ADSORPTION OF DISSOLVED IONS IN MINE WASTEWATER WITH LATERITE AND IRON OXIDE NANOPARTICLES

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MASTER OF SCIENCE

By

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By

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A THESIS APPROVED BY THE MATERIAL SCIENCE AND ENGINEERING DEPARTMENT

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Chief Academic Officer

Date
DECLARATION

I declare that this thesis is my original work. It is being submitted for the MSc Degree of Material Science and Engineering in the African University of Science and Technology and has not been presented for a degree in any other University.

Signature..............................

Date.................................

Ibrahim Jumal
ABSTRACT

This work studies the adsorption capacity of laterite and iron oxide nanoparticles for dissolved ions in solution and therefore its ability to reduce conductivity of mine waste effluent. Three laterite samples were prepared and used as adsorbents. The first laterite adsorbent was used without any treatment, the second was heat treated and the third was mixed with 15 % iron oxide nanoparticles of particle size 100 nm. Laterite and nanoparticle characterization, pH and adsorption tests were conducted to ascertain the composition of laterite and as-prepared iron oxide nanoparticles, the adsorption capacity of the adsorbents and the optimum conditions for adsorption. The X-ray diffraction. (XRD) results of both pure and heat-treated laterite showed the main minerals present to be: Quartz (SiO$_2$), Alumina (Al$_2$O$_3$), Berlinite (AlPO$_4$) and Hematite (Fe$_2$O$_3$). The XRD results for synthesized iron oxide nanoparticles showed the mineral Magnetite (Fe$_3$O$_4$). The adsorption results of heat-treated laterite showed the highest adsorption capacity for total dissolved ions at a pH range of 6.5 - 6.8. Laterite and nanoparticles composite had the highest adsorption capacities for Ca and Mg ions.
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I would like to thank my supervisor, Professor Luke Achenie and Co-supervisor, Dr. A. R. Adetunji for their guidance and support during the course of this project. Secondly to my advisors Professor Winston Oluwole Soboyejo and Professor Addai-Mensah Jonas for their guidance, continual input and motivation, which made this study possible.

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My huge appreciation goes to those I call family, my parents, my brothers, sisters, and Desmond Kofi Sika Ofori, for their inspiration, I am forever grateful to them.

Finally, special thanks to the faculty and staff of the African University of Science and Technology (AUST), Turkish Nile University, PAMI and African Capacity Building Foundation (ACBF) for their benevolence support and sponsorship in every way.
DEDICATION

This work is dedicated to Almighty Allah for his wonderful mercy, strength and protection. Secondly, to Assoc. Professor E. K. Esiam and Mustapha Adams; words cannot express my gratitude. Allah richly bless you.

Finally to my parents Mr. and Mrs. Ibrahim and my siblings for their prayers and support.

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CHAPTER ONE

BACKGROUND

1.1 Introduction

High quality water is a critical resource with invaluable socio-economic and environmental value and significance worldwide. The growing concern with water quality and increasing stringent environmental regulation has brought focus on water recycling, water treatment and minimization of water used in the mining and process industries. Conventional treatments to meet allowable concentrations of contaminants in water before discharge are being challenged due to economics and cost factors in technology and selection. Effective sustainable development must, therefore, ensure uncontaminated streams, rivers, lakes and oceans (Nkwonta and Ochieng 2013). Under current practice, water draining from process industries and base metal mines frequently contain organic, inorganic and heavy metals at high levels. When the contaminants in the effluents become higher than the set standards, disposal becomes a challenge.

As process water from mineral processing accumulates or when the water level overflows the depth of an open pit mine or an underground mine, the water is pumped out of the mine to ensure safety and stability or may be reused for process applications such as make-up water, dust suppression or mill operations, grinding, leaching, and steam generation depending on the water availability and quality. Nevertheless, it has been observed that more than 70% of all pollutants from the mining industry mostly contained in wastewaters are emitted into water bodies (Doll, 2012). With the fast development in industries, a huge quantity of wastewater is been produced and discharged into soils and water systems. The removal of these contaminants before discharge is receiving significant attention. There is, therefore, a growing necessity for finding versatile and low-cost treatment technologies to mitigate these contaminants. Currently, adsorption has emerged as a simple and effective technique for water and wastewater treatment even though its success largely depends on the development and improvement of materials for efficient adsorption. Activated carbon, clay minerals, zeolites, biomaterials and some industrial solid wastes materials have been used as adsorbents for adsorption of dissolved ions and organics in wastewater (Wang and Peng 2009).

In the past, membrane separation processes received much attention and are been applied in different industries especially in wastewater treatment (Mortazavi, 2008). These membrane processes which include: reverse osmosis, nanofiltration, ultrafiltration and
microfiltration are effective (Dessouky and Ettouney, 2002) but considered to be very expensive.

1.2 Problem Definition

The contamination of water by dissolved ions is a significant worldwide problem (Nriagu and Pacyna, 1988) that warrants cost-effective methods for the removal of the undesirable species. This excessive pollution problem results from chemical substance and dissolved constituents from the ore added to the water at concentrations higher than established limits during processing. To make things worse, the regulated discharge limits of industrial wastewater effluents are getting more restrictive with time (Mortula and Shabani, 2012).

As inorganic components dissolve in water, one of the parameters that changes significantly is conductivity. Conductivity is a measure of the ability of water or an aqueous solution to carry an electric current. The current flow in water depends on the presence and concentration of ions in the water and therefore conductivity is often used as an indirect estimate for dissolved solids content of a solution (Coury, 1999). High total dissolved solids (TDS) discharged to rivers and streams can promote eutrophication, destroy sensitive ecosystems and endangers aquatic species (e.g., the cutthroat trout and cui-cui fish) in rivers and lakes (Mortensen et al., 2008). These water bodies can also be rendered unwholesome for both animals and plant usage, especially for people living in catchment areas, who do not only use these waters for drinking but also for other domestic purposes.

In recent years, most mining companies in the Western Region of Ghana have experienced relatively higher conductivity values of about 4000 µS/cm above Environmental Protection Agency (EPA) standard (≤ 1500µS/cm) (US EPA, 2011) for process waters. Since large volumes of wastewater are generated daily, high conductivity in the process water creates discharge problems. Existing wastewater treatment technologies such as oxidation, precipitation, alum coagulation/precipitation, reverse osmosis, nanofiltration, ion exchange, demand high capital investment, operation and maintenance cost (Lesmana et al., 2009).

The applicability of nano-materials and membrane separation processes for the reduction of dissolved ions in contaminated water has been demonstrated in the open literature (Mostafa and Hoinkis, 2012, Carlos et al., 2014, Rytwo, 2012). Reverse Osmosis (RO) and Nanofiltration (NF) are pressure-driven processes that are used to remove TDS and nutrients from water. Many researchers and full-scale applications have established RO as the most effective membrane process for removing dissolved solids (Mortazavi, 2008) and also for reducing the conductivity of water. RO is currently used by most mining companies in Ghana. However, it is considered to be very expensive and can render mining operations
uneconomical. It also generates highly concentrated retentate after filtration. Hence alternatives such as metal- based nano-materials have been explored to remove a variety of inorganic contaminants and heavy metals ions which includes; arsenic, lead, mercury, copper, cadmium, chromium and nickel. Metal oxides such as iron oxide, titanium dioxide and alumina are effective and comparably low-cost adsorbents for the removal of heavy metals ions (Qu et al., 2013).

Numerous adsorbents such as activated carbon, zeolites, clay, mesoporous silica (Feng et al., 1997), diatomaceous earth substrates (Al-Dege et al., 2000 and 2001) and finely layered clay minerals, are employed to remove undesirable metal ions from process water, enabling recycling for reuse. The high cost of some adsorbents can, however, be a major disadvantage for their application. In contrast, lateritic soil is one such naturally available and inexpensive adsorbent. It is known to have high porosity, high permeability, high adsorption and high ion exchange capacity. Various researchers have studied the sorption capabilities of lateritic soil in adsorbing metal ions in solution (Ajith and Jayantha, 2013; Avinash et al., 2009). Of particular interest is the deployment and efficacy of laterite as cheap and environmentally benign adsorbents for mine water treatment and also the improvement of their metal ion adsorption capacities by the incorporation of nanoparticles to replace the costly, conventional methods.

Based on the discussions above, this work aims to employ iron oxide nanoparticles with laterite as adsorbents to reduce the dissolved solids and conductivity of mine wastewater without compromising efficiency at a minimal cost.

1.3 Aims and Objectives of the Research

The objectives of this thesis are;

- To synthesize iron oxide nanoparticle.
- To reduce the dissolved ions (conductivity) of mine waste water using laterite and iron oxide nanoparticles as adsorbents.
- To determine optimum conditions for dissolved ion (conductivity) reduction.
- To determine the adsorption capacity of laterite and iron oxide nanoparticles.

