocatalyst supported on activated carbon using co-precipitation method.

II. To characterize the photocatalyst using XRF, XRD and BET Method.

III. To treat raw tannery effluent using activated carbon (Adsorption).

IV. To treat the same raw tannery effluent using the synthesized photocatalysts

V. To compare the results for adsorption and photocatalysis

1.3 PROBLEM STATEMENT

I. Conventional Methods used for treatment of tannery effluent are usually laborious and often cannot be carried out under ambient conditions and at same time generate large volume of sludge.

II. Conventional photocatalysts such as titanium dioxide (TiO$_2$) and zinc oxide (ZnO) have high band energy making them effective only in the presence of ultra-violet light.

1.4 SCOPE

I. Synthesis and characterization of ZnO-ZnFe$_2$O$_4$ photocatalyst and ZnO-ZnFe$_2$O$_4$ photocatalyst supported on activated carbon.

II. Evaluation of the efficiency of the photocatalysts in the reduction of COD, BOD$_5$ and chromium ions in raw tannery effluent.

III. Comparing the effectiveness of photocatalysis with that of adsorption on activated carbon for treating tannery effluent.

IV. Studying the effects of time, photocatalyst dose, and initial COD, BOD$_5$ and chromium ions contents as well as pH on the adsorption and photocatalytic processes.

V. Using Langmuir-hinshelwood kinetics to explain and develop a kinetic model for the photocatalytic reactions.
1.5 JUSTIFICATION

I. The discharge of tannery effluent into the environment is considerably increasing over the last decades because of increasing industrial activities which has contributed pollution.

II. Zinc Nitrate, Iron Nitrate and ammonium hydroxide which are the reactants for the synthesis of the photocatalyst are readily available and cheap.

III. Photocatalysis can be performed under ambient conditions (room temperature and atmospheric pressure).
CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, a detailed literature review was presented and the discussion focused on the current trends in the following key areas;

- Tanning and Tannery
- Tannery Effluent
- Methods of Treating Tannery Effluent
- Photocatalysis
- Determination of Photocatalytic Efficiency (PE)
- Determination of Surface Area and Crystalline Size of Solids
- Langmuir–Hinshelwood Kinetic Model of Photocatalytic Processes
- Previous Related Works

2.2 TANNING AND TANNERY

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling wastewater. (Thakur, 2006). Tannery is a place where skin and hides are converted to leather products. In the leather manufacturing industry, the term ‘hide’ refers to skins from larger animals, while ‘skin’ refers to that of smaller animals (Sawyer et al, 2003).

The tanning process consists of strengthening the protein structure of the putrescible skin by creating a bond between the peptide chains. The skin is made up of three layers being the epidermis, dermis and subcutaneous layers. The dermis consists between 30-35% protein,
which is mostly collagen, with the remainder being fat and water. It is the dermis that is used to make the leather after the other layers have been removed chemically or mechanically. The whole tanning process uses acids, alkalis, salts, enzymes and tanning agents to dissolve the fats and non-fibrous proteins, as well as chemically bond the collagen fibres. The tanning process also produces a lot of waste which is an environmental concern (Wang et al., 2007).

The generic tanning process involves several steps, depending on the type of skin used and its desired end product. Some of the steps are discussed in subsection 2.1

2.2.1 Curing

This process involves salting and/or drying the skin once it's been stripped from the dead animals. This is an immediate step upon removal and takes place inside the meat-packing industry. Skins can be cured in one of two ways:

(a) Wet salting: Salting the skin and then piling many skins together until a moist bunch is formed. They are then left for a month allowing the salt to be completely absorbed into the skin.

(b) Brine curing: Is more common than wet-salting since it is considered as being faster and easier. During brine-curing, skins are placed in vats and smothered with a mixture of salt and disinfectant. This process takes up to 16 hours with the skins being completely cured to proceed to the next stage.

2.2.2 Soaking

Once cured, the skins are then soaked in water for several hours to several days. The water aids in the removal of salt, dirt, debris, blood and excess animal fats.
2.2.3 Hair Removal

At this stage the animal hair is still present. The skins are transported to another large vat and immersed in a mixture of lime and water, which loosens the hair from the skin. After soaking from 1 to 10 days, the hair is then mechanically removed from the skin.

2.2.4 Scudding

Any stray hairs and fat which were missed are removed with a plastic tool or dull knife, by hand.

2.2.5 Deliming:

After the hair, debris and excess fats have been removed from the skin, the skins are delimed in a vat of acid. After the lime has been pulled from the skin, skins are then treated with enzymes, which smoothens the grain of the leather allowing for a product that is soft and flexible.

The treatment of skins can be repeated several times during the tanning process. The type of tanning procedure depends on the type of skin and the resulting product intended. Wet-blue comes from "hides", wool skins, dewoollled or fell mongered pickled-pelts from sheepskins, finished leather or sole leather.

2.2.6 Vegetable Tanning

Skins are tanned with a vegetable tanning agent solution to produce flexible, but stiff leather. This process involves stringing the skins on large frames, situated in large vats, and exposing them to tannin, a natural product found in wood bark and leaves and fruits from oak, chestnut and hemlock trees. Skins are treated repeatedly with each step involving the skins being soaked in a stronger solution of tannin every time, this type of leather is used in luggage, furniture, leashes, belts, hats and harnesses.
2.2.7 Mineral Tanning

It is the most common tanning type in the world. Mineral or chrome tanning is carried out on skins needed for softer, stretchier leathers. Skins are pickled first in an acid and salt mixture then soaked into a chromium-sulphate solution. Mineral tanning is a faster process than vegetable tanning since it usually takes 1 day. This type of leather is found in purses, bags, briefcases, gloves, shoes, boots, pants, jackets, and sandals.

2.1.8 Dyeing Process

Depending on the desired product, the skins go through a dyeing process which involves replacing moisture back into the skin. Skins that have been vegetable tanned are bleached and then soaked with oils, soaps, greases and waxes to make them more pliable.

(a) Rolling: This involves running the skins through a machine to produce leather that is firm and stronger. After the rolling process, the leather is stretched and dried out in a heat controlled room.

(b) Finishing compound: This is the final step in the tanning process. The process involves covering the grain surface with a chemical compound and then brushing it. Light leathers are buffed and sandpapered to cover any imperfections. Leathers that have been buffed for long periods of time become suede.

2.3 TANNERY EFFLUENT

Tannery effluent is a wastewater generated when hides and skin are converted to leather. They are also of large-scale environmental concern because they colour and diminish the quality of water bodies in which they are released. Their disposal into the environment creates adverse effect by altering the normal physicochemical properties of soil and water. The parameters that
are often considered in a typical tannery effluent are fully discussed in sub-section three of this thesis.

2.3.1 Parameters in Tannery Wastewater

2.3.1.1 Biochemical Oxygen Demand (BOD)

BOD is the amount of oxygen used by organisms while consuming organic matter in a waste water sample. It is possible to assess the performance of a wastewater treatment plant by measuring the BOD$_5$ of the inflow and outflow. Many factors can influence this test, such as temperature of incubation, dilution rate, nitrification, toxic substances, and nature of bacterial seed and presence of anaerobic organisms (McCaffrey, 2001).

2.3.1.2 Chemical Oxygen Demand (COD)

This method measures the oxygen required to oxidise the effluent sample wholly. It sets a value for the materials that would normally be digested in the BOD$_5$ analysis, the longer term biodegradable products, as well as the chemicals that remain unaffected by bacterial activity. The method is very aggressive. A suitable volume of effluent is boiled with a powerful oxidising agent (potassium dichromate) and sulphuric acid. As the effluent components oxidise, they use oxygen from the potassium dichromate, the amount used being determined by titration. This method is often favoured as it provides rapid results (hours as opposed to days). It is more reliable and cost effective as it is easier to manage larger numbers of samples.

2.3.1.3 pH

This is the concentration of hydrogen ions in solution and indicates the level of acidity or alkalinity of an aqueous solution. If the pH of the waste water is outside the range of 5-10, there may be considerable interference with biological processes (McCaffrey, 2001).
2.3.1.4 Salinity

Salinity is a measure of the dissolved salts in the water. Salinity is usually highest during periods of low flows and increases as water levels decrease. Salinity is measured as either TDS (Total Dissolved Solids), which measures the amount of dissolved salts in the water, or as EC (Electrical Conductivity), which is the property of a substance which enables it to serve as a channel or medium for electricity. Salty water conducts electricity more readily than purer water. A sample’s EC can be converted to TDS and vice versa (McCaffrey, 2001).

2.3.1.5 Turbidity

Turbidity is a measure of the ability of light to pass through water, that is, a measure of the water’s murkiness. Measuring murkiness gives an estimate of suspended solids in the water. The series of turbidity-induced changes that can occur in a water body may change the composition of an aquatic community. First, turbidity due to a large volume of suspended sediment will reduce light penetration, thereby suppressing photosynthetic activity of phytoplankton, algae, and macrophytes, especially those farther from the surface. If turbidity is largely due to algae, light will not penetrate very far into the water, and primary production will be limited to the uppermost layers of water. Cyanobacteria (blue-green algae) are favoured in this situation because they possess flotation mechanisms. Overall, excess turbidity leads to fewer photosynthetic organisms available to serve as food sources for many invertebrates. As a result, overall invertebrate numbers may also decline, which may then lead to a fish population decline. Turbidity is measured in Nephelometric Turbidity Units (NTU’s).

2.3.1.6 Chromium (Cr $^{3+}$ and Cr $^{6+}$)

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the retanning system and is displaced from leathers during retanning and dyeing processes.
Chromium is discharged from processes in soluble form; however, when mixed with tannery waste waters from other processes (especially if proteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, which add to sludge generation. If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, Cr$^{3+}$ and Cr$^{6+}$ are toxic to human beings (McCaffrey, 2001).

2.3.1.7 Chlorides (Cl$^-$)

Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Chlorides inhibit the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdowns in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the eco-system and may ultimately end up in the ground water. High salt contents are only acceptable if the effluents are discharged into tidal/marine environments (McCaffrey, 2001).

The level of salt as chloride under acid conditions can be determined by titrating a known volume of effluent with a silver nitrate solution, using potassium chromate as an indicator. Under neutral or alkaline conditions, excess silver nitrate is added. This excess is then determined by retro-titration with potassium thiocyanate, using ferric alum as the indicator.

2.3.1.8 Oils and Grease

During leather manufacture, natural oils and grease are released from within the skin structure. If fat liquor exhaustion is poor, some fatty substances may be produced through inter-reaction when waste waters mingle. Floating grease and fatty particles agglomerate to form ‘mats’
which then bind other materials, thus causing a potential blockage problem especially in effluent treatment systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulsify, they create a very high oxygen demand on account of their bio-degradability.

