KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF SCIENCE

DEPARTMENT OF ENVIRONMENTAL SCIENCE

SEQUESTRATION OF ARSENIC BY *Moringa oleifera* SEEDS AND BAUXITE

THESIS SUBMITTED TO THE DEPARTMENT OF ENVIRONMENTAL SCIENCE IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE

BY

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DECLARATION

I hereby declare that this submission is my own piece of work and that, to the best of my knowledge, it contains no materials previously published by another person nor material which has been accepted for the award of any other degree of a university, except where due acknowledgement has been made in the text.

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ABSTRACT

The ability of *Moringa oleifera* seeds and bauxite to sequester arsenic was studied individually and in combination. The study was in relation to how the bauxite, *Moringa oleifera* seeds and the *Moringa*-bauxite mixture could reduce the concentration of arsenic in aqueous solution. Matured *Moringa oleifera* seeds were dried and processed into powder and the bauxite pulverised. Both sorbents were sieved using 500 *u*m copper sieves. Fifty millilitres each of arsenic solution with concentrations 1, 5, 10, 25, 50 and 100 mg/L were prepared into Erlenmeyer flasks and sorbed with 2g of *Moringa oleifera* seeds. The procedure was repeated with bauxite and *Moringa*-bauxite mixture. The duration of sorption was one and half hours. Both *Moringa oleifera* seeds and the bauxite were good sorbents over the concentration range of arsenic solutions prepared. *Moringa oleifera* recorded a mean sorption of 90.94% at 25 mg/L and bauxite a sorption of 98.60% at 1 mg/L. A combination of the two sorbents recorded a percentage sorption of 85.20% at 1 mg/L. There was also a significant sorption of 82.00% at 25 mg/L when *Moringa oleifera* seeds were combined with bauxite. The results were modelled along the Langmuir and Freundlich sorption isotherms with the latter providing a mathematical evidence that sorption were high for all the sorbents. This piece of work provides a competitive option for the removal of arsenic from aqueous solution particularly for the gold mining companies that process sulphidic gold ores and can be extended to areas of arsenic contamination in general.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

Metal species released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, thus becoming a serious threat to the environment. Pollution of the environment by toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal (Pushpa *et al.*, 2005). Bioremediation processes are the target of recent research and are considered low-cost and use eco-friendly methods that can alleviate the current problems of water decontamination, particularly for remote and rural areas Bioremediation processes involve the use of living organisms such as bacteria, fungus and some plants parts in the sequestration of toxic materials in the environment (Ninlanja, 2008).

Filamentous fungi as a part of microbial communities influence transformation and distribution of metal(loid)s in the environment. Interactions between microorganisms and ions of different metal(loid)s can be divided into two basic categories; transformations, that lead to the mobilization of heavy metals (bioleaching, biological methylation and reduction), and transformations that immobilize metal (loid)s, such as biosorption, or different types of microbial precipitation, or binding of metalloids to macromolecules (Gadd, 2000).

Arsenic, one of the most dangerous heavy metals, is ubiquitous and ranks 20th in its natural abundance, comprising about 0.00005% of the earth's crust, 14th in the seawater, and 12th in the human body. Its concentration in most rocks ranges from 0.5 to 2.5 mg/kg, though higherconcentrations are found in finer grained argillaceous sediments and phosphorites (Mandal and Suzuki, 2002).

Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities. Soil erosion and leaching contribute to 612×108 and 2380×108 g/year of arsenic, respectively, in dissolved and suspended forms in the oceans (Mackenzie *et al.*, 1979). Most environmental arsenic problems are the result of mobilization under natural conditions, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed.

1.2 Statement of problem

Gold for centuries has been a major source of foreign exchange for the country. The gold ore in Ghana is of two types. These are the free milling and the sulphidic gold ores (Hunter *etal.*, 1993). The free milling gold ores are processed by direct leaching with cyanide after crushing and grinding. The sulphidic gold ores are subjected to previously, roasting and more recently, bioxidation. Pyrite (FeS_2) and arsenopyrite (FeAsS) are the major components of sulphidic gold ore but the latter is a major contributor of arsenic in the processing of sulphidic gold ores but these two forms of sulphidic ores are processed together. Mine drainage areas have appreciable level of the toxic metal arsenic (As) in the processing of the sulphidic gold ore (Groza *et al.*, 2008). Unfortunately, the sulphidic gold ore is of a larger belt in Ghana. Such ore is processed by Anglo-Gold Ashanti at Obuasi in the Ashanti Region and Golden Star Resources in the Western Region of Ghana.

Most of the arsenic enters water supplies and soil either from natural deposits in the earth, industrial, agricultural pollution and processing of the suphidic gold ores. Arsenic in drinking water causes bladder, lung and skin cancer, and may cause kidney and liver cancer (NRDC, 1999). It also harms the central and peripheral nervous systems, as well as heart and blood vessels, and serious skin diseases, birth defects and reproductive problems.

Major remediation processes for arsenic has been chemical: precipitation and oxidation amongst others (Mohan and Pittman, 2006). This process is very expensive and turns out to be destructive on living organisms in the soil, which play very important role in soil fertility and in water bodies. More recently, the idea of sorption of arsenic has been an area of much research especially with activated carbon. However, there has been very little focus on biosorption. This study is to determine whether the *Moringa oleifera* seeds powder can be a better sorbent of arsenic if combined with bauxite as compared to the *Moringa oleifera* seeds powder alone or the bauxite alone.

1.3 Justification

The history of arsenic has been overshadowed with its notoriety as a poison in homicides. Arsenic occurs naturally or is introduced into the environment by commercial activities such as mining which cannot be stopped. Therefore it is imperative on researchers to find the most efficient way of reducing the occurrence and consumption of arsenic by man and animals alike. There has been some work done by other researchers on the use of the *Moringa oleifera* seeds powder on the sorption of metals such as cadmium, lead and copper (Sharma *et al.*, 2007).

It is known that by the ingestion of arsenic through contaminated water bodies, bio-magnification through the food chain is reduced. Additionally, the cost involved in management of arsenic will be reduced.

1.4 Main objective

The study will assess the sequestration effect of *Moringa oleifera* seeds by measuring the extent of reduction in concentration of arsenic through sorption when the powder of *Moringa oleifera* seeds is combined with bauxite as compared to sorption due to bauxite alone or the *Moringa oleifera* seeds powder alone.

1.5 Specific objectives

- Measure the reduction in concentration of arsenic in aqueous solution using bauxite.

- Measure the reduction in the concentration of arsenic in aqueous solution using the *Moringa oleifera* seeds powder.
- Measure the reduction in the concentration of arsenic in aqueous solution when *Moringa oleifera* seeds powder is combined with bauxite.

CHAPTER TWO

2.0 LITERATURE REVIEW

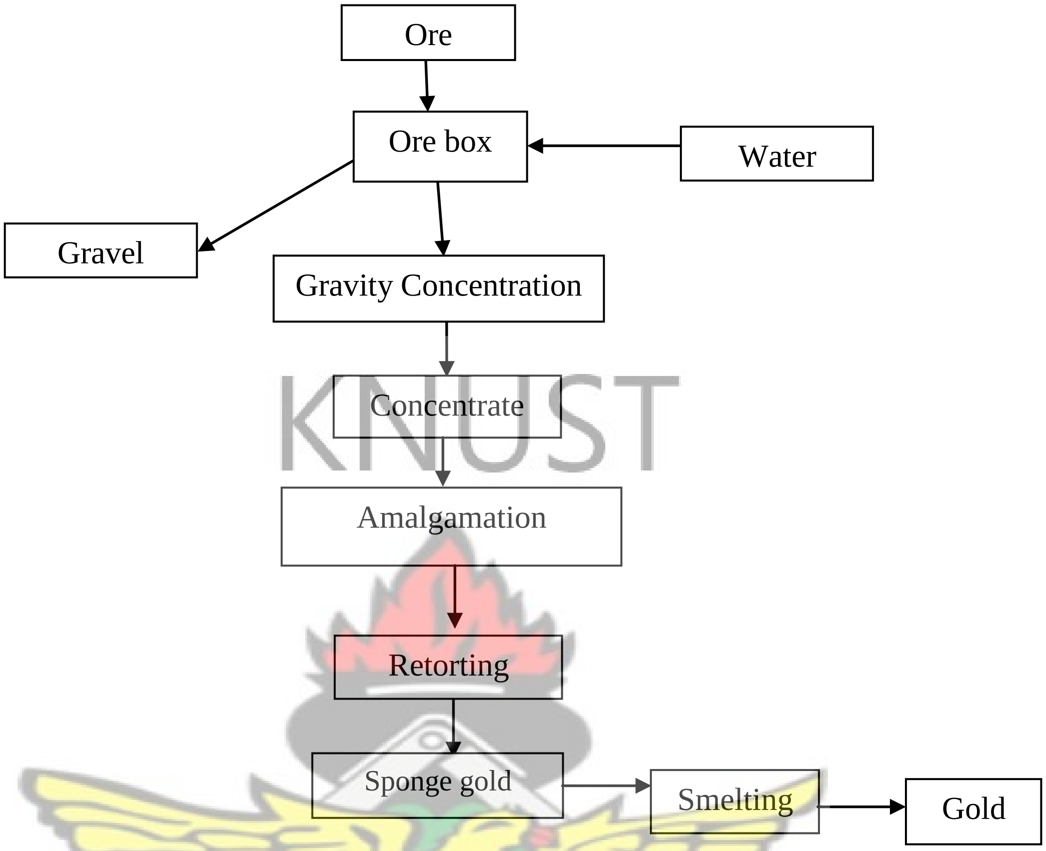
2.1 Types of gold ores in Ghana

There are three types of gold ores (based on complexity of processing) in Ghana. These are alluvial, oxides and sulphidic gold ores. The list is in order of increasing beneficiation complexity. The alluvial gold ores are usually found in water bodies. They are therefore weathered due to the fact that they were transported for a long distance in water. The oxides and sulphides originated from the Tarkwaian rock and the Birimian rock respectively (Kesse, 1985).

2.2 Processing of gold ores

2.2.1 Processing of alluvial gold ores

The processing of alluvial gold begins with the removal of gravels from the ore by subjection of the ore to a water jet. The concentrate is obtained through gravity concentration. Gravity concentration is done through panning or the use of the Knelson concentrator. The Knelson concentrator operates on the principle that two different particles with different densities will travel in the same medium at different velocities. The gold in the concentrate forms an amalgam with mercury. The amalgam obtained is heated in a retort. The mercury evaporates leaving the sponge gold in the retort. Concentrate is obtained in the beneficiation of alluvial gold ore; there is no need for leaching (Amankwah and Anim-Sackey, 2003). Figure 1 shows the stages of alluvial gold ore processing.