1.4 Materials and Methodology:

The methods used include;

- Review of relevant literature
- Synthesis of iron oxide nanoparticles
- Characterization of lateritic soil;
1.5 Expected Outcomes

At the end of the research, it is expected that:

- The total dissolved ions (conductivity) of the mine waste water will be reduced by the adsorbents.
- Factors that can affect the reduction of ions in mine wastewater will be ascertained.
- The adsorption properties of laterite with iron oxide nanoparticles will be determined.
- The adsorption capacity and adsorption isotherm followed by the adsorption will be determined.

1.6 Thesis Organization

The thesis consists of five chapters with each chapter discussing a distinct activity that will be carried out systematically to complete the thesis.

Chapter one will introduce the problem statement, objectives of the research, materials and methodology and expected outcomes.

Chapter two will entail the literature review on conductivity, effects of high conductivity, and causes of conductivity in mine wastewater, mine waste waters, contaminants of mine waste waters, waste water treatment techniques, nanotechnology and nanofiltration, types of nanomaterials for water treatment, laterites and chemical precipitation.

Chapter three will focus on experimental procedure, materials used, sorption test, effluent constituent analysis, measurement of physical parameters, filtration test using laterite with metal nanoparticles.

Chapter four discusses the results obtained. Finally, Chapter five presents the conclusions and recommendations.
CHAPTER TWO

LITERATURE REVIEW

1.7 Introduction
Water is a natural resource, on which every living thing depends for survival. It covers about 75% of the earth’s surface but it becomes scarce when its quality is taken into consideration since it possesses challenges to its users. Water can be used domestically for human activities, in manufacturing industries and mining industries and in the agricultural sector. Each of the above uses of water generates wastewater, which becomes a challenge when it comes to the issue of disposing into the environment. Wastewater is made up of about 99.9% of water with the rest being ions of organic and inorganic component as shown in Table 1.1 below (Anon, 2014). These dissolved ions called TDS affect the quality of water. As the TDS increase, the conductivity of the water also increases. Conductivity is a measure of the ability of an aqueous solution (water) to carry an electric current. Contributors to TDS and Conductivity include inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions (negatively charged ions) or sodium, magnesium, calcium, iron, and aluminium cations (positively charged ions) (Kemker, 2014). The conductivity of most freshwaters ranges from 10 to 1000 µS cm⁻¹ but sometimes exceed 1000 µS cm⁻¹, especially in polluted waters (Chapman and Kimstach, 2005). Organic compounds such as phenol, alcohol, oils and sugar do not conduct much electrical current and therefore have a low conductivity when in aqueous solutions. The current flow in water also depends on molality and valence of the ions, the temperature of measurement and on the pH of the solution (Coury, 1999). The typical conductivity of ultra-pure water is 5.5x10⁻⁶ S/m, drinking water is 0.005-0.05 S/m and sea water is 5 S/m. Conductivity is a parameter use to determine the quality of water and a number of applications that are related to water quality.

1.8 Conductivity and Total Dissolved Solids (TDS)

Electrical conductivity (EC) is used as an estimate of the amount of TDS or the total quantity of dissolved ions in the water. Total Dissolved Solids is a measure of the total ions in solution. TDS in drinking water is derived from many sources including sewage to urban industrial wastewater etc. TDS test is therefore considered in determining the general quality of water (Mohsin et al., 2013). In dilute solution, TDS and EC values are comparable. In streams and rivers, dissolved solids consist of Ca²⁺, Cl⁻, nitrate, Fe²⁺, SO₄²⁻, and other ions that will pass through a filter with pores size of 2 microns (0.002 cm) in size. TDS (in mg/L) can be obtained by multiplying the conductance by a factor, which is commonly
between 0.55 and 0.75. This factor is determined for each water body. The factor is close to 0.67 for waters in which concentration of sodium and chloride are higher and higher for waters containing high concentrations of sulfate (Chapman and Kimstach, 2005).

Conductivity measurement is used to:

1. Determine the mineralization of water or simply the TDS.
2. Determine the variation or changes in natural water and wastewaters.
3. Estimate sample size necessary for other chemical analyses.
4. The amounts of treatment chemicals to be added to a water sample.

Total dissolved solids information gives the overall ionic effect in a water source. Certain physiological effects on plants and animals are often affected by the available ions in the water. An elevated level of TDS does not necessarily indicate that the water presents a health risk. However, elevated levels of specific ions such as nitrate, arsenic, aluminium, copper, or lead, could present health risks. If an indicator test shows elevated TDS, the specific ionic analysis is required for each contaminant to determine potential health effects (Arizona, 2009).

**Table 2.1** Organic and Inorganic Components in Wastewater

<table>
<thead>
<tr>
<th>Organic</th>
<th>Inorganic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin and dieldrin</td>
<td>Arsenic</td>
</tr>
<tr>
<td>Benzene</td>
<td>Cadmium</td>
</tr>
<tr>
<td>Benzo-a-pyrene</td>
<td>Chromium</td>
</tr>
<tr>
<td>Chlordane</td>
<td>Fluoride</td>
</tr>
<tr>
<td>Tetrachlorethylene</td>
<td>Mercury</td>
</tr>
<tr>
<td>DDT</td>
<td>Lead</td>
</tr>
<tr>
<td>1,1 Dichlorethylene</td>
<td>Selenium</td>
</tr>
<tr>
<td>1,2 Dichloroethane</td>
<td>Copper</td>
</tr>
<tr>
<td>Dye</td>
<td>Sodium</td>
</tr>
<tr>
<td>Heptachlor and heptachlor epoxide</td>
<td>Calcium</td>
</tr>
<tr>
<td>Lindane</td>
<td>Potassium</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>Sulfates</td>
</tr>
<tr>
<td>2, 4, 6 Trichloroethylene</td>
<td>Nitrates</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>Chlorides</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Iron</td>
</tr>
<tr>
<td>Trichlorophenol</td>
<td>Zinc</td>
</tr>
</tbody>
</table>

(Source; Anon, 2014)
1.9 Water Pollution

Natural water bodies can be polluted by chemical, physical, or microbial substances. Adverse changes in water quality can lead to illness and deaths, accounting for approximately 50 million deaths per year worldwide (Cunningham and Saigo, 2001). Water contamination may result from natural causes such as sedimentation from severe rainfall, volcanic eruptions and algae bloom. The most problematic of water pollutants are derived from human activities in the environment or overpopulation phenomena, which results in the contamination of water bodies such as lakes, rivers, oceans, and groundwater. Any physical, biological, or chemical change in the quality of water that can affect living organisms or renders water unsuitable for use can be considered pollution (exampleessays, 2002). When toxic substances enter lakes, streams, rivers and oceans, they get dissolved suspended in water causing pollution. This results in the pollution of water which also affects aquatic ecosystems (Cunningham and Saigo, 2001).

1.10 Water Pollutants

Water pollutants are categorized into chemical, physical and biological pollutants. Chemical water pollutants are atoms or molecules, which have been discharged into natural water bodies, usually by human activities. Chemicals in water can be naturally occurring or introduced by human activities and can have serious health effects (Bandal, 2015). Common examples of chemical pollutants include the carbonates, sulfates, chlorides, fluorides, nitrates, and heavy metals. These chemicals form the total dissolved solids, present in water. Radioactive pollutants are a subclass of chemical pollutants.

Physical water pollutants include color, odor, turbidity, taste, temperature and conductivity which constitute the physical quality of water. These materials are not so harmful to human health as chemicals or pathogens, they comprise mainly of the visual impact of water pollution.

Biological water pollutants include algae, fungi, viruses, protozoa and bacteria. The life forms present in water are affected to a large extent by the presence of pollutants. Pathogens introduced into natural water bodies originate from untreated sewage or surface runoff from intensive industrial or agricultural activities. One of the most common disease agents is Giardia lamblia, a parasitic protozoan common in faecal material of many fauna (Hesain, 2015). This microbe is particularly insidious, due to its resistance to conventional sewage treatment. Other protozoans and bacteria are important causes of illness and mortality in developing countries where water scarcity, population density and inadequate sewage treatment combine to widespread parasitic and bacterial disease (eoearth, 2016).
1.11 Effects of High Dissolved Solids in Water

TDS is usually indicative of water pollution regardless of whether the result was caused by manmade or natural sources. Changes in conductivity, salinity and total dissolved solids can have a negative impact on aquatic life and water quality (Kemker, 2014). A high concentration of total dissolved solids affects the water balance in the cells of aquatic organisms. Conductivity values outside of a normal range can result in fish kills due to changes in dissolved oxygen concentrations, osmosis regulation and TDS toxicity (Kemker, 2014). An organism placed in water with a high concentration of solids will shrink somewhat because the water in its cells will move out. This affects the organism's ability to maintain its proper cell density, making it difficult to keep its position in the water. It might float or sink to a depth to which it has not adapted, and it might not survive. Water with high TDS often has bad taste and high hardness and can also result in a laxative effect. Environmental Protection Agency sets a standard of 500 mg/L TDS in drinking water. A high concentration of total solids can make drinking water unpalatable and might have an adverse effect on people. Levels of total solids that are too high can also reduce the efficiency of wastewater treatment plants, as well as the operation of industrial processes that use raw water (US EPA, 2011). Corrosion of metallic surfaces by waters high in dissolved solids causes problems with industrial equipment and boilers, water heaters, washing machines and dishwashers.