The presence of oils and grease is determined by shaking the effluent sample with a suitable solvent and allowing the solvent to separate into a layer on top of the effluent. This solvent dissolves fatty matter, and a quantity can be drawn off and evaporated until dried. The residual grease can be weighed and calculated (McCaffrey, 2001).

2.3.1.9 Total Suspended Solids

Total Suspended solids is an indication of the amount of erosion that took place nearby or upstream. This parameter would be the most significant measurement as it would depict the effective and compliance of control measures e.g. riparian reserve along the waterways. The series of sediment-induced changes that can occur in a water body may change the composition of an aquatic community. First, a large volume of suspended sediment will reduce light penetration, thereby suppressing photosynthetic activity of phytoplankton, algae, and macrophytes. This leads to fewer photosynthetic organisms available to serve as food sources for many invertebrates. As a result, overall invertebrate numbers may also decline, which may then lead to decreased fish populations. In addition, sediment may interfere with essential functions of organisms. The numbers of filter-feeding invertebrates will decline if their filter mechanisms are choked by suspended particles. Some zooplankton suffer decline due to clogged feeding mechanisms. Likewise, fish may suffer clogging and abrasive damage to gills and other respiratory surfaces. Abrasion of gill tissues triggers excess mucous secretion, decreased resistance to disease, and a reduction or complete cessation of feeding. Suspended sediment may also affect predator-prey relationships by inhibiting predators' visual abilities.
2.3.1.10 Colour

Colour is vital as most water users, be it domestic or industrial, usually prefer colourless water. Determination of colour can help in estimated costs related to discolouration of the water. It is measured in Hazen units (McCaffrey, 2001).

2.4 METHODS OF TREATING TANNERY EFFLUENT

2.4.1 Electrocoagulation-Flotation (ECF)

ECF is a treatment process of applying electrical current to treat and flocculate contaminants without having to add coagulants. Coagulation occurs with the current being applied, capable of removing small particles since direct current applied, setting them into motion. Also electrocoagulation could reduce residue for waste production. Electrocoagulation-flotation is a better alternative method to classic chemical coagulation for many reasons. ECF is capable of reducing the need for chemicals due to the fact that the electrodes provide the coagulant. However, many individuals still use chemical coagulants to attempt to enhance treatment. Traditionally, chemical coagulation involves the use of alum (aluminium sulphate), ferric chloride (FeCl₃), or ferrous sulphate (Fe₂SO₄) which can be very expensive depending on the volume of water treated. When applying the coagulant, the coagulant performs a similar function as the electrodes, neutralizing the charge of the particulates, thereby allowing them to agglomerate and settle at the bottom of the tank. In addition, electrocoagulation-flotation is capable of reducing waste production from wastewater treatment and also reduces the time necessary for treatment (Sengil et al., 2009).

2.4.2 Biological Reduction Processes

The processes of biological reduction frequently used is the activated sludge process (ASP) and the upflow anaerobic sludge blanket Process. In general, ASP based treatment is considered
to be energy – intensive and expensive from an operation and maintenance point of view. On the other hand, anaerobic processes claim to offer several advantages especially under tropical climatic conditions (Walenciak et al, 1999).

2.4.3 Precipitation & Foam Fractionation

The electrolytic precipitation process is highly dependent on the chemistry of the tannery waste water, especially its conductivity. In addition other characteristic such as pH, particle size and chemical constituent influence the process. Foam fractionation is experimental method based on the phenomena that surface- active solutes collect at gas-liquid interfaces. However, the chemical costs make this treatment method too expensive (Chang, 2003).

2.4.4 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications for water purification. (Oremusová, 2007).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption
Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to
the surface only through Van der Waals (weak intermolecular) interactions, which are also
responsible for the non-ideal behaviour of real gases.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the
formation of a chemical bond, as opposed to the readily bonded Van der Waals forces which
cause physisorption.

Adsorption is usually described through isotherms, that is, functions which connect the amount
of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can
find in literature several models describing process of adsorption, namely Freundlich isotherm,
Langmuir isotherm, BET isotherm, etc. (Oremusová, 2007).

Activated carbon has long been used as a standard adsorbent for treatment of tannery effluent.
In spite of their importance in various cleaning procedures activated carbon remain expensive;
therefore the development of low cost alternative adsorbent has been the focus of recent
research. Many researchers have used agricultural waste such as banana & orange peel, wheat
straw, sugar cane dust, saw dust, rice husk, waste mud & wood materials, cotton, bark, hair,
coal, sewage sludge based activated carbon, coir pith, almond shell, walnut shell, fly ash,
bottom ash, soil etc. as adsorbent (Oremusová, 2007).

2.4.5 Electrochemical Process

The electrochemical processes have found use in destruction of toxic and non-biodegradable
organic matter by direct or indirect oxidation/reduction. These methods are very promising as
they involve the controlled degradation of the pollutants. They are moreover very effective
towards reduction of chromophoric groups of metals, which is the main disturbing factor for
water recycling in most of the industries (Chandra et al., 2004).
2.5 PHOTOCATALYSIS

The word photocatalysis is of Greek origin comprising of two parts: the prefix “photo” means light and the “catalysis” means break apart or decompose. Hence, photocatalysis can generally be described as a process in which light is used to activate a substance, the photocatalyst that aid this process is itself not involved in the chemical transformation. Photocatalytic reactions are classified into homogeneous photocatalysis in which both the photocatalyst and the substrate are of the same phase and the heterogeneous photocatalysis in which both the photocatalyst and the substrate are in different phases. However, heterogeneous photocatalysis is by far more intensively studied in recent years because of its potential use in a variety of environmental and energy-related application as well as in organic synthesis. The reaction scheme in heterogeneous photocatalysis involves the formation of an interface between a solid photocatalyst (metal or semiconductor) and a fluid containing the reactants and products of the reaction. Therefore, heterogeneous photocatalysis is mainly used in cases where a light-absorbing semiconductor is utilized, which is in contact with either a liquid or a gas phase (Beydoun et al., 1999).

2.5.1 Application of Photocatalysis

Both the technological and economic importance of photocatalysis has considerably increase over the past decades. Improvement in performance have been strongly correlated to advances in nanotechnology. For example, the introduction of nanosized photocatalysts has tremendously enhanced the catalytic efficiency of specific materials. A variety of application ranging from anti-fogging, anti-microbial and self-cleaning surfaces through to water and air purification and solar induced hydrogen production have been developed and many of these
have made their way into commercial products. However, extensive research continues to
further optimize this technology and to widen the spectrum of potential applications. Some of
the application of photocatalysis are given in figure 2.1.

Figure 2.1: Spectrum of Photocatalytic Applications (Source: Serpone and Pellizette,
2000)

2.5.1.1 Self-Cleaning Surfaces

This support the light induced destruction of adherent organic molecules and is of particular
importance for anti-bacterial, anti-viral and fungicidal applications. Particular relevance is
given to surface sterilisation in areas such as biomedical engineering and food preparation.
(Serpone and Pellizette, 2000)

2.5.1.2 Super Hydrophilic Surfaces

Photo-induced hydrophilicity is generated by the exposure of a TiO₂- treated surface to intense
UV light. Water is prevented from forming droplets and instead covers the surface with a
homogeneous thin wetting layer, which penetrates below dirt particles. Hydrophilic surfaces
are thus easy to clean by pure water sprinkling and demonstrate considerable anti-fogging
effects. Wet vehicle rear-view mirrors will therefore impact on the user’s view to a lesser extent (Serpone and Pellizette, 2000).

A combination of both effects generates considerable self-cleaning properties. Organic dirt can easily be washed off, for example by the next rain shower, surfaces remain clean, and moreover possess anti-microbial properties. Photocatalytically active surfaces of glass, metals or ceramics are also widely established.

2.5.1.3 Air Purification

Photocatalytic surfaces have the potential to act against a variety of air pollutants and odours such as microbes, volatile organic carbons (VOC), formaldehyde, ammonia and inorganic gaseous substances such as nitrogen- or sulphur-oxides (NOx, SOx). Meanwhile a variety of technical products are commercially available. Applications include photocatalytic components for air filters, ventilation, and air conditioning systems via active decomposition of cigarette smoke or automotive and industrial exhaust to general air purifying effects of larger photoactive building elements (Portela et al., 2012).

2.5.1.4 Destruction of Warfare Agents

Photocatalysts have the potential to decompose various hazardous substances at least in mild conditions. Researchers have examined the photocatalytic degradation of chemical warfare agents (CWAs), and the results indicated that photocatalysts can support the detoxification of hazardous compounds. However, they must be applied as an additional component within larger decontamination measures (Hitchman et al., 1997).

2.5.1.5 Conversion of Carbon Dioxide

Conversion of carbon dioxide into gaseous hydrocarbons using titanium dioxide in the presence of water. As an efficient absorber in the UV range, titanium dioxide nanoparticles in
the anatase and rutile phases are able to generate excitations by promoting electrons across the Bandgap. The electrons and holes react with the surrounding water vapor to produce hydroxyl radicals and protons. At present, proposed reaction mechanisms usually suggest the creation of a highly reactive carbon radical from carbon monoxide and carbon dioxide which then reacts with the photogenerated protons to ultimately form methane. Although the efficiencies of present titanium dioxide based photocatalysts are low, the incorporation of carbon based nanostructures such as carbon nanotubes and metallic nanoparticles have been shown to enhance the efficiency of these photocatalysts (Varghese et al., 2009).

2.5.1.6 Conversion of Water to Hydrogen

Conversion of water to hydrogen gas by photocatalytic water splitting. An efficient photocatalyst in the UV range is based on a sodium tantalite (NaTaO₃) doped with La and loaded with a cocatalyst nickel oxide. The surface of the sodium tantalite crystals is grooved with so called nanosteps that is a result of doping with lanthanum (3–15 nm range). The NiO particles which facilitate hydrogen gas evolution are present on the edges, the oxygen gas evolves from the grooves (Nathan and Daniel, 2006).