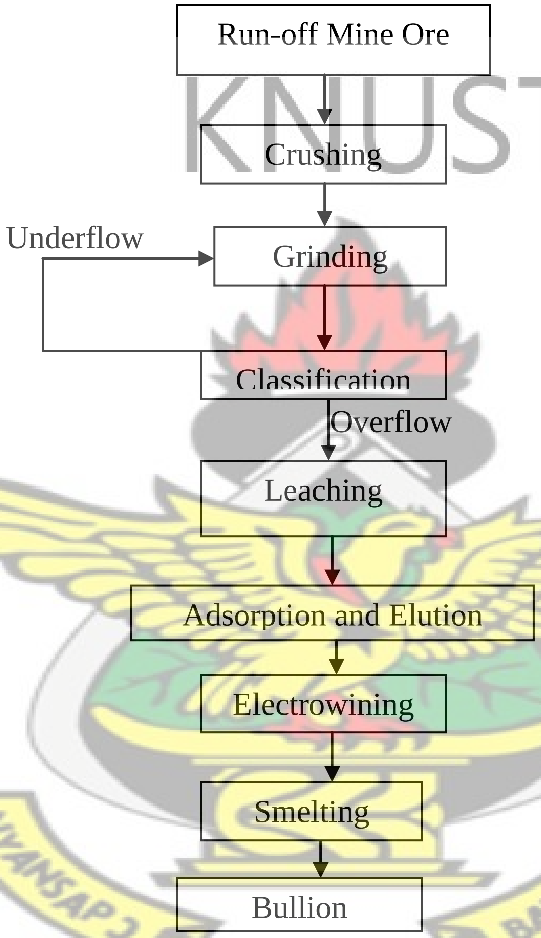


Source: Tabbey-Appiah, 2009 (unpublished)

Fig.1: Flowsheet for the processing of alluvial gold ore.

2.2.2 Processing of Oxides

Oxides are more encapsulated as compared to alluvial gold ore, it is therefore necessary to leach the ore through cyanidation. This is indicated in Fig. 2. In the processing of oxides, the ore is crushed and milled. The milled ore is classified so that the right particle sizes proceed for leaching. Leaching is done by the application of cyanide in the form of sodium cyanide (NaCN), which takes place in leaching tanks (Kondos *et al*., 1995). In some mines, adsorption takes place after leaching. Those processing plants are known as Carbon-In-Leach (CIL). Other companies also leach and adsorb the gold simultaneously. Those processing plants are known as Carbon-In-Pulp (CIP). CIL or CIP obviously depicts the type of material used for the adsorption: activated carbon. The adsorbed gold is desorbed and forwarded to electrowinning cells using steel wool and electrolytic cells. The steel wool containing the gold is smelted and later shaped into bars (Parga *et al.*, 2007).



Source: Tabbey-Appiah (2009).

Fig. 2: Flowsheet for the processing of oxidized gold ore.

2.2.3 Processing of sulphidic gold ores.

Sulphides are more encapsulated than oxides and cannot be subjected to direct leaching after crushing and grinding. Two main constituents make up the sulphidic gold ore. These are pyrite (FeS_2) and arsenopyrite (FeAsS). Since the pyrite cannot be separated from the arsenopyrite, they are processed together. The processing of these types of ore requires pre-treatment. The pre-treatment is a technique used to make the gold particles more and amenable to cyanidation (Afidenyo, 2011). Some of the pre-treatment processes are

- Pressure oxidation
- Bio-leaching
- Chemical oxidation
- Roasting

The bio-oxidation takes place by the use of *Thiobacillus thiooxidans* at temperatures between 30^{o}C to 35^{o}C and has been considered as the most environmentally- friendly process for sulphidic gold processing for now (Groza *et al.*, 2008).

It is very necessary to subject the ore to pre-treatment after crushing and grinding as shown in the flowsheet for sulphidic gold ore processing in Fig. 8. Previously, the ore was subjected to roasting but more recently to bio-oxidation. This is because roasting is deemed to contribute significantly to acid rain. The bio-oxidation process produces a lot of acid according to the equations:

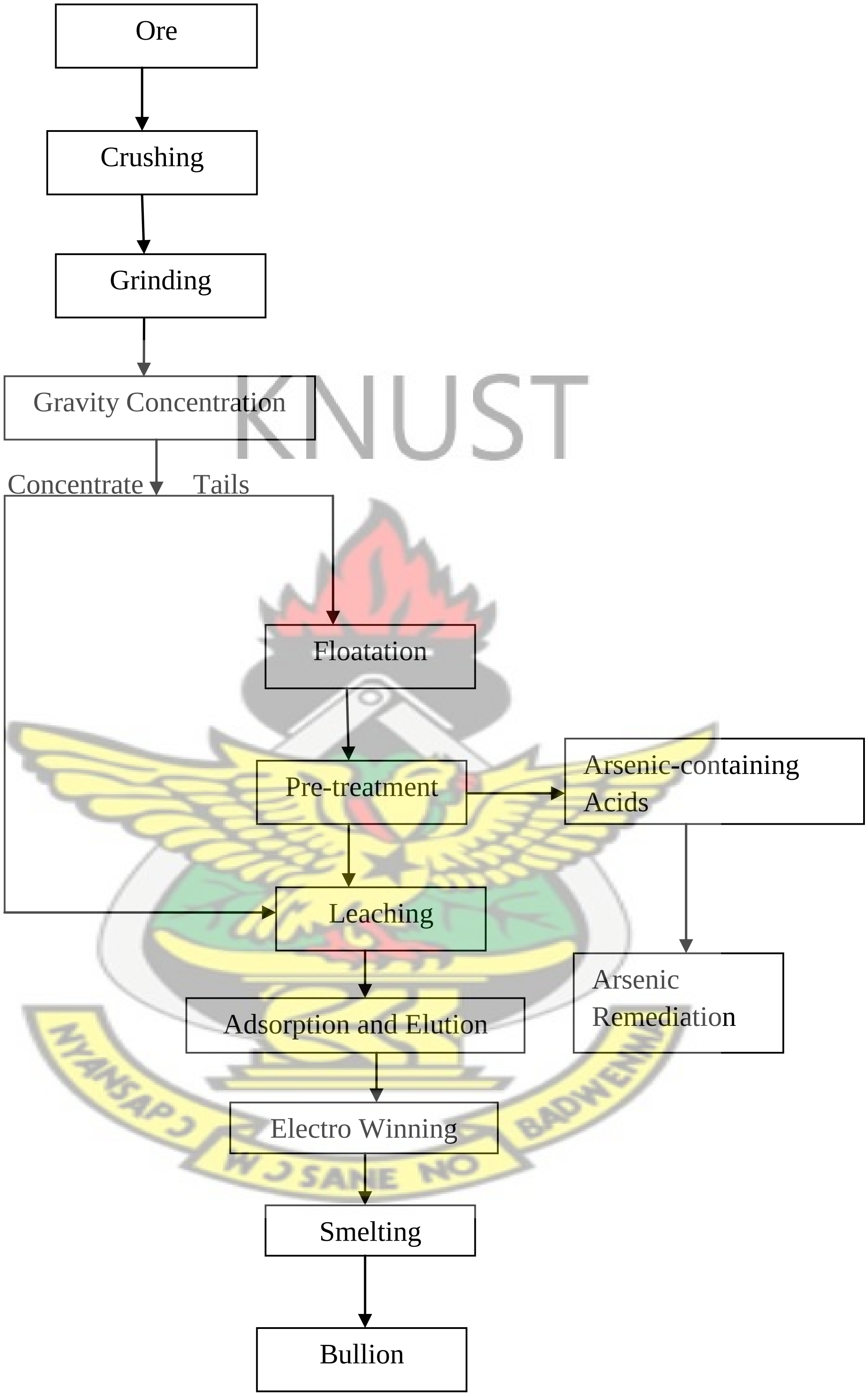
$4FeS_2+15O_2+2H_2O \xrightarrow{} 2Fe_2(SO4)_3+2H_2SO_4$

$2FeAsS+7O_2+H_2SO_4 + H_2O \xrightarrow{} 2H_3AsO_4 + Fe_2(SO4)_3$

$2FeAsS+Fe_2(SO4)_3+6O_2+4H_2O \xrightarrow{} 2H_3AsO_4 + 4FeSO_4 + H_2SO_4$

Source: (Afidenyo, 2011)

In addition to the acid, high level of arsenic is produced. The arsenic is in the form of pentavalent arsenic (AsO_4^{3-} from H_3AsO_4). It is imperative on the company to treat the counter current bio-oxidation liquor, which contains the arsenic before onward forwarding to the tailings dam. The procedure for the remediation of arsenic has been chemical: precipitation. The use of limestone or lime has been prominent in the remediation of the arsenic acid produced. The arsenic acid is the source of (pentavalent) arsenic (Mohan and Pitman, 2006).



Source: Tabbey-Appiah, (2009).

Fig. 3 :Flowsheet for the processing of sulphidic gold ore.

2.3 Other sources of arsenic

As indicated in the previous section, areas of high level arsenic are the mining areas, especially where the mineral is in association with pyrite and arsenopyrite. Minerals with the formula MAsS and MAs_2 (M = Fe, Ni, Co) are the dominant commercial sources of arsenic, together with realgar, an arsenic sulfide mineral and native arsenic. An illustrative mineral is arsenopyrite (FeAsS). Many minor As-containing minerals are known. Arsenic also occurs in various organic forms in the environment (Matschullat and Jörg, 2000).

Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation. On roasting in air of arsenopyrite, arsenic sublimes as arsenic (III) oxide leaving iron oxides, while roasting without air results in the production of metallic arsenic. Further purification from sulfur and other chalcogens is achieved by sublimation in vacuum or in a hydrogen atmosphere or by distillation from molten lead-arsenic mixture (Whelan *et al*., 1960).

Similar to many metalloids, the prevalence of particular species of arsenic depends greatly on the pH and redox conditions of the matrix in which it exists. Speciation is also important in determining the toxicity of arsenic. Arsenic minerals exist in the environment principally as sulphides, oxides, and phosphates (Smedley and Kinniburg, 2002).

2.4 Chemistry of arsenic

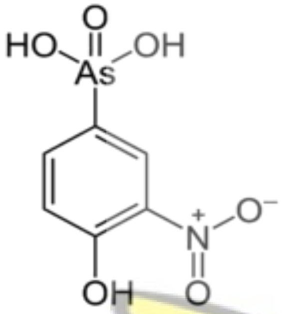
Arsenic is a metalloid. It can exist in various allotropes, although only the grey form has important use in industry. Naturally occurring arsenic is composed of one stable isotope, As. As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is ^{73}As with a half-life of 80.3 days. Isotopes that are lighter than the stable ^{75}As tend to decay by β^+ decay, and those that are heavier tend to decay by β^- decay, with some exceptions. At least 10 nuclear isomers have been described, ranging in atomic mass from 66 to 84 (Emsley, 2001).

Arsenic forms colourless, odourless, crystalline oxides As_2O_3 ("white arsenic") and As_2O_5, which are hygroscopic and readily soluble in water to form acidic solutions. Arsenic (V) acid is a weak acid. Its salts are called arsenates, which is the basis of arsenic contamination of groundwater, a problem that affects many people. A broad variety of sulfur compounds of arsenic are known. Orpiment (As_2S_3) and realgar (As_4S_4) are somewhat abundant and were formerly used as painting pigments (Madelung, 2004).