Agricultural uses of water for livestock watering are limited by excessive dissolved solids ([www.water.nr.state](http://www.water.nr.state)). High TDS levels are also responsible for leaving water spots on dishes and white mineral build up on water faucets and swamp coolers.

1.12 Water Quality Standards

**Table 2.2** WHO Water Quality Standards- Primary and Secondary Maximum Contaminant Level (MCL)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Primary MCL</th>
<th>Secondary MCL</th>
</tr>
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<tbody>
<tr>
<td>PH</td>
<td>6.5-8.5</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Conductivity</td>
<td>500 µS/cm</td>
<td>no limit listed</td>
</tr>
<tr>
<td>TDS</td>
<td>500 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Sulfate</td>
<td>500 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Nitrate</td>
<td>10.0 mg/L</td>
<td>50 mg/L</td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.50 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Chloride</td>
<td>250 mg/L</td>
<td>no limit listed</td>
</tr>
</tbody>
</table>
### 1.13 Sources of High Dissolved Solids in Waste Water

Natural sources of dissolved solids or TDS and high conductivity in water include mineral springs, carbonate deposits, salt deposits and sea water intrusion. Other sources can include sewage, urban and agricultural runoff, industrial wastewater, the piping or hardware used to transport water. TDS is controlled by:

- **Geology** (rock types) composition determines the chemistry of the watershed soil and sometimes the wastewater. For example, limestone leads to higher EC because of the dissolution of carbonate minerals in the basin.

- **Wastewater from sewage treatment plants** (point source pollutants).

- **Wastewater from septic systems and drain field on-site wastewater treatment and disposal systems** (nonpoint source pollutants).

- **Urban run-off from roads** (especially road salt). This may shock organisms with intermittent extreme concentrations of pollutants, which seem low when averaged over a week or month.

- **Agricultural runoff** of water draining agricultural fields typically has extremely high levels of dissolved salts.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>1.5 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Calcium</td>
<td>120 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Sodium</td>
<td>100 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Magnesium</td>
<td>120 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Potassium</td>
<td>no limit listed</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Manganese</td>
<td>no limit listed</td>
<td>0.05 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>0.015 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Arsenic</td>
<td>10 ug/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.005 mg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Zinc</td>
<td>no limit listed</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>0.05 mg/L</td>
<td>1.3 mg/L</td>
</tr>
<tr>
<td>Chromium</td>
<td>3 μg/L</td>
<td>no limit listed</td>
</tr>
<tr>
<td>Iron</td>
<td>no limit listed</td>
<td>0.3 mg/L</td>
</tr>
</tbody>
</table>
- Atmospheric inputs of ions are typically relatively minor except in ocean coastal zones where ocean water increases the salt load (salinity) of dry aerosols and wet (precipitation) deposition.

- Evaporation of water from the surface of a lake concentrates the dissolved solids in the remaining water - and so it has a higher EC. This is a very noticeable effect in reservoirs.

1.14 Causes of High TDS in Waste Water

The major contributors of high TDS in water include the following:

Sulfate - The presence of sulfate in drinking water results in a noticeable change of taste. The lowest taste threshold concentration for sulfate is approximately 250 mg/l. The physiological effects resulting from the intake of large quantities of sulfate are dehydration and gastrointestinal irritation (Asklund and Eldvall, 2005). Water containing magnesium sulfate at levels above 600 mg/l acts as a purgative in humans and may also contribute to the corrosion of distribution systems. Drinking water should not have sulfate levels exceeding 500mg/l (WHO, 2015).

Chloride (Cl\(^{-}\)) - High chloride content in water may indicate pollution by sewage, industrial waste or intrusion of seawater. Chloride occurs in natural waters bodies in varying concentrations. Concentration is usually greater in groundwater than surface water especially if salt deposits are in the area. Water containing chloride concentration above 250 mg/L may taste salty (Nduka et al., 2008). High chloride concentration damage metallic pipes and structure as well as harms growing plants (Mohsin et al., 2013).

Nitrate (NO\(_3^{-}\)) - Nitrate (NO\(_3^{-}\)) is highly soluble in water and stable over a wide range of environmental conditions. It is easily transported in streams and groundwater. Nitrate serve as a source of food to plankton, aquatic plants, and algae, which are then eaten by fish. Excessive concentrations of nitrate and nitrite can be harmful to humans and wildlife (Zollweg, 2006). Nitrite concentrations in freshwaters are usually about 0.001 mg/L, and rarely higher than 1 mg/L. High nitrite concentrations are associated with microbiological quality of water (Chapman and Kimstach, 2005).

Phosphate (PO\(_4^{3-}\)) - The introduction of phosphorus in the form of phosphate in an aquatic environment is a major cause of eutrophication. Phosphorus is a vital nutrient for all living things. Phosphorus occurs naturally, almost as phosphate. Most phosphates are dissolved but
some combine with suspended particles in the water and contribute to turbidity (Nduka et al. 2008).

**Calcium (Ca)** - Calcium salt and calcium ion are among the most commonly occurring in nature. They may result from the leaching of soil and rocks or may come from manmade sources such as industrial wastes. Calcium concentrations in natural waters are typically < 15 mg/L. For waters associated with carbonate-rich rocks, concentrations may reach 30-100 mg l⁻¹. Salt waters have concentrations of several hundred milligrams per litre (Chapman and Kimstach, 2005).

**Sodium (Na)** - Sodium salts are found in almost all food and drinking water. The concentrations of sodium in most potable waters are although less than 20 mg/L, it should be noted that some water softeners can add significantly to the sodium content of drinking water. Concentrations in excess of 200 mg/L may give rise to unacceptable taste. Concentrations of sodium in natural surface waters vary considerably depending on local geological conditions, wastewater discharges and seasonal use of road salt (Chapman and Kimstach, 2005).

**Magnesium (Mg)** - The second most abundant mineral in seawater behind sodium, magnesium is common among many bodies of water. Magnesium is common in natural waters as Mg²⁺, it contributes to water hardness. Mg²⁺ is washed from rock surfaces and circulates into water (Chapman and Kimstach, 2005). Depending on the area, some water contains up to 5mg of magnesium per litre (Chapman and Kimstach, 2005). Negative effects on the environment as a result of magnesium water are generally minor if there are any at all. Because large amounts of magnesium in water make it hard, softeners are often added to the water supply.

**Potassium (K)** - Seawater contains about 400 ppm. Potassium (as K⁺) is found in low concentrations in natural waters since rocks contain potassium. However, potassium salts are widely used in industry and in fertilisers for agriculture and enter freshwaters with industrial discharges and runoff from agricultural land (Chapman and Kimstach, 2005). Intake of a number of potassium compounds can be harmful to our health. For example at higher concentrations, potassium chloride interferes with nerve impulses (puritybay, 2013), which of course affects the functioning of the heart. Potassium alum causes stomach ache and nausea at an even concentration as low as 2 g. Potassium carbonate and potassium dichromate are lethal, while potassium nitrate causes severe intoxication (www.wqa.org).

**Heavy Metals** – heavy metal refers to a metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration (Sigel and Sigel, 2005). Examples of heavy metals include mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), thallium...
(Tl), and lead (Pb). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. Heavy metals can enter our bodies via food, drinking water and air, at higher concentrations they can lead to poisoning. Heavy metals can enter a water supply by industrial and municipal waste, or even from acidic rain dissolving soils and releasing heavy metals into streams, lakes, rivers, and groundwaters (lenntech.com).

1.15 Wastewater and Mine Wastewaters

Wastewater is water containing wastes products originating from residential, commercial, industrial sites etc. Municipal wastewater contains sewage from sinks and showers. Industrial waste effluent is the most common source of water pollution in present day (Ogedengbe and Akinbile, 2004) and it increases yearly due to the fact that most countries are getting industrialized (Ewa et al., 2011).

The processing of metals for economic use involves a series of physical and chemical processes, which involves excavation of the ore that contains the metal through to production of the metal in marketable form (Sangodoyin, 1991). Some mineral processes involve extensive use of organic and inorganic chemicals, partly for the purpose of altering the surface characteristics of the minerals (e.g. in flotation processes) and to obtain solutions and precipitates in leaching processes. In most cases, the added chemicals and in some cases dissolved substances remain in the effluent (Kihlstedt, 2008).