2.5.2 Mechanisms of Photocatalysis

Semiconductors are particularly useful as photocatalysts because of a favourable combination of electronic structure, light absorption properties, charge transport characteristics and excited state lifetimes. A semiconductor by definition is nonconductive in its undoped ground state because an energy gap called bandgap exists between the top of the filled valence band and the bottom of the vacant conduction band as seen in figure 2.2:
Figure 2.2  Mechanism of Photocatalysis (Source: Jos et al., 2004)

Thus, electron transport between these bands must occur only with appreciable energy change. In semiconductor photocatalysis, excitation of an electron from the valence band is accomplished by absorption of a photon of energy equal to or higher than the bandgap energy of the semiconductor. This light-induced generation of an electron-hole pair is a prerequisite step in all semiconductor mediated photocatalytic processes. In this process, photogenerated species tend to recombine and dissipate energy as heat of photons, because the kinetic barrier for the electron-hole recombination process is low. However, conduction band electrons and valence holes can be separated efficiently in the presence of an electric field, such as the one formed spontaneously in the space charge layer of a semiconductor-fluid or a semiconductor metal interface. Therefore, the lifetime photogenerated carriers’ increase and the possibility are offered to these species to exchange charge with substrates adsorbed on the photocatalyst surface and initiate chemical reactions.
Interfacial electron transfer i.e. transfer of electron to or from a substrate adsorbed onto the light-activated semiconductor is probably the most critical step in photocatalytic processes, and it’s efficiency determines to a large extent the ability of the semiconductor for a given redox reaction. The efficiency of electron transfer reactions is in turn, a function of the position of semiconductors conduction and valence band-edges relative to the redox potential of the adsorbed substrates. For desired electron transfer to occur, the potential of the electron acceptor species should be located below (more positive than) the conduction band of the semiconductor, whereas the potential of the electron donor species should be located above (more positive than) the valence band of the semiconductor. Interfacial electron transfer processes are then initiating subsequent (dark) redox reaction to yield the ultimate products. The overall scheme of semiconductor-mediated photocatalytic reaction is described by the following general Equation:

\[ OX_{1\text{ads}} + Red_{2\text{ads}} \rightarrow OX_{2\text{ads}} + Red_{1\text{ads}} \]  

(2.1)

The potential energy required for the chemical transformation to occur is overcome by the large amount of ‘‘free energy’’ supplied with the ultra-violet or visible light quanta (Demeestere and Dewolf, 2007).

A large variety of semiconducting materials, mainly metal oxides and chalcogenides are considered to be good photocatalytic properties. In general, wide –bandgap semiconductors such as titanium oxide (TiO\textsubscript{2}), prove to be better photocatalysts than low-band materials, such as cadmium sulphide (CdS) mainly due to the higher free generated charge carriers of the former and the inherently low chemical and photochemical stability of the Latter. However, low bandgap semiconductors are better adapted to the solar spectrum, thereby offering the significant advantage of potential utilization of a continuous readily available power supply, the Sun. Several methods aiming at the modification of electronic and/or optical properties of
semiconductors, including metal deposition, dye sensitization, doping with transitional metals or non-metallic elements use of composite semiconductor photocatalysts.

2.5.3 General Photocatalytic Reaction Mechanism

In general, the reaction steps leading to the photocatalytic oxidation of hydrocarbons start with the electron-hole pair excitation.

\[ TiO_2 + h_v \rightarrow h^+ + e^- \]  \hspace{1cm} (2.2)

To form the hydroxyl radicals, the hole (h+) reacts with the hydroxides produced from water dissociation (eqn 2.3) or adsorbed water (eqn 2.4) (De Lasa et al., 2005) on the photocatalyst surface:

\[ OH^- + h^+ \rightarrow OH \cdot \]  \hspace{1cm} (2.3)
\[ H_2O + h^+ \rightarrow H^+ + OH \cdot \]  \hspace{1cm} (2.4)

The hydrocarbons are then mineralized by the hydroxyl radicals or the hole itself (eqn 2.5) producing carbon dioxide and water as the final products:

\[ RH + OH \rightarrow intermediate species \rightarrow CO_2 + H_2O \]  \hspace{1cm} (2.5)
\[ RH_2 + h^+ \rightarrow RH^+ + H^+ intermediate species \rightarrow CO_2 + H_2O \]  \hspace{1cm} (2.6)

On the other hand, electrons (e-) trapped transiently on surface or next-to-surface defects can react with the adsorbed oxygen. Evidence of photoelectron emission and impedance spectra suggests that surface-adsorbed oxygen acts as an electron acceptor to create surface states slightly below the conduction band (eqn 2.6) (Lettinga, et al., 2008), forming a one-electron-reduced Oxygen (O\(_2^-\)).

\[ e^- + O_2 \rightarrow O_2^- \]  \hspace{1cm} (2.7)

This one-electron-reduced oxygen (O\(_2^-\)) also possesses an oxidizing potential that can convert the initial products into aldehydes/ ketones (eqn 2.8) or alcohols into carboxylic acids (2.9), which is later converted to oxidation products in the subsequent steps.

\[ RH^\cdot + O_2 \rightarrow R + OH \]  \hspace{1cm} (2.8)
\[ ROH^- + O_2 \rightarrow ROOH \] (2.9)

However, if the mobile electron recombines with the hole, the photocatalytic reaction dies out and energy is released as heat (eqn 2.10) (Lettinga, et al., 2008).

\[ h^+ + e^- \rightarrow TiO_2 + heat \] (2.10)

The mechanism of photocatalytic Cr(VI) reduction is not very clear, but is fairly well described by the capture of photo-excited conduction band electrons followed by reduction, according to Equations (2.1) and (2.2), depending on the pH. In acidic medium

\[ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \] (2.11)

For alkaline solutions

\[ Cr_2O_7^{2-} + 14H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^- \] (2.12)

In the absence of reducing agents, H_2O accepts the valence band holes, and the following photocatalytic redox cycle takes place.

\[ 2H_2O + 14H^+ \rightarrow H_2O_2 + 2H^+ \] (2.13)

**2.6 DETERMINATION OF PHOTOCATALYTIC EFFICIENCY (PE)**

The photocatalytic efficiency (PE) for the removal of COD, BOD_5 and chromium ions was calculated using equation 2.14:

\[ PE = \frac{(C_0 - C_t) * 100}{C_0} \] (2.14)

Where Co and Ct are the initial COD or BOD_5 or Chromium ions concentration and the COD or BOD_5 or Chromium ions concentration after irradiation for a period of time (t), respectively.
2.7 DETERMINATION OF SURFACE AREA AND CRYSTALLINE SIZE OF SOLIDS

2.7.1 Brunauer Emmet Teller Surface Area Measurement

First method to measure the specific surface area of finely divided and porous solids. BET named after Stephen Brunauer, P.H. Emmet and Edward Teller was developed in 1938 as they were working on ammonia catalysts.

Assumptions for BET surface area measurement

1. Homogeneous surface
2. No lateral interactions between molecules
3. Uppermost layer is in equilibrium with vapor phase
4. First layer: heat of adsorption; higher layers: heat of condensation
5. At saturation pressure, the number of layers becomes infinite

The surface area of the catalyst can be determined using adopted BET method developed by Adefila et al., (2003) which employs adsorption of adsorbate (water molecules) on the surface of the adsorbent (samples of catalyst to characterize) using the BET theory. The concept of the theory is an extension of the Langmuir theory, which is a theory of monolayer molecular adsorption, to multilayer adsorption with the following hypothesis (a) Gas molecules physically adsorb on a solid in layers indefinitely; (b) There is no interaction between each adsorption layer and (c) the Langmuir theory can be applied to each layer (Adefila et al., 2003).

The resulting BET equation is expressed by

$$\frac{P}{P_0} = \frac{1}{v_mC} + \frac{C - 1}{v_mC} \left(\frac{P}{P_0}\right)$$  \hspace{1cm} (2.15)

$P$ and $P_0$ are the equilibrium and the saturation pressure of the adsorbate at the temperature of adsorption, $v$ is the adsorbed quantity of the adsorbate, $V_m$ is the monolayer adsorbed gas quantity, $C$ is the BET constant
Equation (2.15) is an adsorption isotherm and can be plotted as a straight line with \( \frac{P}{P_0} \)/V\{1 − \( \frac{P}{P_0} \)\} on the x-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of 0.05 < \( \frac{P}{P_0} \) < 0.35. The value of the slope S and the y-intercept I of the line are used to calculate the monolayer adsorbed gas quantity \( V_m \) and the BET constant C. Equation 2.16 can be used to find intercept, I and slope S

\[
I = \frac{1}{V_mC} \quad \text{and} \quad S = \frac{C-1}{V_mC}
\]  

(2.16)

Upon mathematical manipulations, it follows that:

\[
V_m = \frac{1}{1+S} \tag{2.17}
\]

Employing room temperature and assuming ideal situation,

\[
PV = nRT \tag{2.18}
\]

\[
n = \frac{V_m}{M} \tag{2.19}
\]

\[
V = \frac{V_mRT}{MP} \tag{2.20}
\]

Where, \( R = 8.314 \text{ J/gmol.K} \)

\( T = \text{Room temperature (298 K)} \)

\( M = \text{Molecular mass of the adsorbate (18 g/gmole, for water)} \)

\( V = \text{Standard volume at STP (0.0224 m}^3) \)

\( P = \text{Atmospheric pressure (1.01325*10}^5 \text{ Nm}^{-2}) \)
Area occupied by one volume of adsorbent, $\alpha$ can be derived from first principle:

Assuming, the geometry of the $\alpha$ molecule of the adsorbent is spherical

Then, cross sectional area of a molecule

$$\alpha = \pi R^2$$  \hspace{1cm} (2.21)

Volume of a molecule, $\gamma = \frac{M}{N_0 \rho}$ \hspace{1cm} (2.22)

Where $\rho = $ density of the adsorbate in g/cm$^3$

No = Avogadro’s constant = $6.023 \times 10^{23}$ mol$^{-1}$

Also, $\gamma = \frac{4}{3} \pi r^3$ \hspace{1cm} (2.23)

Equating equations (2.22) and (2.23), we have

$$r = \left(\frac{3M}{4\pi \rho N_0}\right)^{\frac{1}{3}}$$ \hspace{1cm} (2.24)

But $r = R$, Hence, substitute equation (2.24) into (2.21), it follows that

$$\alpha = 1.209\left(\frac{M}{\rho N_0}\right)^{\frac{2}{3}}$$ \hspace{1cm} (2.25)

However, the surface area of the adsorbent is calculated as thus

$$S_g = \left(\frac{V m \ln N_0}{V}\right) \alpha$$ \hspace{1cm} (2.26)

Substituting equations (2.20) and (2.18) into (2.26), Sg can be calculated as thus,

$$S_g = \left(\frac{V m R T}{M P} \times \frac{N_0}{V}\right) \alpha$$ \hspace{1cm} (2.27)

Equation (2.27) can be used to evaluate Sg in m$^2$/g (Adefila et al., 2003)
This method developed by Adefila in 2003 gave an error of 19.826 % (Salahudeen et al., 2010) of the actual BET surface area values expected for the synthesized photocatalysts, this errors was actually due to some inherent error introduced by factors associated with the method such as; ideal situation assumption, efficiency of the desiccator used, purity of the salt used, etc.