The trifluoride, trichloride, tribromide, and triiodide of arsenic (III) are well known, whereas only Arsenic pentafluoride (AsF_5) is the only important pentahalide. Again reflecting the lower stability of the +5 oxidation state, the pentachloride is stable only below −50 C.

2.5 Uses of arsenic

The main uses of metallic arsenic are for strengthening alloys of copper and especially lead (for example, in car batteries). Arsenic is a common n-type dopant in semiconductor electronic devices, and the optoelectronic compound gallium arsenide is the most common semiconductor in use after doped silicon. Arsenic and its compounds, especially the trioxide, are used in the production of pesticides (treated wood products), herbicides, and insecticides. These applications are declining, however (Sabina, 2005). Arsenic is still added to animal feed, in particular in the U.S. as a method of disease prevention and growth stimulation. One example is roxarsone with a chemical structure as indicated in Fig. 4, which is used as a broiler starter by about 70% of the broiler growers since 1995. The Poison-Free Poultry Act of 2009 proposes to ban the use of roxarsone in industrial swine and poultry production (Jones, 2007).



Source: Wolfram Alpha LLC (2011)
Fig. 4: The chemical structure of Roxarsone

Arsphenamine, as well as neosalvarsan was indicated for syphilis and trypanosomiasis, but has been superseded by modern antibiotics. Arsenic trioxide has been used in a variety of ways over the past 500 years, but most commonly in the treatment of cancer. The US Food and Drug Administration in 2000 approved this compound for the treatment of patients with acute promyelocytic leukemia that is resistant to ATRA (Antman, 2001). Recently new research has been done in locating tumours using arsenic-74 (a positron emitter). The advantages of using this isotope instead of the previously used iodine-124 is that the signal in the PET scan is clearer as the body tends to transport iodine to the thyroid gland producing a lot of noise (Jennewein, 2008).

The toxicity of arsenic made it possible to be used as a weapon. According to a Blister Agents' report, after the first world war, the United States built up a stockpile of 20000 tons of lewisite ($ClCH=CHAsCl_2$), a chemical weapon that is a vesicant (blister agent) and lung irritant.

2.6 Dangers of arsenic

Arsenic is known to cause arsenicosis owing to its manifestation in drinking water, "the most common species being arsenate [H_3AsO_4; As(V)] and arsenite [H_3AsO_3 ; As(III)]". The ability of arsenic to undergo redox conversion between As (III) and As(V) makes its availability in the environment more abundant. According to Croal *et al*. (2004), "understanding what stimulates As (III) oxidation and/or limits As (V) reduction is relevant for bioremediation of contaminated sites. The study of chemolithoautotrophic As (III) oxidizers and the heterotrophic As (V) reducers can help the understanding of the oxidation and/or reduction of arsenic.

Arsenic exerts its toxicity by inactivating up to two hundred enzymes, especially those involved in cellular energy pathways and DNA synthesis and repair. Acute arsenic poisoning is associated initially with nausea, vomiting, abdominal pain, and severe diarrhoea. Encephalopathy and peripheral neuropathy are sometimes reported. Chronic arsenic toxicity results in multisystem disease. Arsenic is a well-documented human carcinogen affecting numerous organs. There are no evidence-based treatment regimens to treat chronic arsenic poisoning but antioxidants have been advocated, though benefit is not proven. The focus of water management companies is to reduce arsenic ingestion from drinking water and there is increasing emphasis on using alternative supplies of water (Ratnaike, 2003).

2.7 Metabolism and clinical features of arsenic

If arsenic is absorbed, it undergoes hepatic biomethylation to form monomethylarsonic acid and dimethylarsinic acid that are less toxic but not completely innocuous (Aposhian, 1997). About 50% of the ingested dose may be eliminated in the urine in three to five days. Dimethylarsinic acid is the dominant urinary metabolite (60%–70%) compared with monomethylarsonic acid (Hopenhaven-Rich *et al*., 1993).

A small amount of inorganic arsenic is also excreted unchanged. After acute poisoning electrothermal atomic absorption spectrometry studies show that the highest concentration of arsenic is in the kidneys and liver. In chronic arsenic ingestion, arsenic accumulates in the liver, kidneys, heart, and lungs and smaller amounts in the muscles, nervous system, gastrointestinal tract, and spleen. Though most arsenic is cleared from these sites, residual amounts remain in the keratin-rich tissues, nails, hair, and skin. After about two weeks of ingestion, arsenic is deposited in the hair and nails (Benramdane, 1999).

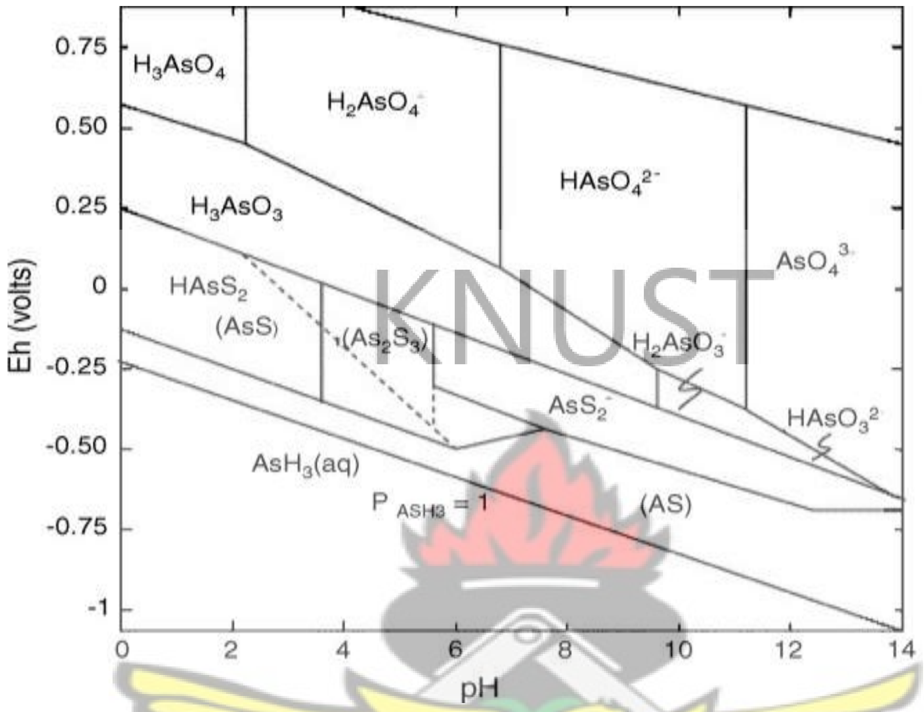
Most cases of acute arsenic poisoning occur from accidental ingestion of insecticides or pesticides. Small amounts (<5 mg) result in vomiting and diarrhoea but resolve in 12 hours and treatment is reported not to be necessary. The lethal dose of arsenic in acute poisoning ranges from 100 mg to 300 mg. The Risk Assessment Information System database states “The acute lethal dose of inorganic arsenic to humans has been estimated to be about 0.6 mg/kg/day”. A 23 year old male who ingested 8 g of arsenic survived for eight days (Opresko, 1992).

2.8 Speciation of arsenic

Arsenic is of many oxidation states. There are four known oxidation states of arsenic, which are -3, 0, +3 and +5. Out of these, +3 oxidation state is the most dangerous one. Mohan further explains that the environmental forms of arsenic are the arsenious acids (H_3AsO_3, $H_3AsO_3^-$ and $H_3AsO_3^{2-}$), arsenic acids (H_3AsO_4, H_3AsO4^- and $H_3AsO_4^{2-}$), arsenates, arsenites methylarsenic acid and arsine. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloid. Apart from pH, Redox potential also affects the speciation of arsenic (Mohan and Pitman, 2006).

The drawing of the Pourbaix diagram has been used to determine the speciation of most metals and metalloids. The Pourbaix diagram, as shown in Fig. 5, is a graph of redox potential (Eh) against pH of a metall(oid) at a fixed temperature and pressure (Smedley and Kinniburg, 2002).

Two forms of arsenic are in natural waters, which are both inorganic-the arsenate (AsO_4^{3}) and the arsenite (AsO_3^{3-}). Pentavalent species predominate and are stable in oxygen-rich or aerobic environments. Trivalent arsenates predominate in moderately reducing anaerobic environments such as groundwater (Greenwood and Earnshaw, 1984).



(Adapted from Mohan and Pitman, 2006).

Fig. 5: The Poubaix diagram (Eh–pH) for arsenic at 25^{o}C

2.9 Adsorption

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid (the absorbent). Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon (Aposhian, 1997).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements of the constituent atoms of the material are filled by other atoms in the material. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction (Ferrali *et al*., 2010).

The material which takes the atoms, ions or the molecules from a solvent is called the adsorbent. The ions, atoms or molecules to be adsorbed from the solvent are referred to as the adsorbate. Some models have been developed to explain the phenomenon of adsorption. The two most popular ones are:

- The Freunlick model
- The Langmuir model

2.9.1 The Freundlich isotherm

The Freundlich isotherm is the most important multisite adsorption isotherm for rough surfaces. The Freundlich isotherm is a model which expects heterogeneous distribution of energy of adsorption sites on sorbent. Freundlich adsorption isotherm has the form: $S_{eq} = K_F C_{eq}^N$, where S_{eq} is the amount of metal (loid) adsorbed per unit sorbent. C_{eq} is the equilibrium concentration of the aqueous solution (Cernansky *et al.*, 2007). The form can be linearised by applying logarithms, which assumes the form $\mathrm{LogSeq} = \log K_F + N \log C_{eq}$. If the log-log diagram is drawn, a straight line is obtained for an adsorption that follows well the Freundlich model.

2.9.2 The Langmuir isotherm

The Langmuir adsorption model is used to quantify the amount of adsorbate as a function of partial pressure or concentration at a constant temperature. It works ideally for solutions with lower concentrations. According to Goldberg (1995), the amount of substance (metal or metalloid) adsorbed onto an adsorbent is given by $x = bkc/(1 + kc)$, where x is the amount of metal(loid) adsorbed per unit mass, c is the equilibrium concentration of the solution, whiles b and k are constants. Goldberg further indicates that the Langmuir isotherm assumes adsorption of gases onto clean solids and implies uniform adsorption sites and absence of lateral interactions. He also agrees with Cernansky *et al.* (2007) on the fact that the Freundlich isotherm assumes heterogeneity of pore sites.

2.10 Bauxite as an ore

2.10.1 Components and formation of bauxite

Bauxite is an aluminium ore and is the main source of aluminium. This form of rock consists mostly of the minerals gibbsite $Al(OH)_3$, boehmite γ-AlO(OH), and diaspore α-AlO(OH), in a mixture with the two iron oxides goethite and hematite, the clay mineral kaolinite, and small amounts of anatase TiO_2 (Plunkert, 2000).

One of the key components of bauxite is aluminium oxides, which can be processed to make aluminium products. Bauxite is mined in several regions of the world by a number of companies that are interested in aluminium products. The companies may sell the raw aluminium ore or process it to generate their own aluminium, depending on the size of the company and its business model.