The wastewater problems of the mineral industry can be listed as follows:

- Destruction of amenities due to the storing of waste piles and the provision of adequate settling ponds.
- Pollution of recipients with slime and precipitates that sterilize the bottom.
- Toxic effects of added inorganic or organic substances that disrupt the normal biological cycle in the recipient.
- Overfertilization of the recipient by excessive discharge of nutrients.
- Water rendered unfit for recreational, communal or industrial use due to the presence of slime, discoloration, objectionable tastes and odors, or objectionable substances in solution.

There is thus a challenge of providing water in adequate quantity and of the required quality for minimizing hazards to human health and conserving the water bodies and the environment.

1.16 Wastewater Treatment Techniques

Methods for water treatment can be divided into four categories: physical, chemical, biological, and membrane. In general, physical treatment requires the least energy but is least
effective in reducing pollutant concentrations. Biological processes have the high energy cost but are effective in reducing conventional pollutants. Chemical processes lie in between the other two both in energy use and effectiveness.

1.16.1 Physical Treatment Methods

- Screening (removal of coarse solids by use of a straining device)
- Sedimentation (gravity settling of pollutants out of the wastewater)
- Flotation (use of small gas bubbles injected into the wastewater which causes pollutant particles in the wastewater to rise to the surface for subsequent removal)
- Air stripping (removal of volatile and semi-volatile organic compounds from wastewater by use of air flow).

1.16.2 Chemical Treatments Methods

- Neutralization (adjustment of alkalinity and acidity to the same concentration pH 7)
- Precipitation (addition of chemicals to wastewater to change the chemical composition of pollutants so that the newly formed compounds settle out during sedimentation)
- Coagulation (use of chemicals to cause pollutants to agglomerate and subsequently settle out during sedimentation)
- Adsorption (use of a chemical which causes certain pollutants to adhere to the surface of that chemical)
- Disinfection (use of a chemical or other methods such as ultraviolet radiation to selectively destroy disease-causing organisms. (Sterilization is the destruction of all organisms)
- Chlorination (addition of chlorine to the level that chloramines will be oxidized to nitrous oxide and nitrogen, and chlorine will be reduced to chloride ions)

1.16.3 Biological Treatment Methods

- Air/Oxygen activated sludge - An aerobic process in which bacteria consume organic matter, nitrogen and oxygen from the wastewater and grow new bacteria
- Aerated pond/lagoon - An aerobic process very similar to air activated sludge. Mechanical aerators are generally used to either inject air into the wastewater or to cause violent agitation of the wastewater and air in order to achieve oxygen transfer to the wastewater
- Trickling filter (fixed film aerobic process) - A tank containing media with a high surface to volume ratio is constructed. Wastewater is discharged at the top of the tank
and percolates (trickles) down the media. Bacteria grow on the media utilizing organic
matter and nitrogen from the wastewater

- Rotating biological contactor (RBC) - A fixed film aerobic process similar to the
trickling filter process except that the media is supported horizontally across a tank of
wastewater. The media upon which the bacteria grow is continuously rotated so that it
is alternately in the wastewater and the air

1.17 Major Treatment Processes
Six categories of wastewater treatment methods were identified as potentially applicable for
industrial processes. These include; chemical treatment methods (precipitation, coagulation
etc.), membrane processes, ion exchange, biological sulfate removal, and adsorption.

1.17.1 Precipitation
To precipitate metal ions in solution, an alkaline solution is added to raise water pH and
supply hydroxides (OH-) so dissolved metals in the water forms insoluble metal hydroxides
and settle out (Opperman, 2008). The pH required to precipitate most metals from water
ranges from pH 6 to 9 except ferric iron which precipitates at about pH 3.5 (Heston and
Wieder, 1990). The types and amounts of metals in the water have much influence in the
selection of a wastewater treatment system (Casper, 2007).

1.17.2 Ion Exchange
This is a well-known method to de-ionize solutions (Heston and Wieder, 1990). The cost of
ion exchange materials compared to the relatively small returns, as well as the inability of
current technology to efficiently deal with vast amounts of effluent has made it unviable
(Buchanan, 2015).

1.17.3 Coagulation-Flocculation
Coagulation and flocculation consists of the addition of chemical products that accelerate
sedimentation with inorganic or organic compounds such as Aluminum sulfate, Aluminum
Hydroxide chloride or high molecular weight cationic polymer (Awaleh and Soubaneh,
2014). The purpose of the addition of coagulant is to remove almost 90% of the suspended
solids from the wastewater at this stage in the treatment process (Sinha and Bharambe, 2008).

1.17.4 Adsorption
The surfaces of solids and liquids possess a residual field of force which allows the uptake of
atoms, molecules, ions from systems in contact. This phenomenon is known as adsorption
(Ingol and Patil, 2013). The system which retains the foreign species or on its surface is
known as the adsorbent and the retained species are referred to as the adsorbate. The
adsorption is categorized on the basis of interactions that take place between the atoms,
molecules or ions (adsorbate) and the adsorbent. The rate of adsorption depends on upon
external mass transfer, internal diffusion and surface adsorption (Kumar and Bandyopadhyay,
2006). Basically, adsorption is a surface phenomenon and it takes place by physical forces
but, sometimes chemical bonding also participates in the adsorption process. Adsorption is
controlled by various parameters such as temperature, nature of the adsorbate and adsorbent,
and the presence of other pollutants along with the experimental conditions (Ali, 2012). Some
of the advantages of using plant wastes for wastewater treatment include simple technique,
requires little processing, good adsorption, selective adsorption of heavy metal ions, low cost,
free availability and easy regeneration.

1.18 Types of Adsorbents
Industrial adsorbents may fall into one of these three classes:
- Oxygen-containing compounds- silica gel, zeolites and laterites
- Carbon-based compounds- activated carbon and graphite
- Polymer-based compounds- polar or non-polar functional groups in a porous polymer
  matrix
- Bio/Agro-adsorbents

1.18.1 Silica Gel
Silica gel is a porous form of silica with a great internal surface area. It is a highly activated
adsorbent that is available in numerous sizes designed for many uses in industry
(nutecoverseas, 2016). It is a chemically unreactive, non-toxic, polar and dimensionally
stable (<400 °C or 750 °F) amorphous form of SiO$_2$ which is prepared by the reaction
between sodium silicate and acetic acid (nutecoverseas, 2016). Silica gel has been used for
the removal of cationic surfactants and for the removal of dyes and herbicide from water after
modification (Suman, 2010).

1.18.2 Zeolites
It is either a natural or synthetic crystalline aluminosilicate which has a repeating pore
network and release water at high temperature. It is manufactured by hydrothermal synthesis
of sodium aluminosilicates or silica source in an autoclave followed by ion exchange with a
cation (Na$^+$, Li$^+$, Ca$^{2+}$, K$^+$, NH$_4^+$). It is then followed by drying of the crystals and pelletizing
with a binder to form a macroporous pellets. It is used in drying of process air, CO$_2$
removal from natural gas, air separation, catalytic cracking, and catalytic synthesis and reforming (Wingenfelder et al., 2005).

1.18.3 Activated Carbon
It is a highly porous, amorphous solid consisting of microcrystalline graphitic structure. Activated carbon can be manufactured from carbonaceous materials such as coal, bituminous, sub-bituminous, lignite, peat and wood in two phases, carbonization and activation. Activated carbon is usually used for adsorption of organic substances, non-polar adsorbates in wastewater treatment (Sekar et al., 2004). It is the most widely used adsorbent since most of its chemical (e.g. surface groups) and physical properties (e.g. pore size distribution and surface area) (shodhganga.inflibnet, 2016) can be altered to suit a need. It also has a large micropore volume resulting in the high surface area.

![Activated Carbon](source: Anon, 2011)

1.18.4 Laterites
Soil contains a variety of oxide minerals and organic matter. These substances possess surface hydroxyl groups which can donate protons to the surrounding solution and can take up metal ions in return. Laterite is a class of soil in which the cementing materials are the sesquioxides and forms not less than 50% of its constituents when the sample is chemically analyzed (Madu, 1975). Sesquioxide is a chemical substance with empirical formula M₂O₃ where M can be potassium, rubidium or caesium and hydrated aluminum and iron oxides (Raheem et al., 2013). Natural laterite mainly consists of a mineral combination of goethite, hematite, aluminium hydroxide, kaolinite mineral and quartz and can easily be found in many regions in Africa. (Rizvi and Hussain. 2014). The lateritic soil has an effective media in which pollutants can be trapped and removed due to it's porous and permeable nature (Manu, 2011). It is a cost effective treatment method, storm water reclamation method, and can also be applied for ground water recharge in both small and large scale. The porous nature of laterite soil can trap suspended and colloidal particles, organic
and inorganics pollutants present in runoff water thereby reducing the pollutant concentrations (Halim et al., 2008).