2.7.2 X-Ray Diffraction

When crystallites are less than approximately 1,000 Å in size, appreciable broadening in the x-ray diffraction lines will occur. These regions may in fact correspond to the actual size of the particles. At other times, however, these regions form “domains” in the larger particle and may be a distinguishing and important feature. In either case, the observed line broadening can be used to estimate the average size. In the simplest case where the particles are stress-free, the size is estimated from a single diffraction peak. But in those cases where stress may be present, a more robust method involving several diffraction peaks is required. X-ray diffraction has found application in corrosion products, forensic analysis, intermetallic contaminants, pharmaceuticals, amorphous/crystalline contents, quality control, phase transformations, catalysts, and fibre analysis (Klug et al., 2004).

2.7.2.1 Scherrer’s equation

X-ray diffraction is a convenient method for determining the mean pore size of nano crystallites in nano crystalline bulk materials. The first scientist, Paul Scherrer, published his results in a paper that included what became known as the Scherrer equation (Langford et al., 1981). Crystalline size is not synonymous with particle size. X-Ray diffraction is sensitive to the crystallite size inside the particles. From the well-known Scherrer formula the average crystallite size, L, is expressed as
\[ L = \frac{K\lambda}{\beta \cos \theta} \] (2.28)

Where \( \lambda \) is the X-ray wavelength in nanometre (0.1542 nm), \( \beta \) is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and \( K \) is a constant related to crystallite shape, normally taken as 0.9. \( \theta \) is the angular position of the peak maximum (diffracting angle). The value of \( \beta \) in 2\( \theta \) axis of diffraction profile must be in radians. The \( \theta \) can be in degrees or radians (Dinilichenko et al., 2002).

2.7.3 X-Ray Fluorescence

An X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron microscope. However, an XRF cannot generally make analyses at the small spot sizes typical of 2-5 microns, so it is typically used for bulk analyses of larger fractions of geological materials. The relative ease and low cost of sample preparation, and the stability and ease of use of x-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals, and sediment (Fitton, 1997).

The XRF method depends on fundamental principles that are common to several other instrumental methods involving interactions between electron beams and x-rays with samples, including: X-ray spectroscopy, X-ray diffraction, and wavelength dispersive spectroscopy. The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behaviour of atoms when they interact with radiation. When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens,
energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample (Potts, 1987).

X-Ray fluorescence is used in a wide range of applications, including research in igneous, sedimentary, and metamorphic petrology, soil surveys, mining (e.g., measuring the grade of ore), cement production, ceramic and glass manufacturing, metallurgy (e.g., quality control), environmental studies (e.g., analyses of particulate matter on air filters), petroleum industry (e.g., sulfur content of crude oils and petroleum products), field analysis in geological and environmental studies (using portable, hand-held XRF spectrometers). X-Ray fluorescence is particularly well-suited for investigations that involve bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment, bulk chemical analyses of trace elements (in abundances >1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment - detection limits for trace elements are typically on the order of a few parts per million. X-ray fluorescence is limited to analysis of relatively large samples, typically > 1 gram, materials that can be prepared in powder form and effectively homogenized, materials for which compositionally similar, well-characterized standards are available, materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood (Rollinson, 1993).

2.8 LANGMUIR–HINSHELWOOD KINETIC MODEL OF PHOTOCATALYTIC PROCESSES

Langmuir-Hinshelwood modified to accommodate reactions occurring at a solid-liquid interface is given by:
\[
    r_o = -\frac{dc}{dt} = \frac{k_rK_eC_o}{1 + K_eC_o}
\]  

(2.29)

Where \( r_o \) is the initial rate of reaction in mg/lmin and is calculated as thus

\[
    r_o = \frac{C_o - C_e}{time}
\]  

(2.30)

\( k_r \) the rate constant for photocatalysis in l/min/mg, \( K_e \) the rate constant for adsorption in l/mg, \( C_o \) the initial concentration of bulk solution in mg/l at adsorption equilibrium \( C_e \) is the equilibrium concentration

Therefore, Equation (2.29) can be linearized as follow

\[
    r_o(1 + K_eC_o) = k_rK_eC_o
\]  

(2.31)

\[
    \frac{1 + K_eC_o}{k_rK_eC_o} = \frac{1}{r_o}
\]  

(2.32)

\[
    \frac{1}{r_o} = \frac{1}{k_rK_eC_o} + \frac{1}{K_r}
\]  

(2.33)

Equation (2.33) is the linearized form of Langmuir-Hinshelwood kinetic model for adsorption involving photocatalytic reactions.

Experimental data on \( 1/r_o \) can be plotted against \( 1/C_o \) for the given parameters (COD, BOD\(_5\) and Cr) and a straight line graph can be obtained from which the values for \( k_r \) and \( K_e \) can be evaluated.

From equation 2.29, if \( K_eC_o \ll 1 \) then

\[
    r_o \sim k_rK_eC_o
\]  

(2.34)

\[
    r_o = K_{app}C_o
\]  

(2.35)
2.9 PREVIOUS RELATED WORKS

Ma et al. (2012) investigated the photocataytic reduction of Cr (VI) using aqueous ions and UV/TiO2 under various operation factors. Experimental result showed that the removal rate of Cr (VI) increased with decreasing solution pH values and with increasing dosage of organic compounds, indicating that the recombination rate of electrons and h+ can be retarded in the reaction systems by the addition of the scavenger, thus raising the reaction rate of Cr (VI). The relationship of the chemical reaction rate of Cr (VI), TiO2 dosage, and change of Cr (VI) concentration was expressed by the pseudo-first-order kinetics equation.

Domenico and Monica (2010) applied TiO2-Photocatalysis to treat tannery wastewaters from biological wastewater treatment plant in order to investigate the feasibility of photocatalysis as a tertiary treatment. Nano sized TiO2 supported on various materials were used as catalysts. Preliminary experiment were performed on laboratory scale using various types of nanoparticle materials coupled with UV light and in aqueous dispersion both in acid and in alkaline conditions. The efficiency of the system was determine in term of chemical oxygen demand (COD) reduction.

Fahim et al. (2006) studied the removal and recovery of chromium using activated carbon prepared from sugar waste. The adsorption process and the extent of adsorption were found to be dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental condition. The effect of pH, particle size and different adsorbent on the adsorbent isotherm of Cr (III) was also studied in batch system and the sorption data fitted well with Langmuir adsorption Model. The results obtained also revealed that the trivalent chromium is significantly adsorbed on activated carbon collected from sugar industrial waste products and the method could be used economically as an efficient technique for removal of Cr (III) and purification of tannery wastewaters.
 Brigatti et al (2000) performed an experiment with aqueous solution by interaction with Fe (II)-bearing solid surfaces using 0.96 * 10^{-3} M Cr (VI) solution and iron-rich clays with different Fe(II)/Fe(III). Experimental results shows that Fe(II)- bearing phyllosilicates reduce aqueous Cr (VI) ions at acidic pH, chlorite, and corrensite, owing to high Fe(II)/Fe(III) ratio which are electrochemically reactive, as rapid due to Cr (VI) reduction. Also, montmorillonite show minimum to zero reactivity towards Cr (VI) while corrensite which is high in both Fe (II)/Fe (III) ratio and exchange capacity, absorbs the greatest amount of chromium. X-ray adsorbed chromium species. The monmorillonite sample, unaffected by treatment with chromium Cr (VI) solution, displays no change at any investigated edge, also edges shape and energy do not change for the Mg and Al spectra in corrensite, and changes are minor in chlorites. By contrast, the Fe K-edge changes both chlorite and corrensite and indicate an increase of Fe(III) in treated samples at the expense of pre-existing Fe(II).Cr K-edge spectral show that chlorite corrensite sorb Cr(III),which implies its reduction from Cr(VI) in interacting Solution.

Yakubu et al (2008) performed experiment which involves activation of carbon obtained from date seed by treatment with zinc chloride and with steam which was then sieved in 250,500 and 1000 um particle sizes It was found that reduction of zinc, nickel and chemical oxygen demand (COD) from tannery effluent was found to decrease with increase in particle size, and the carbon activated by ZnCl2/steam recorded the highest waste removal. The ZnCl2 only activated carbon removed Ni (88%), Zn (90 %); while the ZnCl2/steam activation treatment removed Ni (91%), and Zn (99 %) COD (91 %). The adsorption mechanism has been modelled using by Nernst and Freundlich isotherms with the partition coefficient observed to decrease with temperature. The tannery effluent has lower partition coefficients. The intensity of adsorption (1/n) defined by Freundlich isotherm are greater than 1 in all case, which indicated that the process is favorable.
CHAPTER THREE

MATERIALS AND METHODS

3.1 INTRODUCTION

This chapter consists of two sections namely; materials (section 3.2) and experimental methods (section 3.3). Section 3.2 comprises of lists of equipment (subsection 3.2.1) and reagents (subsection 3.2.2). Section 3.3 is composed of experimental methods and procedure employed in the course of the research.