2.10.2 Production trends

Australia, since 2007, has been the leading producer of bauxite in the world according to a publication by British Geological Survey (2010). Table 1 shows some world bauxite production by countries. From Table 1 again China, Brazil, India and Guinea follow in a decreasing order of production. Even though the demand for bauxite is increasing, the world reserves are enough for a number of centuries. This is due to the fact that aluminium is one of the most recyclable metals.

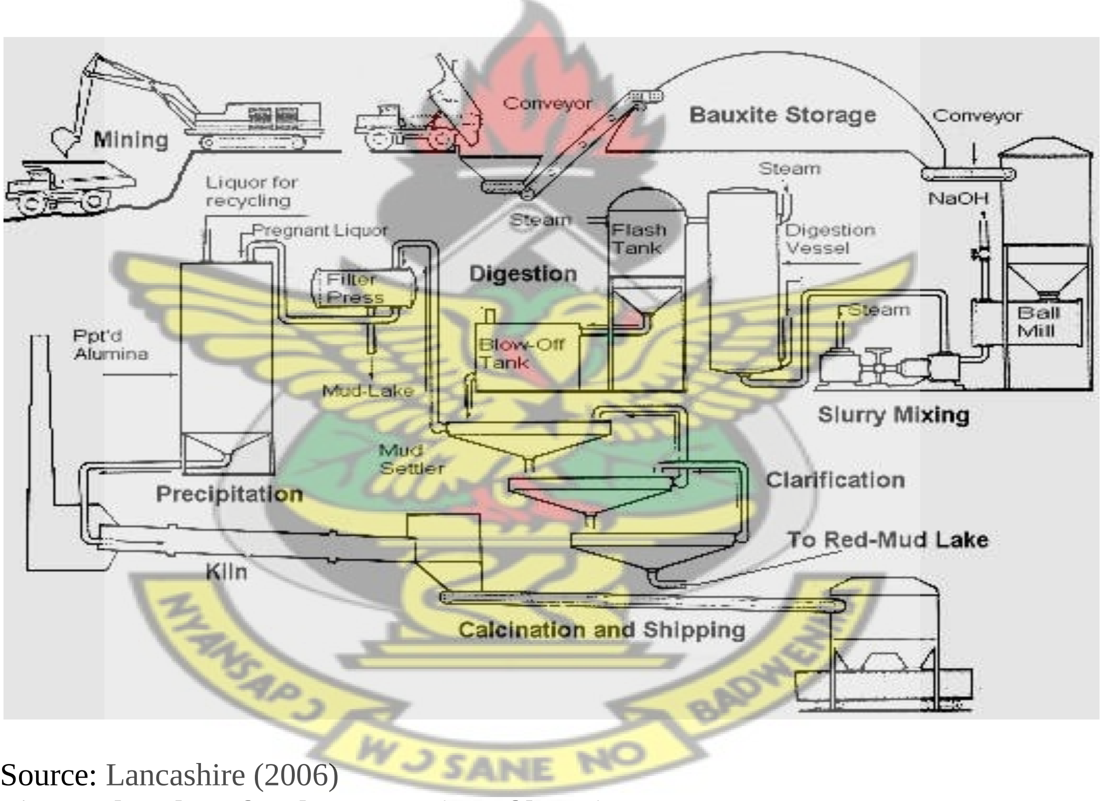
Table 1: Estimate of bauxite production in some countries.

Country	Mine production		Reserves
	2007	**2008**	
Guinea	18000	18000	7400000
Australia	62400	63000	5800000
Vietnam	30	30	2100000
Jamaica	14600	15000	2000000
Brazil	24800	25000	1900000
Guyana	1600	1600	700000
India	19200	20000	770000
China	30000	32000	700000
Greece	2220	2200	600000
Iran	-	500	-
Suriname	4900	4500	580000
Kazakhstan	4800	4800	360000
Venezuela	5900	5900	320000
Russia	6400	6400	200000
United State	NA	NA	20000
Other countries	7150	6800	3200000

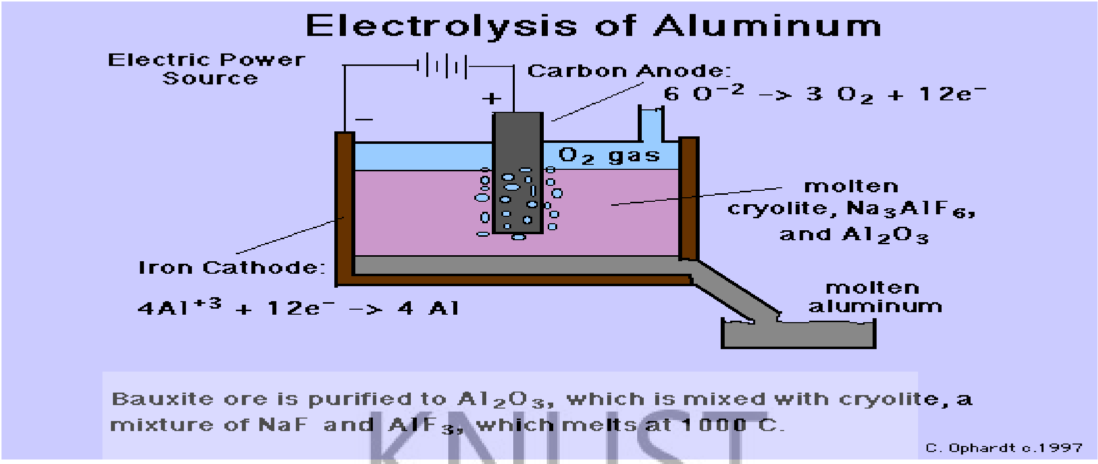
Source: British Geological Survey (2010)

2.10.3 Processing of bauxite

Usually, bauxite ore is heated in a pressure vessel along with a sodium hydroxide solution at a temperature of 150 to 200 °C. At these temperatures, the aluminium is dissolved as an aluminate (the Bayer process). After separation of ferruginous residue (red mud) by filtering, pure gibbsite is precipitated when the liquid is cooled, and then seeded with fine-grained aluminium hydroxide. The gibbsite is usually converted into aluminium oxide, Al_2O_3, by heating. This mineral becomes molten at a temperature of about 1000 °C, when the mineral cryolite is added as a flux. Next, this molten substance can yield metallic aluminium by passing an electric current through it in the process of electrolysis, which is called the Hall–Héroult process after its American and French discoverers in 1886 (Ophardt, 2003). The processing of bauxite involves conversion of the bauxite to alumina (Fig. 6) and conversion of the alumina to aluminium (Fig. 7).



Source: Lancashire (2006)
Fig. 6: Flowsheet for the processing of bauxite



Source: (Ophart, 2003)

Fig. 7: Flowsheet for the processing of alumina

2.10.4 Uses of bauxites

Bauxite is an important ore of industrial benefit. There are two main categories of bauxite according to its uses. These are the metallurgical bauxite and the non-metallurgical bauxite. The metallurgical bauxite is specifically mined and processed into alumina and hence to aluminium. Aluminium is used in the manufactures of cars and aircrafts, saucepans and other cooking utensils whilesnon-metallurgical bauxite are used for refractories, abrasives (including the recently development proppants), high aluminium cements, aluminium chemicals, activated bauxite and alumina(Plunkert, 2000).

Calcination removes the inert moisture and increases the alumina content by converting tri-hydrate and mono-hydrate (gibbsite and boehmite) into anhydrous aluminium oxide by expulsion of water of crystallization. Calcined bauxite is used for different applications that include:

- Refractory bricks

- Grinding media (Abrasives)
- Road surfacing material
- Proppants
- Alumina cement
- Ceramics

Refractory grade calcined bauxite is produced mainly in China, India, Guyana and the USA. The raw bauxite used for calcination should contain alumina of 55 to 60%. Availability of this quality bauxite is limited (Badossy and Aleva, 1990).

2.11 The Moringa plants

The Moringa plant is one of the most popular plants in Africa and Asia. *Moringa oleifera* is the most widely cultivated species of the genus *Moringa*, which is the only genus in the family Moringaceae. Common names include moringa, benzolive tree and West Indian ben. It is also known as drumstick tree, from the appearance of the long, slender, triangular seed pods, horseradish tree, from the taste of the roots which resembles horseradish, or Ben oil tree, from the oil derived from the seeds. It is an exceptionally nutritious vegetable tree with a variety of potential uses (Top Tropicals, 2012). Plate 1 and 2 show matured fruits and young shoot of *Moringa oleifera* respectively.

Source: National Research Council (2006)

Plate 1: The fruits of the *Moringa oleifera.*

Source:National Research Council (2006)

Plate 2 :The *Moringa oleifera* (young) shoot.

2.11.1 Description of the plant.

The tree itself is slender, with drooping branches that grow to approximately 10 m in height. In cultivation, it is often cut back annually to one metre or less and allowed to re-grow so that pods and leaves remain within arm's reach. It can grow in an arid soil and withstands harsh weather conditions. It is an all-year round plant (http://toptropicals.com/html/toptropicals/articles/trees/horseradish.htm)

2.11.2 Other species of Moringa

Compared with *M. oleifera*, the trunk of *M. stenopetala* is considerably thicker at the base, the tree seems more vigorous, the leaves are larger, and if tasted raw the leaves are milder as shown in plate 3. *M. oleifera* develops into a slender tree, *M. stenopetala* into a round shrub-like tree (Jahn, 1986). In spite of the initial rapid growth of *M. oleifera*, in drier years the species has not done well without some watering. The *M. stenopetala*, by contrast, has the lushest green foliage and continued to grow during the exceptionally long dry season. Other species of Moringa include *Moringa peregrina* and *Moringa dourhadii*.

Source: Price (2007)
Plate 3: The *Moringa* stenopetala.

2.11.3 Uses of Moringa plants

The various species of *Moringa* has common and peculiar uses. The plant has been referred to as “The miracle plant.” Food can be stripped from the feathery, fern-like leaves and used in any spinach recipe. They are exceptionally nutritious. Very young plants can also be used as a tender vegetable. In many cultures, the diet consists mainly of a starchy dish or porridge made from corn meal, cassava, millet or the like. Side dishes or "sauces" served with the starchy main dish are therefore very important nutritionally, as they are often the only source of extra protein, vitamins and minerals. *Moringa* leaves could easily be added to such sauces as a potherb or as dried herbs (Price, 2007).

According to Price (2007), in addition to its usefulness as a source of oil, *Moringa* seeds can be used for water treatment**.** Suspensions of ground seed of the Moringa tree are used as primary coagulants. *Moringa oleifera* seeds (Plate 4) can "clarify Nile water of any degree of visible turbidity." At high turbidities their action was almost as fast as that of alum, but at medium and low turbidities it was slower. The doses required did not exceed 250 mg/l. coagulating the solid matter in water so that it can be removed easily. It also removes a good portion of the suspended bacteria (Jahn, 1986).