**Figure 2** Laterite Soil

### 1.18.5 Diatomaceous Earth (DE)

DE is silica-rich, fossilized remains of diatoms formed over several thousand or perhaps million years. This natural silica biomineralization has attracted immense interest from researchers, as it produces intricate 3-D silica architectures with highly ordered nanopores and species characteristic patterns (De Stefano et al., 2005; Gale et al., 2009). Due to its low cost per available surface area, fine DE particles are becoming increasingly attractive as an adsorbent for water decontamination (Hernandez-Ramirez et al., 2008; Yang et al., 2008; Yu et al., 2011). The use of chemically-modified DE particles for metal ions removal from solutions has been exemplified in several studies (Al-Degs et al., 2000 & 2001; Khraisheh et al., 2004; Sheng et al., 2009). **Figure 2.3** displays some of the several varieties of shapes and microporous structures of natural diatomite particles (Losic et al., 2009).
Figure 2.3: Diversified shapes and microporous structures of natural diatomite particles. a–d) and f–i) SEM images of several marine diatom species. e) SEM of fossilized diatom biosilica structures from diatomaceous earth (Losic et al., 2009).

1.18.6 Mesoporous Silica
Mesoporous silica is a porous, 3D structural silica-based materials with highly open spaces interconnected to each other via SiO$_4$ tetrahedral bonds (Walcarius and Mercier, 2010). Mesoporous silica materials possess large specific surface areas (200 - 1500 m$^2$/g), uniform pore sizes and ordered nanochannels, and tunable liquid crystal-like structures (Feng et al., 1997). A major drawback of preparing mesoporous silica materials is the use of rather expensive templates, which constitutes a real restriction in the wide use of such high-efficiency adsorbents.

1.18.7 Agricultural Waste
Agricultural waste is inexpensive and non-living plant materials such as groundnut husk, eggshell, sugarcane husk and citrus peels are considered as potential adsorbents (Zwain et al, 2014). Several agricultural wastes adsorbents have been researched extensively for waste water treatment (Gardea-Torresday et al. 2000). For instance, the application of agro-waste materials, eg. Almond shell, coconut shell, coconut copra and groundnut shell. Pre-treatment of plant wastes can extract soluble organic compounds and improve adsorption efficiency of the product (Gaballah et al., 1997). (Kumar and Bandyopadhyay, 2006) reported that rice husk treated with sodium hydroxide, sodium carbonate and epichlorohydrin enhanced the adsorption capacity of cadmium.

1.18.8 Bio-sorbents
Heavy metals bio-sorption from aqueous solutions is a process that has been verified as a very promising process in the removal of heavy metal contaminants (Zwain et al, 2014). The major advantages of bio-sorption are the use of inexpensive bio-sorbents and its high effectiveness in reducing contaminants (Fua and Wang, 2011). Bio-sorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources as follows (1) non-living biomass such as lignin, shrimp, krill, squid, and crab shell; (2) algal biomass; (3) microbial biomass, for example, bacteria, fungi, and yeast (Zwain et al, 2014).

1.19 Metal Ion Adsorption Mechanisms and Kinetics
Adsorption arises due to the fact that the surface atoms of the adsorbent are not in the same environment as the atoms inside the bulk. Inside the adsorbent all the forces acting between
the atoms are balanced but on the surface the atoms are not surrounded by atoms or molecules on all sides, and hence they possess unbalanced or residual attractive forces (Ingol and Patil, 2013). These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface. The extent of adsorption increases with an increase in surface area per unit mass of the adsorbent at a given temperature and pressure. The rate of adsorption depends on external mass transfer, internal diffusion and surface adsorption (McKay et al., 1988). There are mainly two types of adsorption of gases on solids. If the adsorption on the surface of a solid occurs as a result of weak van der Waals forces, it is termed as physical adsorption or physisorption. When molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption.

### 1.19.1 Chemisorption

Chemisorption is a direct chemical bonding (e.g., covalent or mono/bi-dentate) between similarly or oppositely charged adsorbate (metal ions) and the adsorbent surface. This interaction invariably involves high activation energy changes and leads to a high adsorption density with generally irreversible, monolayer formation. Covalent bonding-mediated chemisorption process experienced through electron exchange or electron orbitals sharing is exemplified by heavy metal ions (e.g., Hg$^{2+}$, Ag$^+$, Cu$^{2+}$ etc.) interactions with amino group functionalized adsorbents (Feng et al., 1997).

### 1.19.2 Physisorption

Physisorption occurs where there is an electrostatic attraction, hydrogen bonding, hydrophobic and van der Waals interactions between the metal ions and the adsorbent surface involves low energy changes. Electrostatic attraction is encountered when metal ions and adsorbent are oppositely charged. In physisorption, the contributions to adsorbate-adsorbent potential are related to (i) dispersion energy, (ii) close range repulsion energy, (iii) induction energy interaction between an electric field and an induced dipole interactions (Masel, 1996). The adsorption of positively charged heavy (e.g., Hg$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$) or alkaline-earth metal ions (e.g., K$^+$ and Na$^+$) onto negatively charged silica and zeolites particles are examples.

### 1.20 Adsorption Isotherms

The relationship between amounts of pollutant adsorbed in water at equilibrium is called an adsorption isotherm. An equilibrium is established when the concentrations of pollutant adsorbed and in water become constant. From literature, several models are used to describe the process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm. These isotherm models are based on almost similar principle with little difference in their approaches.
**Langmuir Adsorption Model** is a common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration. The Langmuir isotherm indicates that a reaction is a reversible phenomenon and assumes monolayer adsorption onto a surface containing a finite number of adsorption sites (Desta, 2013). Once all adsorption sites are filled, no further sorption can take place. This indicates that the surfaces reaches a saturation point where maximum adsorption of the surface will be achieved (Masel, 1996). The isotherm is represented by:

\[
\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}
\]

(Desta, 2013) (2.1)

Where \( q_e \) = the specific adsorption, \( C_e \) = equilibrium concentration, \( q_{max} \) and \( bq_{max} \) are constants and relate to the energy of adsorption and maximum adsorption capacity, and their values are obtained from the slope and interception of the plot.

**Freundlich Adsorption Model** is a modified form of the Langmuir isotherm. It is mathematically expressed as

\[
\ln q_e = \ln K_f - \frac{1}{n} \ln C_e
\]

(Desta, 2013) (2.2)

Where \( q_e \) represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), \( C_e \) represents the equilibrium concentration (mg/L), \( K_f \) and \( n \) are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively.

### 1.21 Nanotechnology and Membrane Processes

Nanotechnology holds great potential in recent water and wastewater treatment to improve treatment efficiency (Qu et al., 2013). Nanoparticles can also be used with various chemical and process applications for the removal of target compounds. It has been found that nanoparticles have unique properties that allow them to be used as high capacity and selective sorbents for metal ions and anions (Tiwari, et al., 2008).

Membranes are thin films of synthetic organic or inorganic materials, which can bring about a very selective separation between a fluid and its components. Membranes provide a physical barrier for constituents based on their size. As the key component of water treatment and reuse, they provide a high level of automation, require less chemical use and the modular
configuration allows flexible design (Qu et al., 2013). The performance of membrane systems is largely dependent on the membrane material. Incorporation of functional nanomaterials into membranes allows the improvement of membrane permeability, fouling resistance, mechanical and thermal stability etc. (Qu et al., 2013). Membrane processes are used on large scale to produce potable water from sea and brackish waters, to treat industrial effluent and recover valuable constituents, to concentrate or purify fractionate macromolecular mixtures in the food and drug industry and to separate gases and vapours in petrochemical processes (Strathmann et al, 2006).

1.22 Classification of Membrane Processes

Membranes are classified into porous membrane and tight (non-porous or dense) membrane. In non-porous membranes, permeants are adsorbed into the membrane material under the influence of their thermodynamic potential and as a result of a driving force exerted. Porous membranes are sub classified as Microfiltration, Ultrafiltration (UF), Gas diffusion, Reverse osmosis (RO), Nanofiltration (NF), Dialysis (Hu, 2014).

1.22.1 Nanofiltration (NF)

NF membranes are membranes that possess a pore size typically of 1 nm which corresponds to a molecular weight cut-off (MWCO) of 300–500 Daltons (Mohammad et al., 2014). NF membranes in contact with aqueous solution acquire charges due to the dissociation of surface functional groups or adsorption of a charge solute from solution (Mohammad et al., 2014). NF has been explored for applications in water and wastewater treatment. Size-dependent properties of nanomaterials relate to high specific surface area, fast dissolution, high reactivity and strong sorption (Qu et al., 2013). NF membranes are usually used in the separation of inorganic salts and small organic molecules from solution (Mohammad et al., 2014).