3.2 MATERIALS

3.2.1 Equipments

The equipment that were used for the experiment with their availability and model are given in the Table 3.1
Table 3.1: Equipment used for the Experiment, their Availability and Model.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>EQUIPMENT</th>
<th>AVAILABILITY</th>
<th>MODEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weighing Scale</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>AEADAM</td>
</tr>
<tr>
<td>2</td>
<td>Beakers</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Measuring Cylinders</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Sample Bottles</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>X-Ray Diffractometer</td>
<td>N. G. R. L Kaduna</td>
<td>Empyrean panalytical B</td>
</tr>
<tr>
<td>6</td>
<td>X-Ray Fluorescence</td>
<td>N. G. R. L Kaduna</td>
<td>Minipal4 energy Disp.</td>
</tr>
<tr>
<td>7</td>
<td>Hot Plate (Magnetic stirrer)</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>GALLENKAMP</td>
</tr>
<tr>
<td>8</td>
<td>Thermometer</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>Mercury in-glass</td>
</tr>
<tr>
<td>9</td>
<td>Distilled Water Machine</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>A4000</td>
</tr>
<tr>
<td>10</td>
<td>pH Meter</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>HANNAH</td>
</tr>
<tr>
<td>11</td>
<td>Halogen Lamp (500W)</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>BRILLANTA QMC 103</td>
</tr>
<tr>
<td>12</td>
<td>Crucibles, mortar, pestle</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Vacuum Pump</td>
<td>Chem. Engr. Dept. ABU Zaria</td>
<td>GEC MACHINES</td>
</tr>
</tbody>
</table>
### 3.2.2 Reagents

Reagents used for the experiment, their supplier and purity level are given in the Table below:

#### Table 3.2: Materials used for the Experiment, their Supplier and Purity Level.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>REAGENTS</th>
<th>SUPPLIER</th>
<th>PURITY LEVEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc Nitrate</td>
<td>BDH CHEMICALS</td>
<td>Zinc nitrate=96.5 %, Chloride = 0.005%</td>
</tr>
<tr>
<td></td>
<td>Zn((NO_3)_{2}\cdot6H_2O)</td>
<td>ENGLAND</td>
<td>Sulphate = 0.001 % Fe = 0.001 % pH= 3.6</td>
</tr>
<tr>
<td>2</td>
<td>Iron Nitrate</td>
<td>BDH CHEMICALS</td>
<td>Iron nitrate=98.5%, Chloride=0.0005 %</td>
</tr>
<tr>
<td></td>
<td>Fe((NO_3)_{3}\cdot9H_2O)</td>
<td>ENGLAND</td>
<td>Zinc=0.001 % Sulphate= 0.001 %</td>
</tr>
<tr>
<td>3</td>
<td>Ammonia Hydroxide</td>
<td>BDH CHEMICALS</td>
<td>Sp.gr = 0.91, Lead=0.0001%, Iron=0.0001%</td>
</tr>
<tr>
<td></td>
<td>((NH_4OH))</td>
<td>ENGLAND</td>
<td>Chloride=0.001 %, Sulphate=0.002%</td>
</tr>
<tr>
<td>4</td>
<td>Activated Carbon</td>
<td>BDH CHEMICALS</td>
<td>S.A =735.00 m² Ash content=2.5 %</td>
</tr>
<tr>
<td></td>
<td>ENGLAND</td>
<td>Water soluble=1.5 %</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Potassium Sulphate</td>
<td>BDH CHEMICALS</td>
<td>Chloride=0.05 % Fe =0.001 %</td>
</tr>
<tr>
<td></td>
<td>ENGLAND</td>
<td>Sodium=1 %</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Calcium Sulphate</td>
<td>BDH CHEMICALS</td>
<td>Chloride=0.03 %, Fe=0.001 %</td>
</tr>
<tr>
<td></td>
<td>ENGLAND</td>
<td>Sodium=2 %</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Sodium Acetate</td>
<td>BDH CHEMICALS</td>
<td>Chloride=0.02 %, Lead = 0.005 %</td>
</tr>
<tr>
<td></td>
<td>ENGLAND</td>
<td>K= 0.01 % Sulphate=0.05 %</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Tannery Effluent</td>
<td>NILEST, ZARIA</td>
<td></td>
</tr>
</tbody>
</table>
3.3 EXPERIMENTAL METHODS

This section consists of material collection and preparation (3.3.1), synthesis of photocatalysts (3.3.2), tannery effluent (3.3.3), adsorption on activated carbon (3.3.4), photocatalytic experiments (3.3.5), blank experiments (3.3.6), determination of specific surface area of the synthesized photocatalysts (3.3.7) and analysis of effluent for COD, BOD₅ and Cr (3.3.8). Figure 3.1 shows a process flow diagram of the research methodology.

![Figure 3.1: Flow Diagram of the Research Methodology](image-url)
3.3.1 Material Collection and Preparation

The Equipments used for the experiment were available in the department of chemical engineering, Ahmadu Bello University Zaria. Reagents used were of analytical grade and purchased at Haddiss chemicals, Samaru Zaria.

3.3.2 Synthesis of Photocatalysts

33.0 g of Zn(NO$_3$)$_2$.6H$_2$O (0.110 moles) and 3.35 g of Fe(NO$_3$)$_2$.9H$_2$O (0.0098 moles) were reacted with 33.5 cm$^3$ of NH$_4$OH and 30.69 cm$^3$ of NH$_4$OH respectively to obtain 2.67 g of Fe$_2$(OH)$_3$ and 22.0 g Zn(OH)$_2$ precipitate; this was done by addition of Zn(NO$_3$)$_2$.6H$_2$O and Fe(NO$_3$)$_2$.9H$_2$O crystals to 100 ml deionised water in a beaker placed in a hot plate which was continuously stirred at a constant temperature of 50 °C and pH of 8 until the precipitate was formed. The equations (3.1 and 3.2) show the precipitation processes of the two oxides:

$$\text{Zn(NO}_3\text{)}_2.6\text{H}_2\text{O(s) + 2NH}_4\text{OH(aq) }\rightarrow \text{2NH}_4\text{NO}_3\text{(aq) + Zn(OH)}_2\text{(s) + 6H}_2\text{O(l) \space (3.1)}}$$

$$\text{Fe(NO}_3\text{)}_2.9\text{H}_2\text{O(s) + 2NH}_4\text{OH(aq) }\rightarrow \text{2NH}_4\text{NO}_3\text{(aq) + Fe(OH)}_2\text{(s) + 9H}_2\text{O(l) \space (3.2)}}$$

The precipitate obtained above was then allowed to stand for 24 hours after which it was washed with deionised water filtered using watman filter paper and buchner funnel. The precipitate was further drain with vacuum pump to remove water and other products.

The filtrate obtained after vacuum filtration was dried in the oven at a temperature of 110 °C so as to dry it. After drying the product obtained is then calcined in a furnace at a temperature of 1000 °C. The calcination steps is described by the equations (3.3 and 3.4):

$$\text{Zn(OH)}_2\text{(aq) }\rightarrow \text{ZnO(s) + H}_2\text{O(l)} \quad \text{(3.3)}$$

$$\text{Zn(OH)}_2\text{(aq) + 2Fe(OH)}_2\text{ }\rightarrow \text{ZnFe}_2\text{O}_4\text{(s) + H}_2\text{O(l)} \quad \text{(3.4)}$$
3.3.3 Tannery Effluent

The effluent used was collected from the tanyard of NILEST. The effluent was filtered to remove suspended solids. The pH, COD, BOD$_5$ and chromium contents of the effluent are listed in Table 3.3

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3 – 5</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>2560</td>
</tr>
<tr>
<td>BOD$_5$ (mg/l)</td>
<td>650</td>
</tr>
<tr>
<td>Cr (mg/l)</td>
<td>3.9</td>
</tr>
</tbody>
</table>

3.3.4 Adsorption on Activated Carbon

100 ml of the effluent was collected and placed in a beaker, 0.1 g of activated carbon was then added, placed on a hot plate and magnetically stirred for two hours under ambient conditions. Sample of the adsorbed effluent after 2 hours of adsorption was taken and analysed for COD, BOD$_5$ and Cr at intervals of 5 min, 10 min, 15 min, 20 min, 30 min, 60 min and 120 min.

3.3.5 Photocatalytic Experiments

100 ml of the effluent was collected and placed in a beaker, 0.1 g of the photocatalyst was then added, placed on a hot plate and magnetically stirred for two hours in the dark. Sample of the adsorbed effluent after 2 hours of adsorption in the dark was taken and analysed for COD, BOD$_5$ and Cr. Immediately after adsorption in the dark stage for two hours, the mixture of effluent and the photocatalyst in the beaker was exposed to visible light irradiation by a 500 W
halogen lamp under stirring. Samples were taken after 5 min, 10 min, 15 min, 20 min, 30 min, 60 min and 120 min from the start of irradiation and analysed for BODs, COD and chromium.

To determine the effect of catalyst dose, 100 ml of the effluent was measured and placed in a beaker, 0.05 g of the catalyst was then measured and added to content of the beaker, the beaker was then placed in a hot plate and magnetic stirrer was introduce into the beaker, the content of the beaker was continuously stirred in the dark for two hours after which a 5 ml of the sample was taken for analysis. The content of the beaker was then exposed to light while it was continuously stirred for another two hours and again 5ml sample was then collected for analysis, the same procedure was repeated for 0.10 g, 0.15 g and 0.20 g of catalysts.

To determine the effect of pH, 100 ml of the effluent was measured and placed in a beaker, sodium hydroxide solution whose concentration is known was added to it to adjust the pH of the effluent. For any addition of sodium hydroxide, a pH meter was used to determine the pH of the effluent until the pH of 3 is obtained, a 5 ml of effluent was then taken for analysis, the effluent was then magnetically stirred in the dark for two hours and again 5ml sample was collected for analysis. The effluent was further exposed to light for another two hours and again 5 ml sample of the effluent was taken for analysis. The same procedure was repeated for pH 7 and pH 10.

To determine the effect of light, 100 ml of the effluent was measured and placed in a beaker, exposed to 100 W tungsten lamp and continuously stirred for two hours, 5 ml of the sample of the effluent was then taken for analysis. This procedure was repeated for 200 W tungsten lamp.

To determine the effect of initial concentration of COD, BODs, and Cr, 100 ml of the effluent was measured with a cylinder and poured into a beaker and samples are taken for analysis to determine the COD, BODs and Cr. 0.1 g of activated carbon was then added to the
effluent which was then stirred for 2 hours and again samples were taken for analysis of the aforementioned parameters which were later recorded. Another 50 ml of the effluent was also measured and poured in a beaker and 50 ml of water was added to it and samples were taken for analysis, again 0.1 g of activated carbon was added to it and it was stirred for 2 hours and samples were taken for analysis of aforementioned parameters. This was repeated for 25ml of effluent/75 ml of water, 10 ml of effluent/90 ml of water and samples were in each case taken for analysis.

Similarly, 100 ml of effluent was measured and 0.1 g of 20 g AC ZnO-ZnFe$_2$O$_4$ catalyst was added and photocatalysed for two hours after 2 hours adsorption without light, after which samples were taken for analysis in each case for COD, BOD$_5$ and Cr. The same procedure was repeated for 50 ml of effluent/50 ml of water, 25 ml of effluent/75 ml of water, 10 ml/90 ml of water and samples were taken for after adsorption for 2 hours without light and after adsorption for 2 hours with light.

**3.3.6 Blank Experiments**

Another experiment was conducted in darkness in which 100 ml of effluent was poured in a beaker and then magnetically stirred for 2 hours without light, sample were then collected for analysis of the three parameters (COD, BOD$_5$ and Cr).