Source: Price (2007)

Plate 4: ***Moringa oleifera*** **(dark) and** ***Moringa stenopetela*** **(white) seeds.**

Anwar (2007) also summarises the benefits of the Moringa plants as follows: *"Moringa oleifera* is a highly valued plant, distributed in many countries of the tropics and subtropics. It has an impressive range of medicinal uses with high nutritional value. Different parts of this plant contain a profile of important minerals, and are a good source of protein, vitamins, *β*-carotene, amino acids and various phenolics. The *Moringa* plant provides a rich and rare combination of zeatin, quercetin, *β*-sitosterol, caffeoylquinic acid and kaempferol. In addition to its compelling water purifying powers and high nutritional value, *M. oleifera* is very important for its medicinal value. Various parts of this plant such as the leaves, roots, seed, bark, fruit, flowers and immature pods act as cardiac and circulatory stimulants, possess antitumor, antipyretic, antiepileptic, anti-inflammatory, antiulcer, antispasmodic, diuretic, antihypertensive, cholesterol lowering, antioxidant, antidiabetic, hepatoprotective, antibacterial and antifungal activities, and are being employed for the treatment of different ailments in the indigenous system of medicine, particularly in South Asia."

2.12 Some previous works done on biosorption.

As indicated in the previous chapter, the remediation of arsenic has been chemical. The idea of sorption is a recent development. The process has been with the use of activated carbon. The study of sorption by the use of materials obtained from living organisms has been more recent.

Araújo *et al.* (2010) worked on "Characterization and use of *Moringa oleifera* seeds as biosorbent for removing metal ions from aqueous effluents." The abstract of the work reads: "*Moringa oleifera* seeds were investigated as a biosorbent for removing metal ions from aqueous effluents. The morphological characteristics as well as the chemical composition of *M. oleifera* seeds were evaluated using Fourier Transform Infrared (FT-IR) Spectroscopy, Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The FT-IR spectra showed the presence of lipids and protein components. Scanning electron micrographs showed that Moringa seeds have an adequate morphological profile for the retention of metal ions. The results suggest that *Moringa oleifera* seeds have potential application in Cd(II), Pb(II), Co(II), Cu(II) and Ag(I) decontamination from aqueous effluents".

Ghebremichael *et al.* (2010) also worked on the "Performance of *Moringa oleifera* as a biosorbent for chromium removal." Not only as a biosorbent for heavy metals, *Moringa oleifera* has been tested for its ability as a coagulant, thus reducing appreciably turbidity of effluents.

Bhatia *et al.* (2007), also investigated the pre-treatment of palm oil mill effluent (POME) using *Moringa oleifera* seeds as natural coagulant. He made some interesting findings indicated in his abstract as written: "*Moringa oleifera* seeds, an environmentally friendly and natural coagulant are reported for the pre-treatment of palm oil mill effluent (POME). In coagulation-flocculation process, the *M. oleifera* seeds after oil extraction (MOAE) is an effective coagulant with the removal of 95% suspended solids and 52.2% reduction in the chemical oxygen demand (COD). The combination of MOAE with flocculant (NALCO 7751), the suspended solids removal increased to 99.3% and COD reduction was 52.5%. The coagulation-flocculation process at the temperature of 30 degrees C resulted in better suspended solids removal and COD reduction compared to the temperature of 40, 55 and 70 degrees C. The MOAE combined with flocculant (NALCO 7751) reduced the sludge volume index (SVI) to 210 mL/g with higher recovery of dry mass of sludge (87.25%) and water (50.3%)".

Moringa is not the only biosorbent for heavy metals. Cernansky *et al*. (2007) also investigated the ability of *Aspergilus clavatus,* a fungus on the biosorption of cadmium and arsenic. *Phanerochaete chrysosporium,* which is also a fungus, has been used to sequester heavy metals such as lead and cadmium. Ninlanja *et al.* (2008), reviewed biosorption using different materials. It was indicated that different materials from living sources can be used as biosorbent. It was pointed out that apart from fungus, other materials from living sources can be used as biosorbent. Some of these materials are bacteria, algae, plants, yeast and waste materials of food and agricultural industry.

CHAPTER THREE

3.0 MATERIALS AND METHODS

The summary of the methodology is shown in Fig. 8, which includes the preparation of the *Moringa oleifera* seed and bauxite samples through to Atomic Absorption Spectrophotometer (AAS) analysis.

3.1 Moringa seeds and bauxite samples

Matured *Moringa oleifera* pods were harvested, washed with tap water and with double distilled water to remove all adhering dirt. The seeds were sun-dried, dehusked, crushed using a blender and sieved through a 500 *u*m copper mesh. The powder was kept until ready to be used.

The stock solution of arsenic (3.0973 g/L) was obtained from the Metallurgical Department of Anglo-Gold Ashanti, Obuasi. One litre of the stock solution was mixed with 10 ml of Conc. HNO_3. The solution was kept until ready to be used. Bauxite was obtained from The Department of Mineral Engineering, University of Mines and Technology, Tarkwa. One and a half kilogram (1.5 kg) of bauxite was crushed using a porcelain mortar and pestle and sieved through a 500 *u*m copper mesh. Fifty grams (50 g) of the bauxite undersize was mixed with 50 g of the Moringa seeds powder. The mixture was shaken thoroughly to form a uniform mixture. The mixture was kept until ready to be used.

3.2. Preparation of arsenic solutions

Fifty millilitres each of desired concentrations of arsenic (1, 5, 10, 25, 50 and 100 mg/L) were prepared from stock solution of arsenic (3.0973 g/L) through serial dilutions. The stock solution was shaken before a sample from it was taken. Prior to the preparation of the solutions, each Erlenmeyer flask was labelled according to the type of sorbent and the concentration of the arsenic solution. Thus Mx, Bx and Cx, where x is the concentration of the arsenic solution and M, B and C represented *Moringa* seeds, Bauxite and *Moringa*-bauxite mixture.

3.2.1 Preparation of 100 mg/L arsenic solution

Six point four five millilitres (6.45 mL) of the arsenic stock solution (3.0973 mg/L) was measured into a measuring cylinder. Distilled water was added to the 200 mL mark. The distilled water was added gradually whilst swirling. Fifty millilitres of the solution was measured into an Erlenmeyer flask to form 50 mL of 100 mg/L arsenic solution.

3.2.2 Preparation of 50 mg/L arsenic solution

The excess 100 mg/L solution was used in the preparation of the 50 mg/L arsenic solution. Hundred millilitres of the excess 100 mg/L arsenic solution was measured into a measuring cylinder and topped up gradually to 200 mL with distilled water whilst swirling. Fifty millilitres of this solution was poured into an Erlenmeyer flask to form 50 mL of 50 mg/L arsenic solution

3.2.3 Preparation of 25 mg/L arsenic solution

The excess 50 mg/L solution was used in the preparation of the 25 mg/L arsenic solution. Hundred millilitres of the excess 50 mg/L arsenic solution was measured into a measuring cylinder and topped up gradually with distilled water up to the 200 mL mark, whilst swirling. Fifty millilitres of this solution was measured into an Erlenmeyer flask to form 50 mL of 25 mg/L arsenic solution.

3.2.4 Preparation of 10 mg/L arsenic solution

The excess 25 mg/L solution was used in the preparation of the 10 mg/L arsenic solution. Eighty millilitres of the excess 25 mg/L arsenic solution was measured into a measuring cylinder and topped up gradually with distilled water up to the 200 mL mark, whilst swirling. Fifty millilitres of this solution was measured into an Erlenmeyer flask to form the 10 mg/L arsenic solution.

3.2.5 Preparation of 5 mg/L arsenic solution

The excess 10 mg/L solution was used in the preparation of the 5 mg/L solution. Hundred millilitres of the excess 10 mg/L solution was measured into a measuring cylinder and topped up gradually with distilled water up to the 200 mL mark, whilst swirling. Fifty millilitres of this solution was measured into an Erlenmeyer flask to form the 5 mg/L arsenic solution.

3.2.6 Preparation of 1 mg/L arsenic solution

The excess 5 mg/L solution was used in the preparation of 1 mg/L arsenic solution. Twenty millilitres of the excess 5 mg/L solution was measured into a measuring cylinder. Distilled water was added gradually up to the 100 mL mark. Fifty millilitres of the resulting solution was measured into an Erlenmeyer flask to form 1 mg/L solution.

3.3 pH measurement

The pH of all solutions prepared were measured and recorded without pH modification to the solutions.

3.4 Sorption

3.4.1 Sorption with bauxite

Six Erlenmeyer flasks were used in each run of experiment. The desired concentrations of arsenic solutions (1, 5, 10, 25, 50 and 100 mg/L) were prepared into the Erlenmeyer flasks according to the label on the flask. The flask labelled B_1contained 50 mL of 1 mg/L arsenic solution. The flask labelled B_5 contained 50 mL of 5 mg/L arsenic solution in that order.

Two grams of the bauxite powder was measured into each of the flasks. Each flask was swirled for ten seconds. The stopwatch was started immediately. Each flask was swirled every fifteen minutes for a period of one and a half hours. Each solution was then filtered using a Whatman 42 filter paper. Each filtrate was stored with 1 mL of Conc.HNO_3. The procedure was done in triplicate.

3.4.2 Sorption with *Moringa oleifera* powder

Six Erlenmeyer flasks were used in each run of experiment. The desired concentration of arsenic (1, 5, 10, 25, 50 and 100 mg/L) were prepared into the Erlenmeyer flasks according to the label on the flask. The flask labelled M_1contained 50 mL of 1 mg/L arsenic solution. The flask labelled M_5 contained 50 mL of 5 mg/L arsenic solution in that order.

Two grams of the *Moringa oleifera* powder was measured into each of the flask. Each flask was swirled for ten seconds. The stopwatch was started immediately. Each flask was swirled every fifteen minutes for a period of one and a half hours. Each solution was then filtered using a whatman 42 filter paper. Each filtrate was stored with 1 mL of Conc.HNO_3. The procedure was done in triplicate.

3.4.3 Sorption with *Moringa*-bauxite powder

Six Erlenmeyer flasks were used in each run of experiment. The desired concentrations of arsenic (1, 5, 10, 25, 50 and 100 mg/L) were prepared into the Erlenmeyer flasks according to the label on the flask. The flask labelled C_1contained 50 mL of 1 mg/L arsenic solution. The flask labelled C_5 contained 50 mL of 5 mg/L arsenic solution in that order.

Two grams of the *Moringa*-bauxite powder was measured into each of the flasks. Each flask was swirled for ten seconds. The stopwatch was started immediately. Each flask was swirled every fifteen minutes for a period of one and a half hours. Each solution was then filtered using a 42 Whatman filter paper. Each filtrate was stored with 1 mL of Conc.HNO_3. The procedure was done in triplicate.

3.5 Digestion of filtrate and analysis for arsenic

Each filtrate was heated on a hot plate for 20 minutes after which filtrates were topped up with distilled water to 50 mL mark. Each solution was analysed for arsenic levels using the Perkin-Elmer Atomic Absorption Spectrometer model 1100.