1.22.2 Reverse Osmosis (RO)

Reverse Osmosis or RO, is a process of demineralization or deionization of water by pushing it under pressure through a semi permeable reverse osmosis membrane (Puretec, 2016). RO membranes have pore sizes of 0.1-1.0 nm and thus are very effective at retaining dissolved inorganic and organic pollutants with a molar mass below 1000 Daltons (Aimar et al., 1993). However, high pressures are required to operate both RO and NF membranes. Conversely, Ultrafine (UF) membranes require lower pressures (Tiwari, et al., 2008). RO can remove nearly all inorganic contaminants from water. RO can also remove radium, natural organic substances, pesticides, bacteria and viruses (mrwa.com, 2005). RO is more effective when used in series with multiple units.
1.22.3 Microfiltration (MF)

MF is used for particle separation of particles in the range size of 0.08 to about 2.0 μ (Hassan and Price, 2014). It is usually used as a filter for suspended particulates, bacteria or large colloids from solution (Tiwari, et al., 2008).

1.22.4 Ultrafiltration (UF)

UF membranes can be made from both organic and inorganic materials usually for removal of particles and molecules of 1000 in molecular weight to about 500,000 Daltons (Aimar et al., 1993). It is commonly used in industrial applications such as food and pharmaceutical industries to filter dissolved macromolecules, such as proteins and polymers, from solution (Tiwari, et al., 2008). Ultrafiltration is proven to be a competitive treatment compare with conventional ones.

1.22.5 Gas Diffusion:

Gas diffusion depends on the pore sizes and the molecular weights of particles. The membrane pores are in the range of 5-20 Å in diameter, which is within the range of the thermal motion of the polymer chains (Tiwari, et al., 2008).

1.23 Nano-Materials for Waste Water Treatment

The efficiency of conventional adsorbents is usually limited by the surface area, active sites and lack of selectivity. Nano-adsorbents offer significant improvement in water treatment with their extremely high specific surface area and short intraparticle diffusion distance (Kiriakos et al., 2013) and tunable pore size and surface chemistry (Pan and Xing, 2008). Nano-adsorbents can also be incorporated into existing treatment processes in slurry reactors or adsorbers. When applied in the powder form, nano-adsorbents in slurry reactors can be

Figure 2.4 How Reverse Osmosis Works (Puretec, 2016)
highly efficient since all surfaces of the adsorbents are utilized to facilitate mass transfer. However, an additional separation unit is required to recover the nanoparticles.

1.23.1 Carbon Based Nano-Sorbents
Carbon nano-tubes (CNTs) have shown higher efficiency than activated carbon for adsorption of various chemicals in water (Pan and Xing, 2008). CNTs have high adsorption capacity because of their small size and large specific surface area. CNT aggregates contain interstitial spaces and grooves, which have high adsorption energy sites for organic molecules (Lu et al., 2006). Oxidized CNTs have high adsorption capacity for metal ions with fast kinetics. The surface functional groups (e.g., carboxyl, hydroxyl, and phenol) of CNTs are the major adsorption sites for metal ions, mainly through electrostatic force of attraction and chemical bonding (Rao et al., 2007). Studies show that CNTs are better adsorbents than activated carbon for heavy metals

1.23.2 Polymeric Nano-Sorbents
Polymeric nano-materials or dendrimers are engineered adsorbents that are capable of removing both organics and heavy metals. Their interior shells can be hydrophobic for sorption of organic compounds while the exterior branches can be tailored to have (e.g., hydroxyl- or amine-terminated) for adsorption of heavy metals (Tiwari et al., 2008). The sorption is based on complexation, electrostatic interactions, hydrogen bonding, hydrophobic effect etc (Crooks et al., 2001).

1.23.3 Metal Based Nano-Sorbents
Metal oxides such as iron oxide, titanium dioxide, manganese oxide and alumina are effective and low-cost adsorbents for metals ions. The sorption is due to the complexation between dissolved metals and the oxygen in metal oxides (Koeppenkastrop and Decarlo, 1993). Nanoscale metal and metal oxides are promising alternatives to activated carbon and other effective adsorbents to remove heavy metals ions in water. Metallic nanoparticles have a high specific surface area, short intraparticle diffusion distance and are compressible without a significant reduction in surface area (Gehrke et al., 2015). Some of these nanoscale metal oxides (eg, nanomaghemite) possess superparamagnetic properties, which facilitates separation and recovery. The magnetic property of iron oxide nanoparticles enables easy separation of adsorbents from the system and could be reused for further application (Pragnesh and Lakhan 2014). Nanosilver is one that exhibits a strong antimicrobial activity that is being applied to pointofuse water disinfection systems and anti-biofouling surfaces (Gehrke et al., 2015). Nanotitanium dioxide (TiO), features high chemical stability and low
human toxicity at a cheap price in the disinfection and decontamination processes (Nora and Mamadou, 2005). Metal based nano-materials have been explored to remove a variety of heavy metals such as arsenic, lead, mercury, copper, cadmium, chromium, nickel, and have shown great potential in some cases than activated carbon (Sharma et al., 2009). Magnetic nanoparticles for separation of water pollutants have already been established in ground water remediation, in particular for the removal of arsenic.
CHAPTER THREE

EXPERIMENTAL PROCEDURE

1.24 Materials
In this project, laterite and iron oxide nanoparticles were employed. The lateritic materials used were sampled from Gwagwalada, airport road near AUST, Abuja. Iron oxide nanoparticles were synthesized in AUST multifunctional laboratory, Abuja - Nigeria. Other apparatus that were employed include transparent column, plastic buckets, beakers, stirrers, volumetric flasks, conductivity meter and pH meter were used for pH modification test. Nitric acid and deionized water were used to simulate wastewater. Hot plate, magnetic stirrer, oven and weighing scales were also employed.

1.25 Synthesis of Nanoparticles
Iron oxide nanoparticles were synthesized from ferric chloride salt and ferrous chloride salt at the AUST multifunctional laboratory. Ferric chloride and ferrous chloride salts were mixed into 100 ml deionized water in the ratio of 2:3. The mixture was stirred with a magnetic stirrer for 5 min. 1 M sodium hydroxide solution was added dropwise to the mixture until a black precipitate was formed. The mixture was allowed to stir for 30 min. The particles were washed several times with deionized water and allowed to settle. The particles were then filtered, dried and ground to form a powder. The reaction step is given by;

\[ FeCl_2 + FeCl_3 + NaOH \rightarrow Fe_3O_4 + NaCl \]  

(3.1)

Figure 3.5 Steps for Nanoparticle Synthesis

1.26 Preparation of Adsorbents
Three different types of adsorbents were prepared to determine their adsorption capacity of ions in solution. One adsorbent was made from laterite and iron oxide nanoparticles while
two were made from laterite. The laterite sample was dried, heat treated at 600°C for 2 hrs and sieved to 90% passing 150 µm. Samples of laterite and nanoparticles were blended in the proportion (percentage ratios of laterite to nanoparticles) as 85:15 %.

![Figure 3.6 Sieve (British Standard)](image)

![Figure 3.7 (A) Heat-Treated Laterite and (B) Pure Laterite](image)

**1.27 Sample Characterization Experiment**

Samples of laterite and ION were characterized with XRD and XRF at EMDI (Engineering Materials Development Institute, Naseni Center of Excellence on Nanotechnology) Akure-Nigeria. This experiment was carried out to establish the composition and crystallinity of the adsorbent materials. Samples were ground to a powder form and mixed with the Licowax C Micropowder PM (Hoechstwax) in order to make the lateritic soil become a lump. Subsequently, the Fluxana (film) was put on the surface and below the sample. The sample was then compacted into a round shape solid form before analysis with a spectrometer. The sample was bombarded with high-energy gamma rays; the detector recorded the spectrum, which was matched with an element that was in the instrument’s database.
1.28 Preparation of Synthetic Wastewater

Synthetic wastewater was prepared from MgSO₄, NaCl, KNO₃, Ca(NO₃)₂ and Pb(NO₃)₂. The initial concentration used was 200mg/L for Mg²⁺, 300mg/L for K⁺, 20mg/L Ca²⁺, 250mg/L for Na⁺, 100mg/L for Pb²⁺, 300mg/L for SO₄²⁻, 600mg/L for Cl⁻ and 300mg/L NO₃⁻. A stock solution of each ion was prepared in deionized water with their individual salts. All working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. The pH of the effluent was adjusted to a pH of 6 to prevent hydrolysis. The concentration of metal ions in the effluent was analyzed by an Atomic Absorption Spectrophotometer.

1.29 Physico-chemical Measurement and Ionic Analysis

These analyses were carried out to ascertain the physico-chemical parameters and the concentrations of the different anions and cations in the wastewater. Physico-chemical analysis was conducted to establish the effect of the different parameters on adsorption. These included; conductivity, temperature, pH and TDS.

1.29.1 TDS and Conductivity Measurement

A conductivity meter probe (Figure 3.3) was cleaned with deionized water and wiped with a clean cloth. The probe was inserted into the sample to be read and the “Run” button was pressed. The results were recorded when the reading was stable. The unit of measurement was micro Siemens per centimeter (µS/cm).
1.29.2 PH and Temperature Test
The meter probe (Figure 3.4) was cleaned with distilled water and wiped with a clean cloth. The probe was inserted into the sample to be read. The result was recorded when the reading was stable.