**3.3.7 Determination of Specific Surface Area of the Synthesized Photocatalysts**

An approximate method developed by Adefila *et al* (2003) was used. In this method an adsorbate of constant relative humidity was established as a relative humidity of water vapour obtained from a saturated salt solution in water. This relative humidity was proved to be equal to $\frac{P}{P_0}$ as in equation 2.15
Firstly, two saturated solution of four different kind of salts were prepared, one for each salt was kept in a desiccator and the other left open in the laboratory, the two were left for 24 hours, while their respective weight at the beginning and at the end of 24 hours were noted. The relative humidity of the saturated salt solution for each of the salt were then evaluated as the ratio of the weight differences of salt solution in the desiccator (at initial point and after 24 hrs.) to the weight differences of salt solution left open (at initial point and after 24 hours.). The salts used are CaSO₄, K₂SO₄, CH₃COONa, and MgCl₂. After the determination of value of $\frac{P}{P_0}$ for each salt, a saturated solution for each salt were then prepared and kept in a desiccator with 1 g of the adsorbent (synthesized catalyst) evenly spread on a petri dish and kept together with the saturated salt solution in an air tight desiccator for 24 hours while maintaining room or ambient temperature. The weight gain of the catalyst was determined at the end of 24 hours. to represent $\nu$ in equation 2.15. The procedure was repeated for the remaining catalysts and equations (2.15 to 2.27) were used to determine the specific surface area of the catalyst synthesized.

3.3.8 Analysis of Effluent for COD, BOD₅ and Cr

The analysis of COD, BOD₅ and Cr were carried at National Research Institute for Chemical Technology (NARICT), Zaria.

3.3.8.1 Measurement of COD

To measure the COD a filtered sample of the effluent is heated with a strong oxidizing agent (potassium dichromate) and sulphuric acid for two hours. As the organic substances in the effluent are oxidized, they reduce the potassium dichromate, forming Cr³⁺. The amount of dichromate remaining is determined by titration and this is indirectly a measure of the organic component in the waste water.
3.3.8.2 Measurement of BODs

Analyse sample of the effluent is diluted in water, the pH is adjusted to 6 and it seeded with bacteria, the sample are then incubated in the dark for five days @ 20 °C. The bacteria use the oxygen dissolved in the water as they degrade the organic matter. The oxygen remaining after five days is determined and the BODs was calculated by comparison with the oxygen in the blank sample.

3.3.8.3 Measurement of Chromium Content

The amount of Chromium content of the effluent was carried out using atomic absorption spectrophotometer (AAS) analyser. In this analysis, light of specific wavelength is passed through the atomic vapour on element of interest (in this case – chromium) and measurement is made of the attenuation of the intensity of the light as a result of adsorption
CHAPTER FOUR

RESULTS AND DISCUSSION OF RESULTS

4.1 INTRODUCTION

This chapter presents the results generated from chapter three, the results were also discussed accordingly.

4.2 XRD PATTERNS OF THE SYNTHESIZED PHOTOCATALYSTS.

Analysis of the XRD patterns was performed by comparing the obtained patterns of the two synthesized photocatalysts (Figures 4.1 and 4.2) with standard patterns (Pei., 1977) of the expected component. The diffractogram is dominated by the characteristic peak of hexagonal wurtzite structure of ZnO (31.7°, 34.4°, 36.2°, 47.5° and 69.1°) and minor peaks due to cubic spinel structure of ZnFe₂O₄ (30.0°, 35.3°, 43.2° and 53.7°). The XRD pattern is characterised by sharp peaks, indicative of high crystallinity of ZnO and ZnFe₂O₄. The diffractogram does not feature any peak that can be attributed to activated carbon due to its amorphous nature.

![Figure 4.1: XRD Pattern of the Prepared ZnO-ZnFe₂O₄ Composite Photocatalyst](image)

F = Franklinite(ZnFe₂O₄)
Z = Zincite (ZnO),

Counts

F
Z
Z
Z
Z
Z
Z
Z
Z
Z

POSITION [°2Theta]

0 10 20 30 40 50 60 70 80

8000 7000 6000 5000 4000 3000 2000 1000

0

43
The composition of the synthesized ZnO-ZnFe$_2$O$_4$ photocatalyst is summarized in Table 4.1. It shows that aside the major components (Zinc and Iron), there are other components which constitute impurity, this is expected as there were certain amount of impurity in the substances used in their synthesis as shown in Table 3.2.

**Figure 4.2: XRD Pattern of the Prepared ZnO-ZnFe$_2$O$_4$/AC Photocatalyst**

**4.3 CHEMICAL COMPOSITION OF THE SYNTHESIZED PHOTOCATALYSTS**

F = Franklinite (ZnFe$_2$O$_4$)
Z = Zincite (ZnO),
**Table 4.1: Chemical Composition of the Synthesized Photocatalysts (% wt.)**

<table>
<thead>
<tr>
<th>Synthesized Catalysts</th>
<th>Zn</th>
<th>Fe</th>
<th>Si</th>
<th>P</th>
<th>Ca</th>
<th>Cr</th>
<th>Ni</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-ZnFe$_2$O$_4$</td>
<td>93.06</td>
<td>5.81</td>
<td>0.72</td>
<td>0.24</td>
<td>0.12</td>
<td>0.044</td>
<td>0.026</td>
<td>100</td>
</tr>
<tr>
<td>ZnO-ZnFe$_2$O$_4$/AC</td>
<td>91.87</td>
<td>6.81</td>
<td>0.42</td>
<td>0.53</td>
<td>0.31</td>
<td>0.052</td>
<td>0.032</td>
<td>100</td>
</tr>
</tbody>
</table>

**4.3.1. Percentage Removal of the Effluent Parameters**

From figures 4.3-4.5, the percentage reduction of the three parameters for each of the synthesized photocatalyst is shown and it is observed that the catalyst with 20 g activated carbon has the highest efficiency in the reduction process. Hence, it is selected for the study of effect of lamp power, pH and catalyst dose on the photocatalytic treatment of the effluent.

Also obtained were result of the blank experiments (Table A9) which shows zero percentage removal of the parameters when the effluent sample was magnetically stirred for two hours without the photocatalyst, this shows that photocatalytic degradation of the effluent can only proceed via light absorption by the photocatalyst placed in the Effluent. Similar observations were made when the effluent was treated with photocatalyst under ambient condition, in which there is very low degradation of the effluent sample because of it’s non - exposure to direct light as shown in Table A10.
Figure 4.3: Percentage COD Removal using AC, ZnO- ZnFe$_2$O$_4$, ZnO- ZnFe$_2$O$_4$/AC.

Figure 4.4: Percentage BOD$_5$ Removal using AC, ZnO- ZnFe$_2$O$_4$, ZnO- ZnFe$_2$O$_4$/AC.
Figure 4.5: Percentage Cr Removal using AC, ZnO-\(\text{ZnFe}_2\text{O}_4\), ZnO-\(\text{ZnFe}_2\text{O}_4\), ZnO-\(\text{ZnFe}_2\text{O}_4/\text{AC}\).

Table 4.2: Surface Area and Crystallite Size of the Synthesized Photocatalysts

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Crystallite Size (nm)</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-(\text{ZnFe}_2\text{O}_4)</td>
<td>45.5</td>
<td>27.84</td>
</tr>
<tr>
<td>ZnO-(\text{ZnFe}_2\text{O}_4/\text{AC})</td>
<td>49.1</td>
<td>361.73</td>
</tr>
</tbody>
</table>
4.3.2. Effect of Catalyst Loading on Percentage Removal of the Parameters

From the results obtained (Figures 4.6-4.8), it is shown that the rate of photocatalytic degradation of effluent for the three parameters (COD, BOD$_5$ and Cr) increase linearly with catalyst loading up to 0.10 g/l. Above this loading, there is an increase in turbidity of the effluent solution which reduces the light transmission through the solution, while below it, it is assumed that the catalyst surface area and the adsorption of light by the catalyst are limiting factors. The optimum catalyst is found to be dependent on the initial solute concentration. Hence, higher amount of catalyst may not be useful both in view of possible aggregation as well as reduced irradiation due to increase in light scattering.

![Graph showing effect of catalyst dose on percentage removal of BOD$_5$.](image)

**Figure 4.6: Effect of Catalyst dose on %Removal of BOD$_5$ using ZnO-ZnFe$_2$O$_4$/AC.**
Figure 4.7: Effect of Catalyst Dose on %Removal of COD using ZnO-ZnFe$_2$O$_4$/AC.

Figure 4.8: Effect of Catalyst Dose on %Removal of Cr using ZnO-ZnFe$_2$O$_4$/AC.
4.3.3. Effect of pH on Percentage Removal of the Parameters

The pH of the effluent was varied between 3 and 10 (Figures 4.9 – 4.11) and photocatalytic activity was found to increase with increase in pH up to 10 and then it was almost constant even though the photocatalytic reduction of the effluent is low at alkaline pH. It is thus concluded that photocatalytic reaction occur not only on the catalyst surface but also in the close vicinity of the catalyst surface. The acid-base property of the metal oxide surface can have considerable implication on their photocatalytic activity. The point of zero charge is pH 9 and above this value, ZnO-ZnFe₂O₄ is negatively charged by means of adsorbed OH⁻ ions.

![Figure 4.9: Effect of pH on the Percentage Removal of COD using ZnO-ZnFe₂O₄ / AC](image-url)
Figure 4.10: Effect of pH on the Percentage Removal of BOD$_5$ using ZnO-ZnFe$_2$O$_4$/AC.

Figure 4.11: Effect of pH on the Percentage Removal of Cr using ZnO-ZnFe$_2$O$_4$/AC.
4.3.4. Effect of Lamp Power on Percentage Removal of the Parameters

The light intensity for the photocatalytic activity was varied between 100W and 200W tungsten bulbs. It was found that the photocatalytic activity increases with increase in lamp power as can be seen from Figures 4.12-4.14.

![Figure 4.12: Effect of Lamp Power on Percentage Removal of COD using ZnO-ZnFe₂O₄/AC](image-url)
Figure 4.13: Effect of Lamp Power on Percentage Removal of BOD₅ using ZnO-ZnFe₂O₄/AC

Figure 4.14: Effect of Lamp Power on % Removal of Cr using ZnO-ZnFe₂O₄/AC.
4.3.5. Langmuir-Hinshelwood Kinetics

From the experiment that was carried out for Langmuir-Hinshelwood plot, values for $r_o$, $1/C_o$ and $1/r_o$ were obtained and were later used to plot graphs (Figures 4.15- 4.17). The equations for these graphs shows a very good $R^2$ after their linearization and subsequently their slope and intercept were used to calculate rate constants $k_r$ and equilibrium adsorption constant $K_e$. The values for the $K_e$ and $k_r$ are very low and from literatures, it indicate that photocatalysis as a treatment technology for tannery effluent is very Effective. The $k_r$ value is highest for chromium removal while the $K_e$ is lowest and this indicate that of the parameters considered the rate of chromium removal is the fastest.

Table 4.3: Calculated Values of $r_o$, $1/C_o$ and $1/r_o$ for the Langmuir-Hinshelwood Kinetic Plot.