3.6 Experimental control

Fifty millilitres of arsenic solution with concentrations of 1, 5, 10, 25, 50 and 100 mg/L were put in six Erlenmeyer flasks. Each Erlenmeyer flask was given initial swirling of 10 seconds. These were allowed one and half hour stay with a fifteen-minute intermittent swirling. The solutions were then filtered and the filtrate transferred into six other sample containers, with their labels in the same order T1-----T1, T2------T2 etc. Each solution was filtered and the filtrates stored with 1 mL of Conc.HNO_3. Each filtrate was heated on a hot plate for 20 minutes in glass beakers. The heated solution was topped up to 50 mL mark with double distilled water. The solution was then analysed for arsenic levels using the Perkin-Elmer Atomic Absorption Spectrometer model 1100.

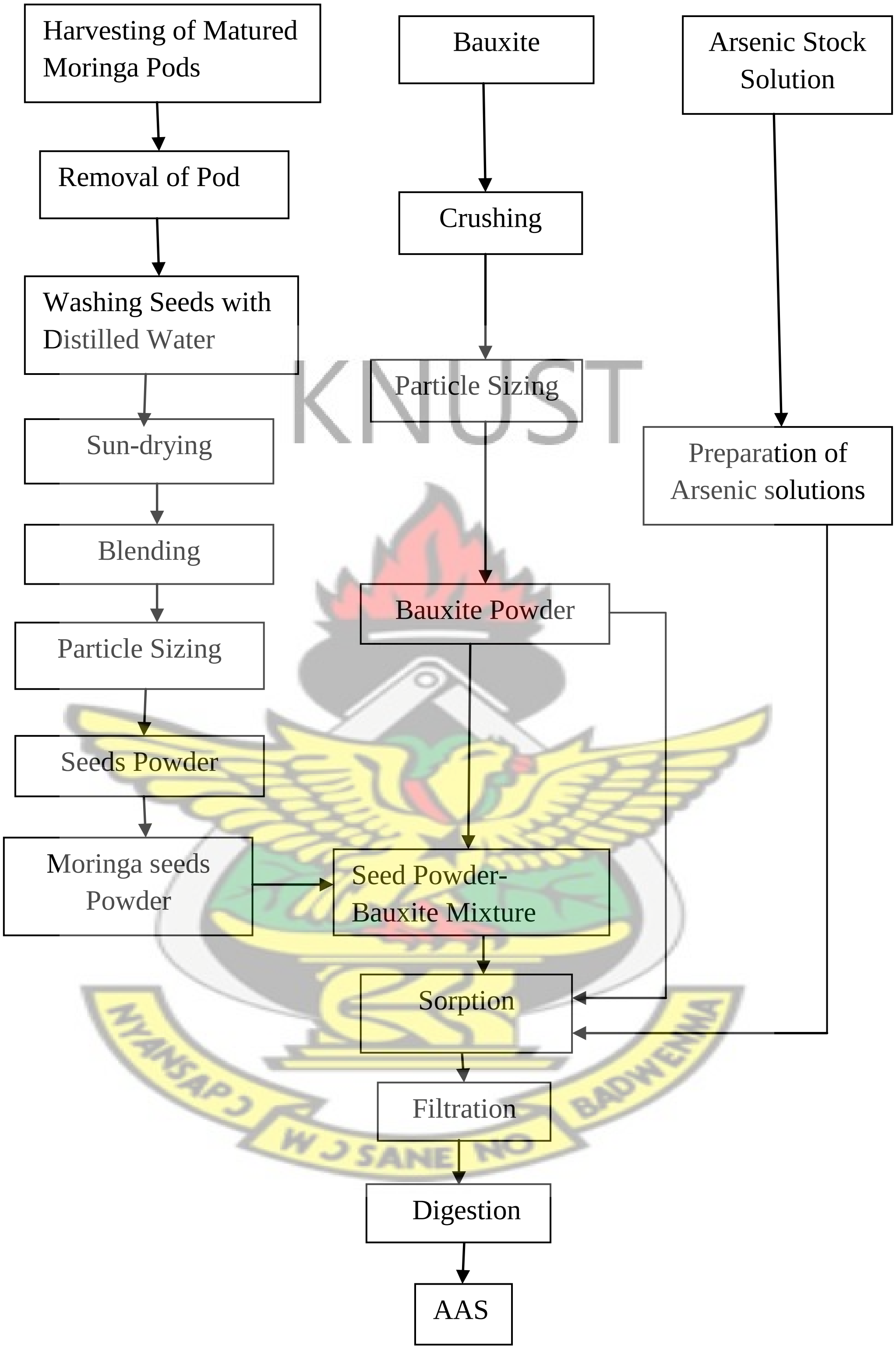


Fig. 8: Flowsheet for the methodology.

3.7 Statistical Analysis

Data was subjected to analysis of variance (ANOVA) using GenStat Discovery (Edition 4). Unless otherwise stated, B1, M1 and C1 denote bauxite, *Moringa* and bauxite-*Moringa* mixture, which are the sorbents used in conducting the experiment.

Data was also modelled in accordance with the Langmuir sorption isotherm, as described by Cernansky *et al.*, (2007) and Ninlanja, (2008). The Langmuir model is given by $Ce/M=1/kb + Ce/k$, where Ce is the equilibrium concentration (mg/L), M is the mass of the sorbed metal per gram of the sorbent (mg/g), b is the ratio of adsorption and desorption rates, k is the maximum uptake of the metal corresponding to site saturation. Ce/M was plotted as the response variate and Ce as the explanatory variate in a linear regression menu of GenStat (Discovery Edition 4).

Additionally, the data was modelled along the Freundlich isotherm. The Freundlich isotherm as described by Ninlanja, (2008), Goldberg (1995) and Cernansky *et al.* (2007) is given by $M = KCe^N$, where M is the mass of metal adsorbed per unit adsorbent (mg/g) and Ce is the equilibrium concentration (mg/L). K and N are Freundlich constants. The model was linearized by applying logarithm to both sides, since the model is not linearized. The linearized form is given by $\log M = \log K + N\log Ce$. This modified model follows the equation of a straight line: $y = mx + c$. logM was plotted as the response variate and logCe as the explanatory variate in a linear regression menu of a statistical software called GenStat (Discovery Edition 4)

CHAPTER FOUR

4.0 RESULTS

4.1 Sorption capacities of sorbents

4.1.1 Sorption capacity of bauxite

Figure 9 shows the sorption capacity of arsenic by bauxite at a pH of 7±0.3 and room temperature (25^{o}C). The highest mean percentage sorption by bauxite was 98.60%. The maximum sorption was recorded when the concentration of the arsenic solution was 1 mg/L and the lowest sorption of 58.65% was recorded at a concentration of 100 mg/L. At a confidence interval of 95%, mean percentage sorption by bauxite followed a steady decline as concentration of the arsenic solution increased.

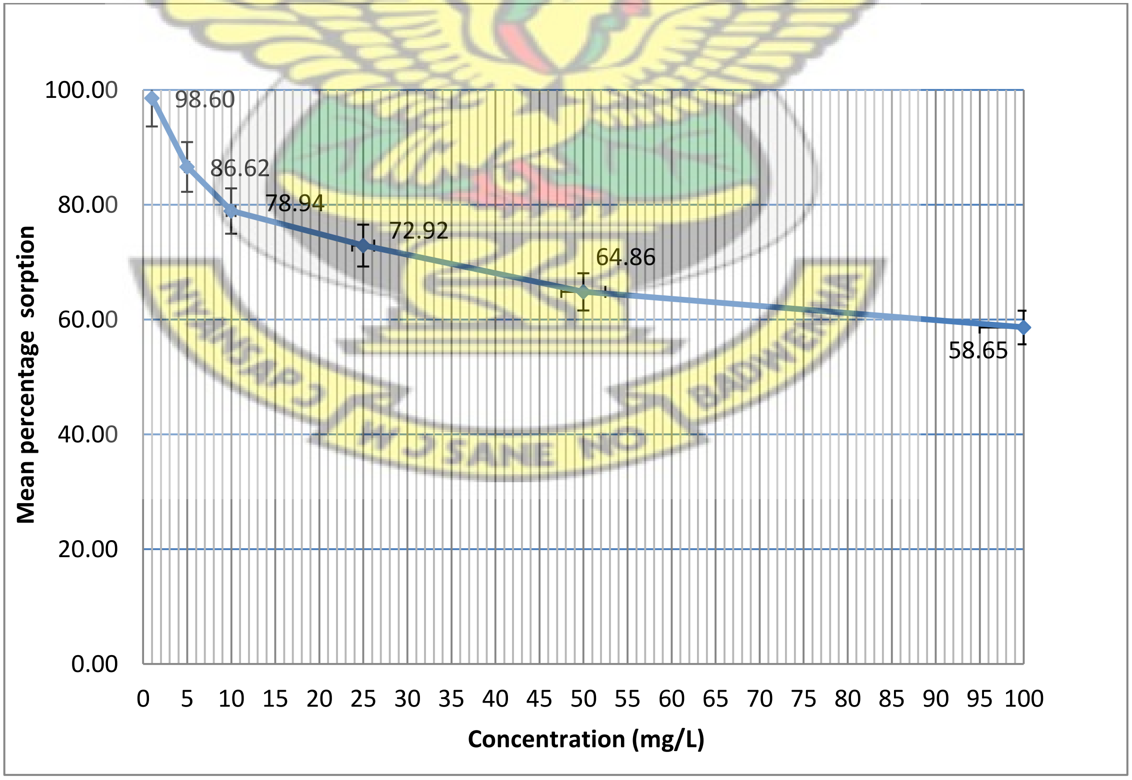


Fig. 9: Sorption capacity of bauxite for arsenic

4.1.2 Sorption capacity of *Moringa oleifera*

Using *Moringa oleifera* seeds powder as the sorbent for arsenic at a pH of 7±0.3 and room temperature (25^{o}C), there was an initial steady rise in the mean percentage sorption from 1 mg/L to 5 mg/L as shown in Fig. 10. This was followed by a sharp increase in mean percentage sorption from 5 mg/L to 10 mg/L through to 25 mg/L, reaching an optimum level of 90.94%. However, there was a sharp decline in mean percentage sorption from 25 mg/L to 50 mg/L and then a gradual fall from 50 mg/L to 100 mg/L.