1.30 Cation and Anion Analysis
The anions determined were chloride ions (Cl⁻), nitrate ions (NO₃⁻) and sulfate ions (SO₄²⁻). Dissolved metals (cations) measured include Sodium (Na⁺), Potassium (K⁺), Magnesium (Mg⁺), Lead (Pb²⁺), and calcium (Ca²⁺). The eluate sample was filtered using filtration paper. 100 ml of each sample was taken into a sample container and digested with 1 ml of 0.1M nitric acid. The solution was mixed by swirling. Dissolved metal ion was then read with an Atomic Absorption Spectrometer using a specific hollow cathode lamp.

1.31 Adsorption Test
300 g of each of adsorbent (dry) was weighed into a transparent (cylinder) column. Plastic tubes were used to transport the wastewater into the columns containing the adsorbents. The wastewater was allowed to flow under gravity at a flow rate of 1 ml/min through the columns packed with the adsorbent. The eluate was collected into a clean volumetric flask. 100 ml of the eluate was collected after every 3 hours over a range of 36 hours for atomic absorption spectrometer analysis. Figure 3.4 shows the set up for the adsorption experiment.

Figure 3.11 Adsorption Test
CHAPTER FOUR

RESULTS AND DISCUSSION

1.32 Results

1.32.1 Properties of Laterite

The X-ray diffraction (XRD) results of both pure laterite and heat-treated laterite showed the main minerals present as; Quartz (SiO$_2$), Alumina (Al$_2$O$_3$), Berlinite (AlPO$_4$) and Hematite (Fe$_2$O$_3$). XRD results for synthesized ION showed mainly the mineral Magnetite (Fe$_3$O$_4$).

The particle size distribution of laterite was 212–150 μm (30%), 150–75 μm (70%). The result of mineral contents analysis is shown in Tables 4.1- 4.3, giving the main chemical composition of samples. Samples also exhibited small diffraction peaks characteristics of aluminium and iron silicate.
Figure 4.12 XRD for Non-Heat Treated Laterite

Figure 4.13 XRD for Heat Treated Laterite
Figure 4.14 XRD for Iron Oxide Nanoparticle

### Table 4.3 Mineral Content of Heat-Treated Laterite

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>23.71</td>
<td>48.50</td>
<td>0.29</td>
<td>0.37</td>
<td>0.55</td>
<td>0.07</td>
<td>1.85</td>
<td>0.07</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CoO</th>
<th>Fe₂O₃</th>
<th>ZnO</th>
<th>WO₃</th>
<th>MoO₂</th>
<th>SnO₂</th>
<th>Sb₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>0.27</td>
<td>29.68</td>
<td>0.10</td>
<td>0.02</td>
<td>0.29</td>
<td>0.98</td>
<td>0.90</td>
<td>7.652</td>
</tr>
</tbody>
</table>

### Table 4.4 Mineral Content of Non-Heat-Treated Laterite

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>28.61</td>
<td>55.66</td>
<td>0.33</td>
<td>0.68</td>
<td>0.60</td>
<td>0.12</td>
<td>1.39</td>
<td>0.05</td>
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</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CoO</th>
<th>Fe₂O₃</th>
<th>ZnO</th>
<th>WO₃</th>
<th>MoO₂</th>
<th>SnO₂</th>
<th>Sb₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>0.13</td>
<td>20.35</td>
<td>0.13</td>
<td>0.03</td>
<td>0.32</td>
<td>1.27</td>
<td>1.33</td>
<td>11.0</td>
</tr>
</tbody>
</table>

### Table 4.5 Mineral Content of Iron Oxide Nanoparticles

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>0.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CoO</th>
<th>Fe₂O₄</th>
<th>ZnO</th>
<th>WO₃</th>
<th>MoO₂</th>
<th>SnO₂</th>
<th>Sb₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>0.04</td>
<td>95.43</td>
<td>0.06</td>
<td>0.00</td>
<td>0.07</td>
<td>0.13</td>
<td>0.08</td>
<td>3.738</td>
</tr>
</tbody>
</table>
1.32.2 Physico-Chemical Parameters

The dissolved ion concentration, conductivity and pH of the wastewater and the eluate emanating from each column were measured on time interval over a period of 36hrs. The results are presented in Figures 4.4, 4.5, 4.6 and 4.7.

Figure 4.15 Total Dissolved Ion Concentration (mg/L) of Eluate against time (hrs) for Pure Laterite (PL), Heat-Treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles Composite (NL)

Figure 4.16 Conductivity (µS/cm) and pH of Eluate against Time (hrs) for Pure Laterite (PL) Sample
Figure 4.17 Conductivity (µS/cm) and pH of Eluate against Time (hrs) for Heat Treated Laterite (HL) Sample

Figure 4.18 Conductivity (µS/cm) and pH of Eluate against Time (hrs) for Laterite and Iron Oxide Nanoparticles Composite (NL)

1.32.3 Ionic Analysis

Sodium (Na)
Figure 4.19 Sodium (Na) Concentration against Time (hrs) for Pure Laterite (PL), Heat-Treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles (NL)

Figure 4.20 Calcium (Ca) Concentration against Time (hrs) for Pure Laterite (PL), Heat treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles Composite (NL)
Magnesium (Mg)

Figure 4.21 Magnesium (Mg) Concentration of Eluate against Time (hrs) for Pure Laterite (PL), Heat treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles Composite (NL)

Chloride (Cl)

Figure 4.21 Chloride (Cl) Concentration of Eluate against Time (hrs) for Pure Laterite (PL), Heat treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles Composite (NL)
**Figure 4.22** Chloride (Cl) Concentration of Eluate against Time (hrs) for Pure Laterite (PL), Heat treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles Composite (NL)

**Lead (Pb)**

![Graph showing lead concentration over time for different samples](image)

**Figure 4.23** Lead (Pb) Concentration of Eluate against Time (hrs) for Pure Laterite (PL), Heat treated Laterite (HL) and Laterite and Iron Oxide Nanoparticles Composite (NL)

### 1.32.4 Adsorption Isotherm Models

Adsorption isotherms were studied to establish the favorable isotherms for the removal of dissolved ions using laterite, heat-treated laterite and iron oxide nanoparticles. Freundlich and Langmuir isotherm models were used in this study. The popular method used to determine the best-fitting isotherm is linear regression and the method of least squares. Adsorption studies with the laterite can be confirmed to follow Freundlich isotherm if the adsorption of the species conforms to equation 2.2 with $R^2$ equal/close to 1 or Langmuir isotherm if the adsorption of an ion conforms to equation 2.1 with $R^2$ equal/close to 1. Results of Freundlich and Langmuir adsorption plots are shown in **Figures 4.13-4.16.**
Figure 4.24 Freundlich and Langmuir Isotherm for Calcium (Ca)

Figure 4.25 Freundlich and Langmuir Isotherm for Sodium (Na)
Figure 4.26 Freundlich and Langmuir Isotherm for Lead (Pb)

Figure 4.27 Freundlich and Langmuir Isotherm for Chloride (Cl−)
Table 4.6 Equilibrium Constants of Langmuir and Freundlich Isotherm Models for Ionic Adsorption on Laterite and Iron Oxide Nanoparticles

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Ca</th>
<th>Na</th>
<th>Pb</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.96689</td>
<td>0.41255</td>
<td>0.9999</td>
<td>0.8682</td>
</tr>
<tr>
<td>$q_{max}$</td>
<td>0.02674</td>
<td>0.00520</td>
<td>0.4673</td>
<td>0.0005</td>
</tr>
<tr>
<td>$bq_{max}$</td>
<td>-0.0195</td>
<td>-3.52E-05</td>
<td>-98.23</td>
<td>-9.26E-06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Freundlich</th>
<th>Ca</th>
<th>Na</th>
<th>Pb</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.8787</td>
<td>0.7054</td>
<td>0.2841</td>
<td>0.1935</td>
</tr>
<tr>
<td>$n$</td>
<td>2.7317</td>
<td>0.1585</td>
<td>0.0221</td>
<td>0.7697</td>
</tr>
<tr>
<td>$\ln K_f$</td>
<td>-2.5676</td>
<td>29.959</td>
<td>-33.224</td>
<td>3.7535</td>
</tr>
</tbody>
</table>

1.33 Discussions

1.33.1 Dissolved Ions Adsorption Mechanism

It was observed in all the concentrations studied that the concentration of dissolved ions decreased rapidly with time for the first 3 hours and the curves started to increase until they flattened (i.e. reached equilibrium). The high concentration difference between the bulk solution and adsorption sites initiated the rapid removal at the initial hours (Rahman et al., 2008). Thereafter the rate tended to slow down with the saturation of the adsorbent sites. This increase in eluate concentration after 3 hours of contact with adsorbent indicates that there is a reversible physical reaction between the adsorbent and the adsorbate. This process occurs when the ions are held to the surface of the adsorbent by weak Vander Waal’s and electrostatic force of attraction. This observation in the adsorption trend is indicated by the total metal ion concentration of eluate after 3 hours onwards to 36 hours, as presented in Figure 4.8-4.12, for most of the ions and adsorbents used, this indicates a physisorption mechanism. The total ion concentration removal rate (%) as a function of time is observed to be approximately 87%, 78% and 48% of the total ions from the bulk solution adsorbed by Heat-Treated Laterite (HL), Pure Laterite (PL) and Laterite Iron Oxide Nanoparticles composite (NL) respectively within the initial 3 hours. This implies that, the heat treated laterite can be used to treat similar constituents with higher adsorption rates and lower conductivity (< 1500 µm) thereby meeting the discharge limits.