<table>
<thead>
<tr>
<th>Composition of Effluent/water Ratio</th>
<th>$r_o$ (mg/l/min)</th>
<th>$1/C_o$</th>
<th>$1/r_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COD</td>
<td>BODs</td>
<td>Cr</td>
</tr>
<tr>
<td>100ml/0ml</td>
<td>4.075</td>
<td>1.79</td>
<td>0.027</td>
</tr>
<tr>
<td>50ml/50ml</td>
<td>3.167</td>
<td>1.48</td>
<td>0.015</td>
</tr>
<tr>
<td>25ml/75ml</td>
<td>3.100</td>
<td>1.24</td>
<td>0.010</td>
</tr>
<tr>
<td>10ml/90ml</td>
<td>2.533</td>
<td>1.08</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Figure 4.15: Plot of $1/r_0$ versus $1/C_0$ for COD Removal with Effluent Treated with ZnO-ZnFe$_2$O$_4$/AC Photocatalyst

Figure 4.16: Plot of $1/r_0$ versus $1/C_0$ for BOD$_5$ Removal with Effluent Treated with ZnO-ZnFe$_2$O$_4$/AC Photocatalyst
Figure 4.17: Plot of $1/r_o$ versus $1/C_o$ for Cr Removal with Effluent Treated with ZnO-ZnFe$_2$O$_4$/AC Photocatalyst

Table 4.4: Kinetic Rate Constant Obtained from Langmuir Plots using ZnO-ZnFe$_2$O$_4$/AC

<table>
<thead>
<tr>
<th></th>
<th>$K_e*10^{-4}$, (mg/lmin)</th>
<th>$K_r$, (l/min/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>BOD$_5$</td>
<td>Cr</td>
</tr>
<tr>
<td>2.752</td>
<td>4.749</td>
<td>2.548</td>
</tr>
<tr>
<td>COD</td>
<td>BOD$_5$</td>
<td>Cr</td>
</tr>
<tr>
<td>1.5805</td>
<td>4.037</td>
<td>7.267</td>
</tr>
</tbody>
</table>

Langmuir-helshinwood kinetic models equations obtained from the experimental data for the three pollutants are given below:

From the linearized form of Langmuir-helshinwood equation (equation 2.31)

$$\frac{1}{r_o} = \frac{1}{k_r K_e C_0} + \frac{1}{k_r}$$

(2.32)
Substituting for $k_e$ and $K_e$ into 2.31

For COD:

$$\frac{1}{r_o} = \frac{1}{1.5805 \times 2.752 \times 10^{-4}C_o} + \frac{1}{1.5805} \quad (4.1)$$

For BOD$_5$:

$$\frac{1}{r_o} = \frac{1}{4.037 \times 4.749 \times 10^{-4}C_o} + \frac{1}{4.037} \quad (4.2)$$

For Cr:

$$\frac{1}{r_o} = \frac{1}{7.267 \times 2.548 \times 10^{-4}C_o} + \frac{1}{7.267} \quad (4.3)$$
CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 INTRODUCTION
This chapter comprises of a summary of conclusions observed in the work (section 5.2); recommendation were also given in section 5.3

5.2 CONCLUSIONS

The following conclusions were made after the photocatalytic treatment of effluent using the synthesized catalysts

1. The photocatalysts ZnO-ZnFe$_2$O$_4$ composite and ZnO-ZnFe$_2$O$_4$ composite on activated carbon support were successfully synthesized.

2. The specific surface area of the synthesized photocatalysts (362m$^2$/g and 274 m$^2$/g) are substantially smaller than the surface area of the activated carbon (735m$^2$/g) used because of sintering of ZnO: ZnFe$_2$O$_4$ particles on the surface of the activated carbon.

3. The adsorption of the effluent with activated carbon alone under ambient conditions show percentage removal of 60.02 % for COD, 72.77 % for BOD$_5$, 64.10 % for Cr of effluent after 2 hour.

4. The percentage removal of the three parameters when the effluent was treated with ZnO-ZnFe$_2$O$_4$/AC under ambient conditions for two hours are 5.47% for COD, 15.38% for BOD$_5$ and 17.94% for Cr.

5. The addition of a commercial activated carbon to ZnO-ZnFe$_2$O$_4$ under visible light increased adsorption and photocatalytic degradation of the effluent by 87.50 % for COD, 90.92 % for BOD$_5$ and 92.31 % for chromium.
6. There was no degradation of the effluent sample when the effluent was adsorbed in the dark for two without photocatalyst.

7. The calculated values of the apparent reaction rate constant \( (k_r) \) are 1.5805 l/min/mg for COD, 4.037 l/min/mg for BOD\(_5\), and 7.267 min/mg for Cr while that of apparent equilibrium of adsorption constant \( (K_e) \) are 2.752 * 10\(^{-4}\) g/lmin for COD, 4.749 * 10\(^{-4}\) mg/lmin for BOD\(_5\), 2.548 * 10\(^{-4}\) mg/lmin for Cr. The values indicate that adsorption of the three parameters (COD, BOD\(_5\) and Cr) is the rate controlling step of the photocatalytic processes because the value of \( k_r \) is substantially higher than of \( K_e \).

8. The experimental data obtained for photocatalysis nicely fitted the Langmuir–Hinshelwood kinetics hence a model equation were obtained for the photocatalytic process.

5.3 RECOMMENDATIONS

1. Photocatalyst composition and process parameters should be optimised using design of experiment.

2. A pilot plant for treatment of tannery effluent based on photocatalysis should be developed.
REFERENCES


Oremusová, J. (2007) “Manual for Laboratory Practice in Physical Chemistry for Student of Pharmacy”, Department of Physical Chemistry, Faculty of Pharmacy, Comenius University, Bratislava, in Slovak


APPENDIX A

Table A1: Effect of Contact Time on the Removal of COD, BOD$_5$ and Cr via Adsorption on Activated Carbon.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>Time(min)</th>
<th>COD(mg/l)</th>
<th>BOD$_5$(mg/l)</th>
<th>Cr(mg/l)</th>
<th>Percentage Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% COD % BOD$_5$ % Cr</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2560</td>
<td>650</td>
<td>3.9</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>2115</td>
<td>612</td>
<td>3.6</td>
<td>17.38 5.85 7.69</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1980</td>
<td>597</td>
<td>3.4</td>
<td>22.66 8.15 12.80</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>1670</td>
<td>457</td>
<td>2.8</td>
<td>34.77 29.69 28.21</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>1575</td>
<td>370</td>
<td>2.5</td>
<td>38.48 43.08 35.89</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>1290</td>
<td>285</td>
<td>1.9</td>
<td>49.61 56.15 51.28</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>987</td>
<td>197</td>
<td>1.7</td>
<td>61.45 69.69 56.41</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>870</td>
<td>177</td>
<td>1.4</td>
<td>60.02 72.77 64.10</td>
</tr>
</tbody>
</table>

Table A2: Effect of Irradiation Time on the Removal of COD, BOD$_5$ and Cr Content of Raw Tannery Effluent using ZnO-ZnFe$_2$O$_4$ after 2 hours of Adsorption in the Dark.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>Time(min)</th>
<th>COD(mg/l)</th>
<th>BOD$_5$(mg/l)</th>
<th>Cr(mg/l)</th>
<th>Percentage Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% COD % BOD$_5$ % Cr</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2256</td>
<td>525</td>
<td>3.5</td>
<td>11.88 19.23 10.26</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1980</td>
<td>450</td>
<td>2.8</td>
<td>22.66 30.77 20.21</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>838</td>
<td>378</td>
<td>2.5</td>
<td>67.27 41.85 35.89</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>735</td>
<td>205</td>
<td>2.0</td>
<td>71.29 68.46 48.72</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>607</td>
<td>176</td>
<td>1.4</td>
<td>76.29 72.92 64.10</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>540</td>
<td>135</td>
<td>0.8</td>
<td>78.91 79.23 79.49</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>445</td>
<td>97</td>
<td>0.6</td>
<td>82.62 85.08 84.62</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>390</td>
<td>75</td>
<td>0.4</td>
<td>84.76 88.46 89.74</td>
</tr>
</tbody>
</table>
Table A3: Effect of Irradiation Time on the Removal of COD, BOD$_5$ and Cr Content of Raw Tannery Effluent using ZnO-ZnFe$_2$O$_4$ / AC after 2 hours of Adsorption in the Dark.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>Time(min)</th>
<th>COD(mg/l)</th>
<th>BOD$_5$(mg/l)</th>
<th>Cr(mg/l)</th>
<th>Percentage Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>%COD</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2149</td>
<td>590</td>
<td>3.4</td>
<td>16.05</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1920</td>
<td>470</td>
<td>2.8</td>
<td>25.00</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>805</td>
<td>390</td>
<td>2.2</td>
<td>68.55</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>720</td>
<td>290</td>
<td>1.7</td>
<td>71.88</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>520</td>
<td>180</td>
<td>0.8</td>
<td>79.69</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>490</td>
<td>148</td>
<td>0.5</td>
<td>80.86</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>406</td>
<td>85</td>
<td>0.4</td>
<td>84.14</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>320</td>
<td>59</td>
<td>0.1</td>
<td>87.50</td>
</tr>
</tbody>
</table>
Table A4: Effect of ZnO-ZnFe$_2$O$_4$ / AC Dose on the Photocatalytic Degradation of the Effluent after Adsorption for Two hours in the Dark.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>Catalyst dose (g)</th>
<th>Experiments</th>
<th>COD (mg/l)</th>
<th>BOD$_5$ (mg/l)</th>
<th>Cr (mg/l)</th>
<th>%COD removal</th>
<th>%BOD$_5$ removal</th>
<th>%Cr removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05g of catalyst</td>
<td>Adsorption for 2 hrs</td>
<td>1930</td>
<td>450</td>
<td>3.0</td>
<td>24.61</td>
<td>30.77</td>
<td>23.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2 hrs</td>
<td>300</td>
<td>55</td>
<td>1.6</td>
<td>91.54</td>
<td>88.28</td>
<td>58.97</td>
</tr>
<tr>
<td>2</td>
<td>0.10g of Catalyst</td>
<td>Adsorption for 2 hrs</td>
<td>1920</td>
<td>470</td>
<td>2.8</td>
<td>25.00</td>
<td>22.69</td>
<td>28.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2 hrs</td>
<td>185</td>
<td>58</td>
<td>0.7</td>
<td>92.77</td>
<td>91.02</td>
<td>82.05</td>
</tr>
<tr>
<td>3</td>
<td>0.15g of catalyst</td>
<td>Adsorption for 2 hrs</td>
<td>1870</td>
<td>270</td>
<td>1.3</td>
<td>26.95</td>
<td>58.46</td>
<td>66.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2 hrs</td>
<td>230</td>
<td>47</td>
<td>0.7</td>
<td>91.60</td>
<td>89.10</td>
<td>70.58</td>
</tr>
<tr>
<td>4</td>
<td>0.20g of catalyst</td>
<td>Adsorption for 2 hrs</td>
<td>2100</td>
<td>310</td>
<td>2.5</td>
<td>17.97</td>
<td>52.30</td>
<td>35.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2 hrs</td>
<td>280</td>
<td>50</td>
<td>1.0</td>
<td>91.20</td>
<td>88.67</td>
<td>60.98</td>
</tr>
</tbody>
</table>
Table A5: Effect of pH on the Photocatalytic Degradation of the Effluent using ZnO-ZnFe$_2$O$_4$ / AC after Adsorption for Two hours in the Dark.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>pH Values</th>
<th>EXPERIMENTS</th>
<th>COD (mg/l)</th>
<th>BOD$_5$ (mg/l)</th>
<th>Cr (mg/l)</th>
<th>%COD removal</th>
<th>%BOD$_5$ removal</th>
<th>%Cr removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>Raw effluent @ pH 3</td>
<td>2350</td>
<td>500</td>
<td>2.9</td>
<td>8.20</td>
<td>23.08</td>
<td>25.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption for 2hrs</td>
<td>1890</td>
<td>398</td>
<td>2.4</td>
<td>21.68</td>
<td>38.77</td>
<td>38.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2hrs</td>
<td>760</td>
<td>250</td>
<td>2.0</td>
<td>70.31</td>
<td>61.54</td>
<td>48.72</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>Raw effluent @ pH 7</td>
<td>2000</td>
<td>470</td>
<td>2.4</td>
<td>27.69</td>
<td>38.46</td>
<td>38.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption for 2 hrs</td>
<td>1900</td>
<td>220</td>
<td>2.0</td>
<td>25.78</td>
<td>66.15</td>
<td>48.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2 hrs</td>
<td>270</td>
<td>90</td>
<td>1.8</td>
<td>89.45</td>
<td>86.15</td>
<td>53.84</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>Raw effluent @ pH 10</td>
<td>1970</td>
<td>320</td>
<td>1.7</td>
<td>23.05</td>
<td>50.77</td>
<td>56.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption for 2 hrs</td>
<td>1690</td>
<td>156</td>
<td>0.7</td>
<td>37.50</td>
<td>76.00</td>
<td>82.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photocatalysis for 2 hrs</td>
<td>200</td>
<td>55</td>
<td>0.2</td>
<td>92.19</td>
<td>91.54</td>
<td>94.87</td>
</tr>
</tbody>
</table>