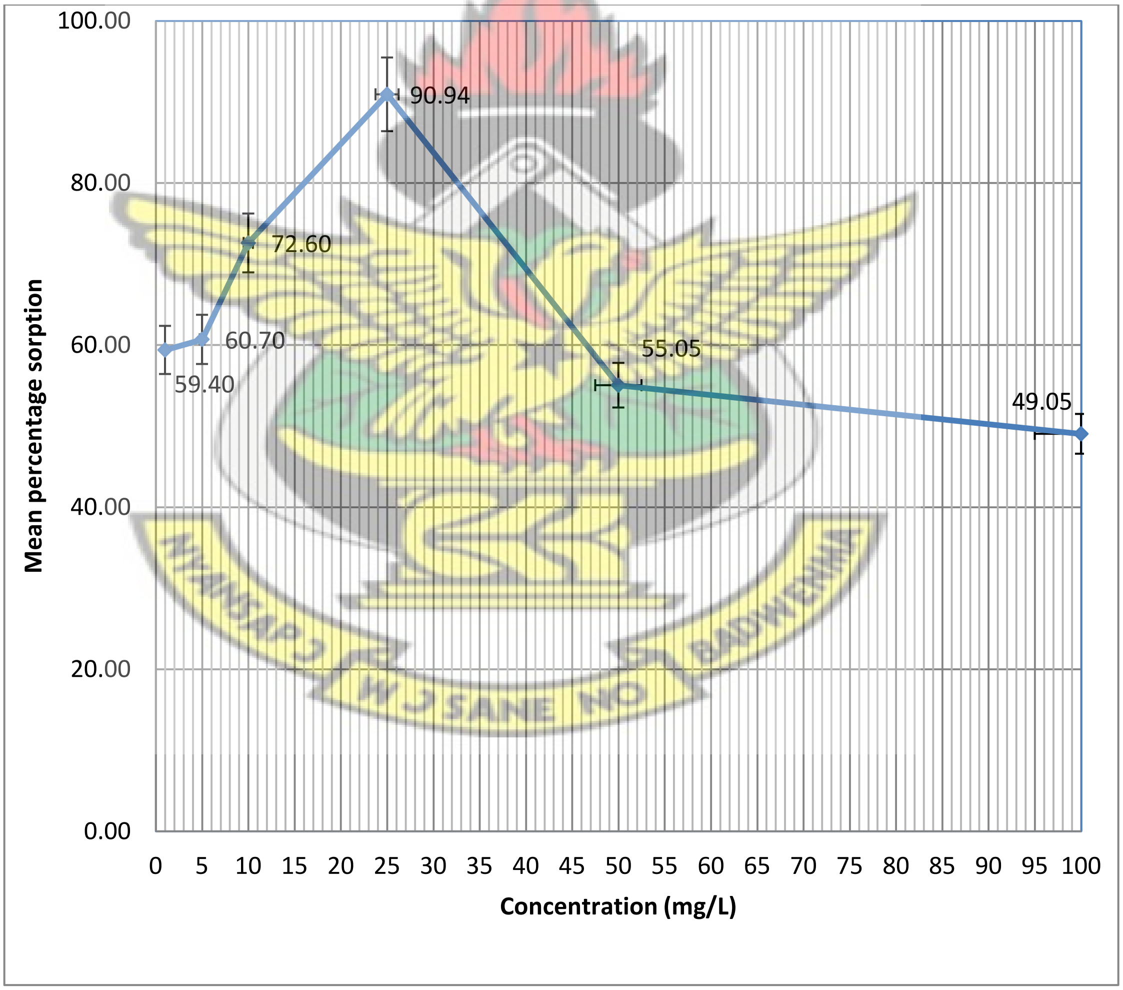


Fig. 10: Sorption capacity of *Moringa oleifera* seeds powder for arsenic.

4.1.3 Sorption capacity of *Moringa*-bauxite mixture

When bauxite-*Moringa* powder mixture was used as the sorbent at a pH of 7±0.3 and room temperature (25^{o}C) and at a confidence interval of 95%, there was optimum sorption at 1 mg/L (Fig.11). Sorption was also high at 25 mg/L. At 1 mg/L, mean sorption was 85.20% while at 25 mg/L, mean sorption was 82.00%. The sorption by the bauxite-*Moringa* mixture showed a trend which was similar to combined sorption trends of bauxite and *Moringa oleifera* seeds.

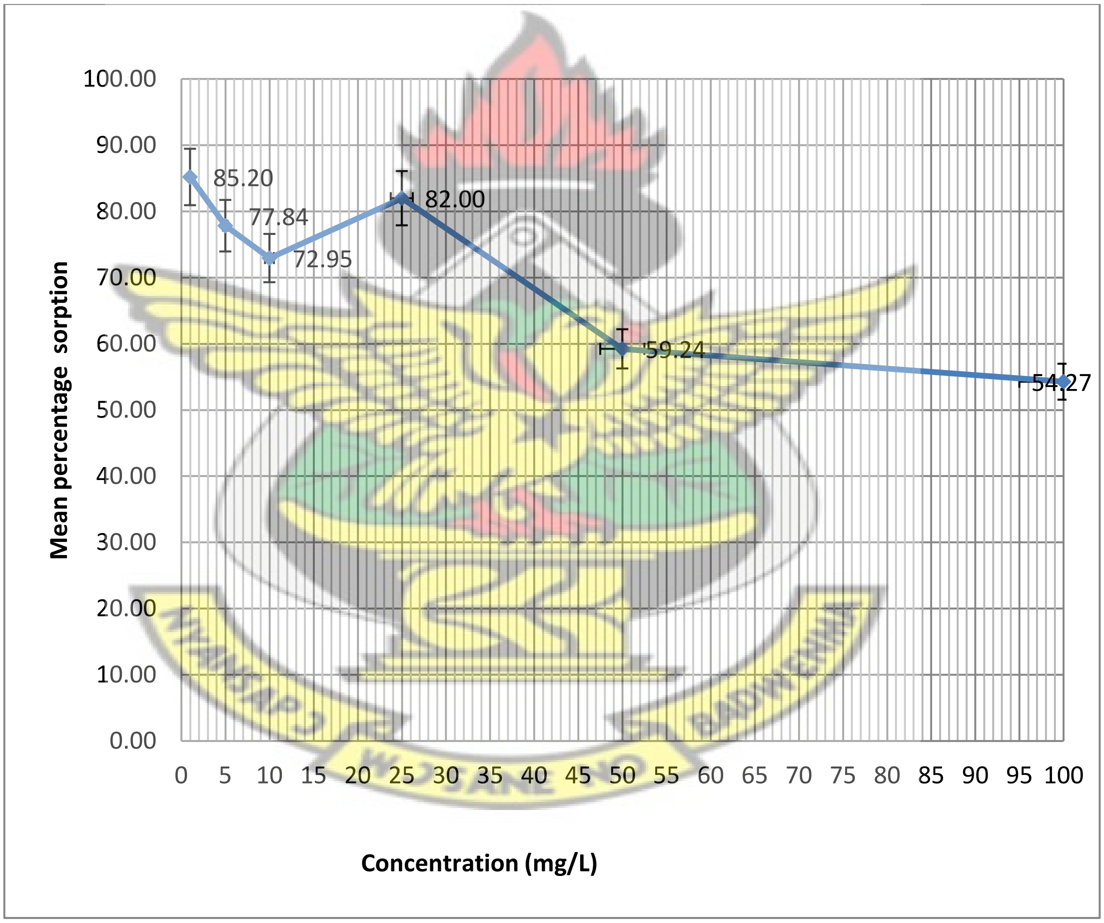


Fig. 11: Sorption capacity of Moringa-bauxite mixture for arsenic.

4.1.4 Comparison of sorption capacities of sorbents at various concentrations

Using column graphs with five percent (5%) error bars to show a comparative analysis of the sorption capacities of the different sorbents at the different concentrations from 1 mg/L to 100 mg/L, there were no statistically significant differences ($p > 0.05$) between the sorption levels of the bauxite and the *Moringa*-bauxite mixture at the 1 mg/L concentration (Fig. 12). However *Moringa oleifera* seeds alone showed significant difference. This was also true for the sorption levels for the sorbents at 5 mg/L. For all the other concentrations studied, there were no statistically significant differences ($p > 0.05$) among the sorption levels of the sorbents.

At concentrations of 1 mg/L, 5 mg/L, 50 mg/L and 100 mg/L, bauxite produced the highest mean percentage sorption, followed by the *Moringa*-bauxite mixture and the least sorption was when *Moringa oleifera* was used alone. At 10 mg/L, percentage sorption for *Moringa oleifera* seeds and the *Moringa*-bauxite mixture were about the same but bauxite still had the highest mean percentage sorption. However, at 25 mg/L, *Moringa oleifera* produced the highest percentage sorption with the least sorption being bauxite.

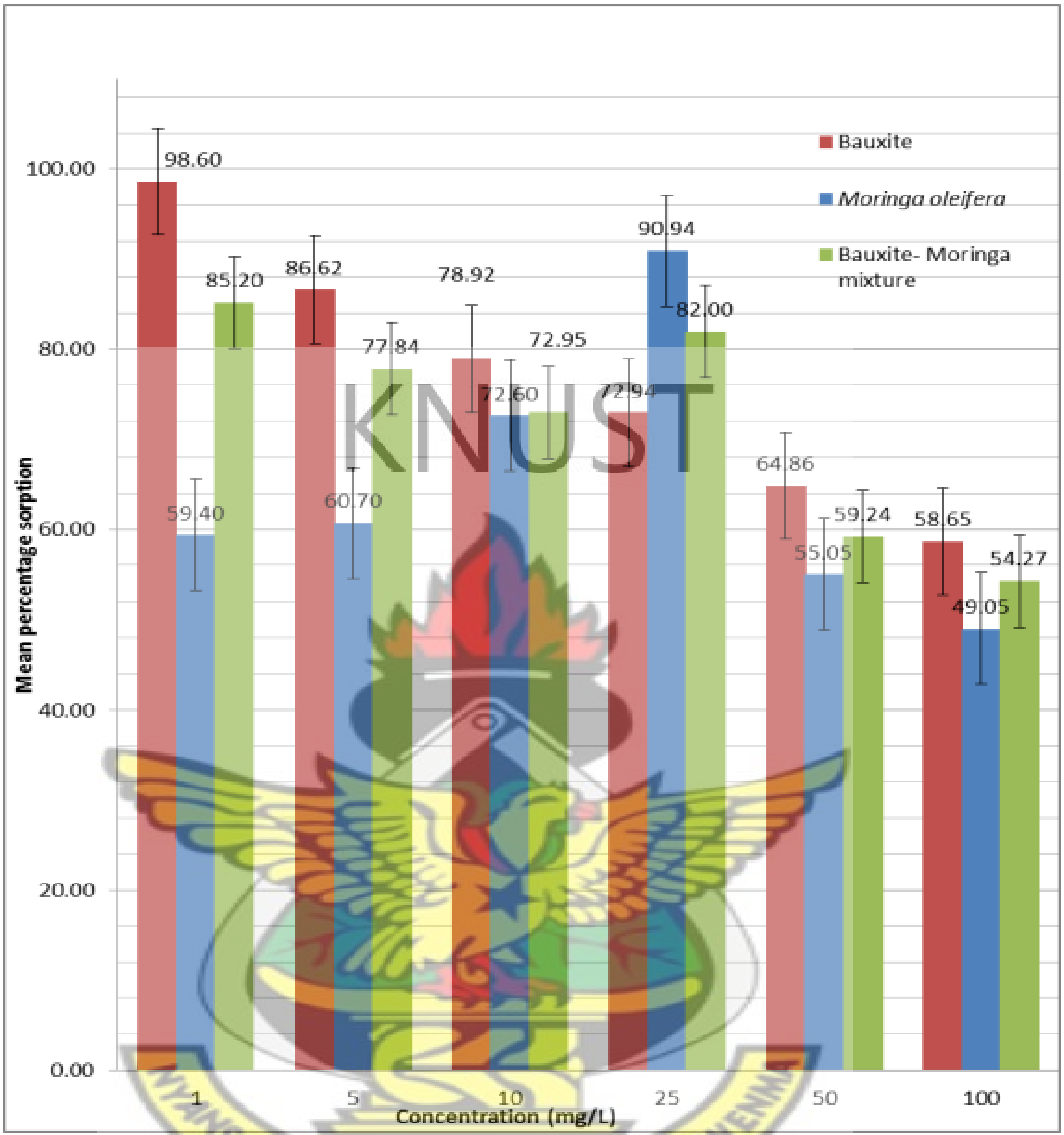


Fig. 12: Comparison of sorption at each concentration for the different sorbents.