The trends in Figure 4.9 - 4.11 showed a nonspecific adsorption on the laterite samples by electrostatic phenomenon where the ions from the bulk solution are exchanged for ions near
the surface of the adsorbent (Smith, 1999). This explains why Ca ions were increasing because the Ca in the adsorbent were been exchanged for other ions in solution.

1.3.3.2 Effect of Adsorbent Compositions on Adsorption

The relative mineral contents in the laterite and iron oxide nanoparticles are shown in Figures 4.1 - 4.3. Different mineral compositions in the laterite cause differences in the adsorption capacity of laterite (Yu et al., 2009). It was observed minerals in laterite were modified after heat-treatment as indicated by the peaks of the minerals in Figure 4.2 compared to Figure 4.1. The SiO$_2$ and Al$_2$O$_3$ were higher than Fe$_2$O$_3$ in the PL sample as indicated in Table 4.2. After heat treatment, the percentage of Fe$_2$O$_3$ increased. Heat treatment resulted in the removal of volatile and organic constituents in the laterite. These changes lead to the increase in pore volume and specific surface area of the HL laterite which in turn increased its adsorption capacity compared to PL grains.

According to (Somasundaran, 2006), less than pH 8-9, the surface of alumina is positively charged and silica (greater than 2-4), negatively charged in which case adsorption of anions on alumina and adsorption of cations on silica is favored by electrostatic force due to charge difference in adsorbent and adsorbate. The adsorption test was carried out between pH 6.5-6.8, which therefore explains the physisorption trends in the graphs.

The surface of iron oxides is neutral at neutral pH (Ahmad et al., 2010). Metal cation adsorption increases with increasing pH as the surface charge becomes more negative and more positive at lower pH. As the surface charge becomes more negative with increasing pH, the surface attracts bivalent metal cations for adsorption as shown in results for Cu$^{2+}$ adsorption on iron oxides (Ahmad et al., 2010; Li and Wua, 2010). In this case, Fe$_2$O$_3$ will tend to adsorb more anions in solution since the pH of the solution was below 7. Therefore, both this effect and that from Al$_2$O$_3$ and SiO$_2$ synergistically enhanced the physisorption mechanism demonstrated earlier.

The XRD results indicated the presence of AlPO$_4$. Metal phosphates like FePO$_4$, AlPO$_4$, and CrPO$_4$ behave as weak acid cation exchangers and possess appreciable exchange capacities for alkali, alkaline earth, and divalent transition metal (Naeem et al., 2002). This theory explains the cationic exchange behavior demonstrated by Ca ions in Figure 4.9.
1.33.3 Cation Removal
From Figure 4.8-4.10 and 4.12, all the three adsorbents were able to remove Na, Ca, Mg and Pb from solution within the first 3 hours. However, as time passed, an increase in ionic concentration was observed. It was also observed that NL sample showed a high ion removal for Ca, Mg and Pb with a release of more Na ions into solution. The release of Na ions into solution was due to residual Na in iron oxide nanoparticles during synthesis.

1.33.4 Anion Removal
From Figure 4.11, chloride concentration of the eluate for the three types of adsorbents PL, HL, and NL decreases after 3 hours of adsorption with percentage adsorption of 81.8 %, 97.9 % and 76.9 % respectively and rises continuously. However, the concentration values for the HL were generally lower than the other two sorbents. This makes HL the best sorbent for ion reduction compared to PL and NL.
Removal of anions is a limitation for most of the soil based natural systems for wastewater purification. Attachment of anions onto the soil is very weak (due to weak van der Waal’s force of attraction) as the soil is negatively charged due to silicates (Avinash, 2009). Cl removal was favored by the presence of the iron oxide and alumina. This charge repulsion due to the high content of silica was a major barrier in the anionic adsorption onto the soil.

1.33.5 Conductivity and pH
The conductivity and pH of the eluate emanating from each column were measured for the corresponding time of sampling. The results are presented in Figure 4.5-4.7. It was observed from Figure 4.5-4.7 that pH reduces with a reduction in conductivity and vice versa. This trend indicates that increase in ionic content increased pH, which could be as a result of an increase in Ca and CO\textsubscript{3} from the soil to the solution. The highest adsorption was achieved at pH of 6.8. The trend in Figure 4.7 was opposite to that observed in Figure 4.5 and 4.6. In Figure 4.7, as the pH increased, the conductivity decreased due to reduction in ion mobility and as the pH decreased, the conductivity increased showing more mobility of the ions in solution.

1.33.6 Isothermal Adsorption
The adsorption isotherm in Figure 4.13 – 4.16 represents Freundlich and Langmuir isotherms for Ca, Na, Pb and Cl. Equilibrium Constants of the two Isotherm Models for Ionic Adsorption on Laterite and Iron Oxide Nanoparticles are presented in Table 4.4. The R\textsuperscript{2} values in the table indicate that adsorption of Ca, Pb and Cl ions obey the Langmuir isotherm
model using heat treated laterite for Pb and Cl and laterite with iron oxide nanoparticles for Ca ions. The coefficient of determinant, $R^2$ for Freundlich was found to be 0.8787, 0.2841 and 0.1935 while that of Langmuir was 0.96689, 0.9999 and 0.8682 respectively. The low values for Freundlich isotherm show that there is a bad correlation between the adsorbent and the adsorbate. Since that for Langmuir correlates better (approaches 1) it implies that the adsorption of Ca, Pb and Cl obeys Langmuir adsorption isotherm more so than Freundlich adsorption isotherm. $R^2$ for Na was found to be 0.7054 for Freundlich and 0.41255 for Langmuir. Na adsorption, therefore, follows the Freundlich isotherm model using heat-treated laterite as an adsorbent.
CHAPTER FIVE

CONCLUSIONS AND FUTURE WORKS

1.34 Conclusion

This study was conducted on synthetic wastewater for the removal of dissolved ion constituents using adsorption by laterite and iron oxide nanoparticles. It was also to determine optimum conditions for ion removal (conductivity reduction) and the adsorption capacity of laterite and iron oxide nanoparticles.

Laterite and nanoparticle characterization, pH and adsorption tests were conducted to ascertain the composition of laterite and as prepared iron oxide nanoparticles, the adsorption capacity of the adsorbents and the optimum conditions for adsorption. XRD results of both pure and heat-treated laterite showed that the main minerals present were Quartz (SiO₂), Berlinite (AlPO₄), Alumina (Al₂O₃) and Hematite (Fe₂O₃) while XRD results for synthesized nano iron oxide showed the mineral Magnetite (Fe₃O₄). The adsorption results indicated that heat-treated laterite showed the highest adsorption capacity for total dissolved ions at a pH range of 6.5-6.8.

From the discussions, it can be concluded that, although all the three types of adsorbents tested can be used to treat mine wastewater, heat treated laterite (HL) was the most efficient having the highest total ion removal of 87% corresponding to 3.399 mg/g for the first 3 hours of adsorption. The adsorption isotherm for Ca, Pb and Cl adsorption using laterite and iron oxide as an adsorbent fitted well with Langmuir adsorption isotherm while that for Na obeys Freundlich adsorption isotherm.

Although the adsorption capacity of the soils is not too high compared to other treatment processes such as reverse osmosis, their availability in large amounts and low costs make them potential candidates for the dissolved ion removal.

It is recommended that adsorption carried out with the adsorbents in this research be limited to a time of 3 hours since the best adsorption was achieved at this time.

1.35 Future Work

It is suggested that for future work, conditions such as pH, temperature, flow rate, adsorbent dosage be considered to determine their effect on adsorption. Metal ions tend to stay in solution in acidic medium and sometimes precipitate at high pH. Also, high temperatures favour transport of ions in solution and therefore pH and temperature can affect the adsorption depending on temperature and the ion concentration, which is affected by the pH.
It is also suggested that studies should be carried out on desorption of adsorbed ions and heat reactivation to allow reuse of the adsorbent material.

Also, the reduction in SiO$_2$ and Al$_2$O$_3$ against the increase in Fe$_2$O$_3$ content shown in the mineral content analysis is not yet understood, further studies are therefore encouraged.
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