Table A6: Effect of Lamp Power on the Photocatalytic Degradation of the Effluent using ZnO-ZnFe$_2$O$_4$ / AC after Adsorption for Two hours in the Dark.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>Lamp (Watts)</th>
<th>COD (mg/l)</th>
<th>BOD$_5$ (mg/l)</th>
<th>Cr (mg/l)</th>
<th>%COD removal</th>
<th>%BOD$_5$ removal</th>
<th>%Cr removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>345</td>
<td>60</td>
<td>0.6</td>
<td>87.30</td>
<td>90.77</td>
<td>84.62</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>325</td>
<td>75</td>
<td>0.68</td>
<td>86.52</td>
<td>88.46</td>
<td>82.56</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>238</td>
<td>46</td>
<td>0.46</td>
<td>92.53</td>
<td>91.90</td>
<td>92.31</td>
</tr>
</tbody>
</table>
Table A7: Effect of Dilution on the Photocatalytic Removal COD, BODs and Cr from Tannery Effluent using ZnO-ZnFe₂O₄/AC.

<table>
<thead>
<tr>
<th>Composition of Effluent/Water Ratio</th>
<th>Initial Values for the effluent (mg/l)</th>
<th>After 2hrs of Adsorption (mg/l) (C₀)</th>
<th>After 2hrs of Photocatalysis (mg/l) (Cₑ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COD</td>
<td>BOD₅</td>
<td>Cr</td>
</tr>
<tr>
<td>100ml/0ml</td>
<td>2260</td>
<td>605</td>
<td>3.3</td>
</tr>
<tr>
<td>50ml/50ml</td>
<td>1960</td>
<td>590</td>
<td>2.5</td>
</tr>
<tr>
<td>25ml/75ml</td>
<td>1750</td>
<td>470</td>
<td>2.1</td>
</tr>
<tr>
<td>10ml/90ml</td>
<td>1500</td>
<td>450</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table A8: Blank Experiment of the Effluent Sample for Two hours in the Dark without Photocatalyst.

<table>
<thead>
<tr>
<th>S/NO</th>
<th>EXPERIMENT</th>
<th>COD(mg/l)</th>
<th>BOD₅(mg/l)</th>
<th>Cr(mg/l)</th>
<th>%COD</th>
<th>%BOD₅</th>
<th>%Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Adsorption in Darkness for two hours</td>
<td>2560</td>
<td>390</td>
<td>3.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table A9: Effect of Contact Time on the Effluent Sample for Two hours with Photocatalyst ZnO-ZnFe₂O₄/AC under Ambient Conditions

<table>
<thead>
<tr>
<th>S/NO</th>
<th>EXPERIMENT</th>
<th>COD(mg/l)</th>
<th>BOD₅(mg/l)</th>
<th>Cr(mg/l)</th>
<th>%COD</th>
<th>%BOD₅</th>
<th>%Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Photocatalysis under ambient conditions.</td>
<td>2420</td>
<td>330</td>
<td>3.2</td>
<td>5.47</td>
<td>15.38</td>
<td>17.94</td>
</tr>
</tbody>
</table>
Table A10: Data for the Determination of Relative Humidity of Salt Solutions

<table>
<thead>
<tr>
<th>SALT</th>
<th>CaSO₄</th>
<th>K₂SO₄</th>
<th>CH₃COONa</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD1</td>
<td>10.68</td>
<td>24.22</td>
<td>10.26</td>
<td>22.67</td>
</tr>
<tr>
<td>QD2</td>
<td>10.43</td>
<td>24.16</td>
<td>9.88</td>
<td>22.48</td>
</tr>
<tr>
<td>QO1</td>
<td>18.24</td>
<td>25.43</td>
<td>8.22</td>
<td>20.78</td>
</tr>
<tr>
<td>QO2</td>
<td>8.24</td>
<td>24.41</td>
<td>4.61</td>
<td>20.02</td>
</tr>
<tr>
<td>RH</td>
<td>0.0250</td>
<td>0.0584</td>
<td>0.1050</td>
<td>0.2500</td>
</tr>
</tbody>
</table>

QD1 = Initial weight of salt solution in desiccator
QD2 = Final weight of salt solution in desiccator after 24 hours
QO1 = Initial weight of salt solution opened to atmosphere
QO2 = Final weight of salt solution opened to atmosphere after 24 hours

\[
\text{RH} = \frac{(\text{QD2} - \text{QD1})}{(\text{QO2} - \text{QA1})}
\]

\[
\text{RH} = \frac{P}{P_0}
\]

Table A11: BET Isotherm of Synthesized Catalysts

<table>
<thead>
<tr>
<th>CATALYST SAMPLES</th>
<th>CaSO₄</th>
<th>K₂SO₄</th>
<th>CH₃COONa</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V(g)</td>
<td>Y(g-1)</td>
<td>V(g)</td>
<td>Y(g-1)</td>
</tr>
<tr>
<td>ZnO-ZnFe₂O₄</td>
<td>0.00115</td>
<td>0.045</td>
<td>0.00359</td>
<td>0.0579</td>
</tr>
<tr>
<td>ZnO-ZnFe₂O₄/AC</td>
<td>0.00189</td>
<td>0.074</td>
<td>0.00754</td>
<td>0.1216</td>
</tr>
</tbody>
</table>
Figure B1: BET Isotherm Plot for ZnO-ZnFe$_2$O$_4$ Photocatalyst

Figure B2: BET Isotherm Plot for ZnO-ZnFe$_2$O$_4$/AC Photocatalyst
Figure B3: The Peaks for Evaluating $\beta$ and $\theta$ for ZnO-ZnFe$_2$O$_4$ Photocatalyst

Recall

$$L = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} 2.27

$\beta = (36.296 - 36.114) \times \frac{\pi}{180}$ \hspace{0.5cm} K = 0.9 \hspace{0.5cm} \lambda = 1.54 \text{ Å}

= 0.00318

$$L = \frac{0.9 \times 1.54 \text{ Å}}{0.00316 \times \cos \left(\frac{36.192}{2}\right)}$$

= 458.48 Å

= 45.5 nm
Figure B4: The Peaks for Evaluating $\beta$ and $\theta$ ZnO-ZnFe$_2$O$_4$ / AC Photocatalyst

Similarly,

$\beta = (36.35 - 36.18) \pi / 180 \quad K = 0.9 \quad \lambda = 1.54 \text{ Å}$

$= 0.00297$

$$L = \frac{0.9 \times 1.54 \text{ Å}}{0.00297 \times \cos \left(\frac{36.265}{2}\right)}$$

$= 491.06 \text{ Å}$

$= 49.1 \text{ nm}$
APPENDIX C - CALCULATIONS

The Photocatalytic efficiency for the three parameters were evaluated using equation (2.14):

\[
PE = \frac{(C_0 - C_t) \times 100}{C_0}
\]

(2.14)

The initial concentration \(C_0\), for COD = 2560 mg/l

\[\text{BOD}_5 = 650 \text{ mg/l}\]

\[\text{Cr} = 3.9 \text{ mg/l}\]

For Example; from Table A1

At any time \(t\), the concentration is \(C_t\).

Hence at 5min, \(C_5\) for COD = 2115 mg/l

\[\text{BOD}_5 = 612 \text{ mg/l}\]

\[\text{Cr} = 3.6 \text{ mg/l}\]

Therefore:

\[\%\text{COD Removed} = \frac{(2560 - 2115)}{2560} \times 100 = 17.38 \%\]

\[\%\text{BOD}_5 \text{ Removed} = \frac{(650 - 612)}{650} \times 100 = 5.85 \%\]

\[\%\text{Cr} \text{ Removed} = \frac{(3.9 - 3.6)}{3.9} \times 100 = 7.69 \%\]

Similar calculations were carried out for the determination photocatalytic efficiency of the three parameters at any time \(t\) for to obtained \(C_t\) and the results obtained are tabulated in Tables A1 – A9.