Generally, there was significant differences among the residual arsenic levels (not sorption levels) for the sorbents (p<0.05). The variations are due to the differences in the initial concentration of arsenic solutions as shown in Table 2, 3 and 4.

Table 2: Differences in residual arsenic levels using *Moringa oleifera* seeds

Concentration (mg/L)	Final reading (mg/L) (Mean±SD)	Range
1	0.41^{a}±0.01	0.40-0.41
5	1.97^{b}±0.01	1.96-1.97
10	2.74^{c}±0.06	2.70-2.80
25	2.27^{c}±0.01	2.25-2.28
50	22.48^{d}±0.44	21.10-22.86
100	50.95^{e}± 0.09	50.84-51.01

Means along the same column with the same letters are not significantly different from each other.

Table 3: Differences in residual arsenic levels using bauxite as sorbent.

Concentration (mg/L)	**Final reading(mg/L) (Mean±SD)**	**Range**
1	0.01^{a}±0.00	0.013-0.016
5	0.67^{b}±0.02	0.644-0.689
10	2.11^{c}±0.02	2.090-2.125
25	6.77^{d}±0.21	6.605-7.003
50	17.57^{e}±0.02	17.54-17.59
100	41.35^{f}±0.05	41.30-41.90

Means along the same column with the same letters are not significantly different from each other.

Table 4: Differences in residual arsenic levels using Moringa-bauxite as sorbent.

Concentration (mg/L)	Final reading(mg/L) (Mean±SD)	Range
1	0.15^{a}±0.01	0.138-0.157
5	1.11^{b}±0.02	1.089-1.129
10	2.71^{c}±0.14	2.548-2.789
25	4.50^{d}±0.06	4.512-4.621
50	20.38^{e}±0.16	20.257-20.558
100	45.73^{f}±0.09	45.635-45.801

Means along the same column with the same letters are not significantly different from each other.

The means plot produced by the ANOVA (Fig. 13), indicates that the bauxite produced the lowest residual mean(11.41 mg/L) of arsenic as compared to the *Moringa oleifera* (13.66 mg/L) and the *Moringa*-bauxite mixture (12.42 mg/L). Lower value of residual means shows more effective sorption. Therefore bauxite was comparably the most effective sorbent over the concentration range.

Fig. 13: **Type of sorbent with corresponding residual means.**

4.2. Relevance of the sorption models.

Quantitative evaluation of biosorption using equilibrium adsorption models is important for constructing and optimizing parameters of adsorption system for removal of target metal (arsenic) from aqueous solution.

The experimental results for sorption poorly followed the Langmuir sorption model. This was true for all sorbents, thus *Moringa oleifera* seeds, bauxite and Moringa-bauxite powder. Fig. 14, 15 and 16 indicate the sorption models. However, Freundlich sorption model was well-followed by experimental results for all sorbents. This is indicated by the high linearity of the data when fitted into the Freundlich model as shown in fig. 17, 18 and 19. The high linearity recorded with the Freundlich model provides a mathematical evidence or quantitative evaluation that sorption capacities of all sorbents are high and that target metal (arsenic) can be separated from aqueous solution using the sorbents.

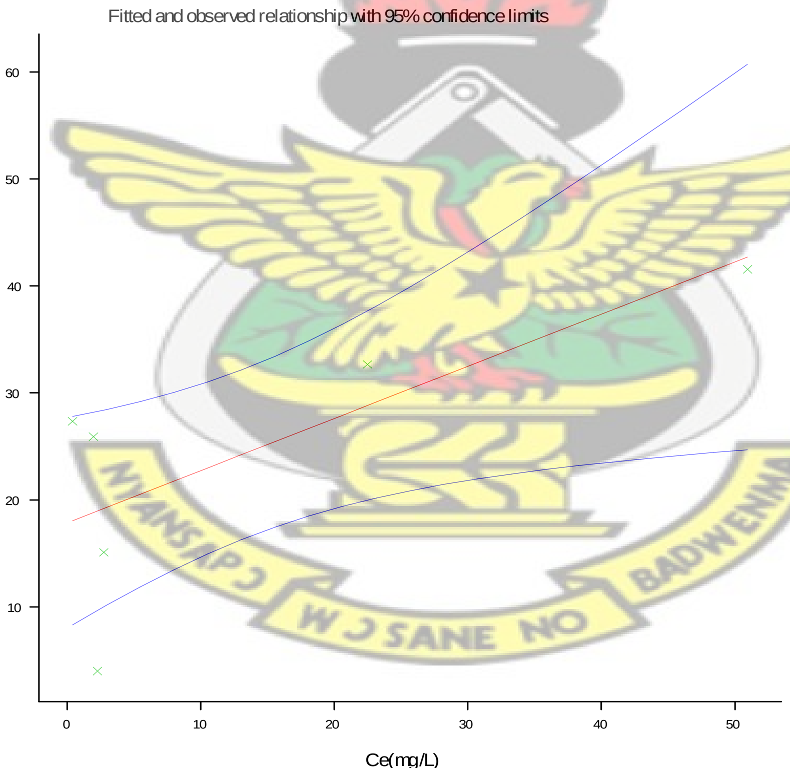


Fig. 14: The fitted Langmuir model for sorption with *Moringa oleifera* as sorbent.

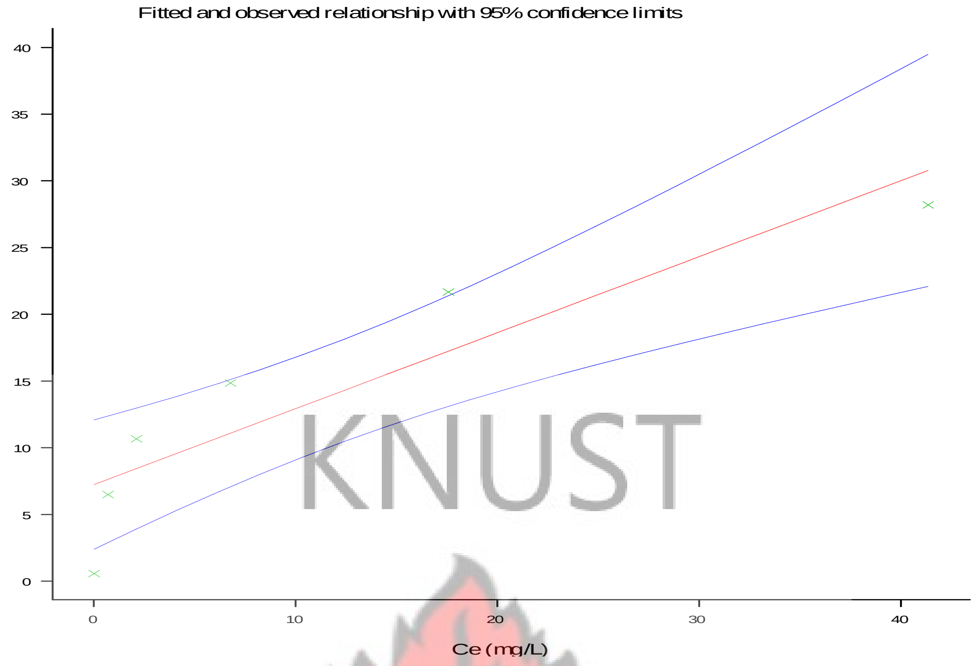


Fig. 15: The fitted Langmuir model for sorption when bauxite was the sorbent.

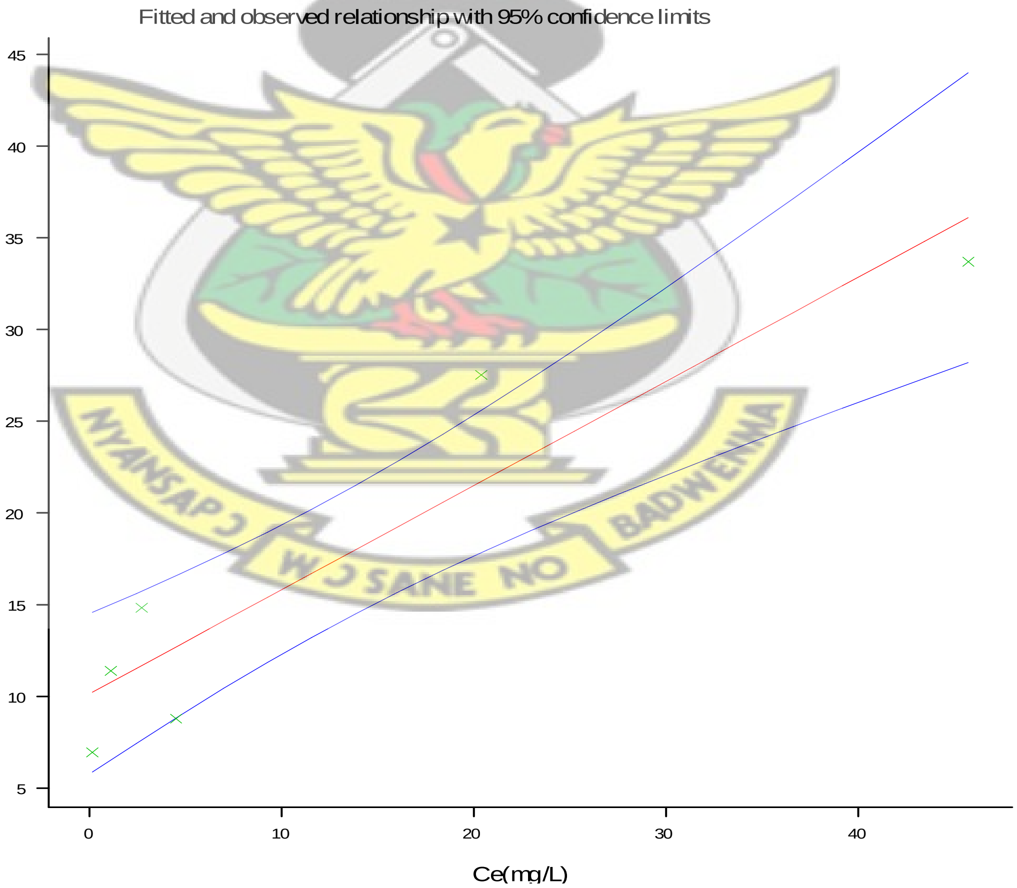


Fig. 16: The fitted Langmuir isotherm for Moringa-bauxite mixture.

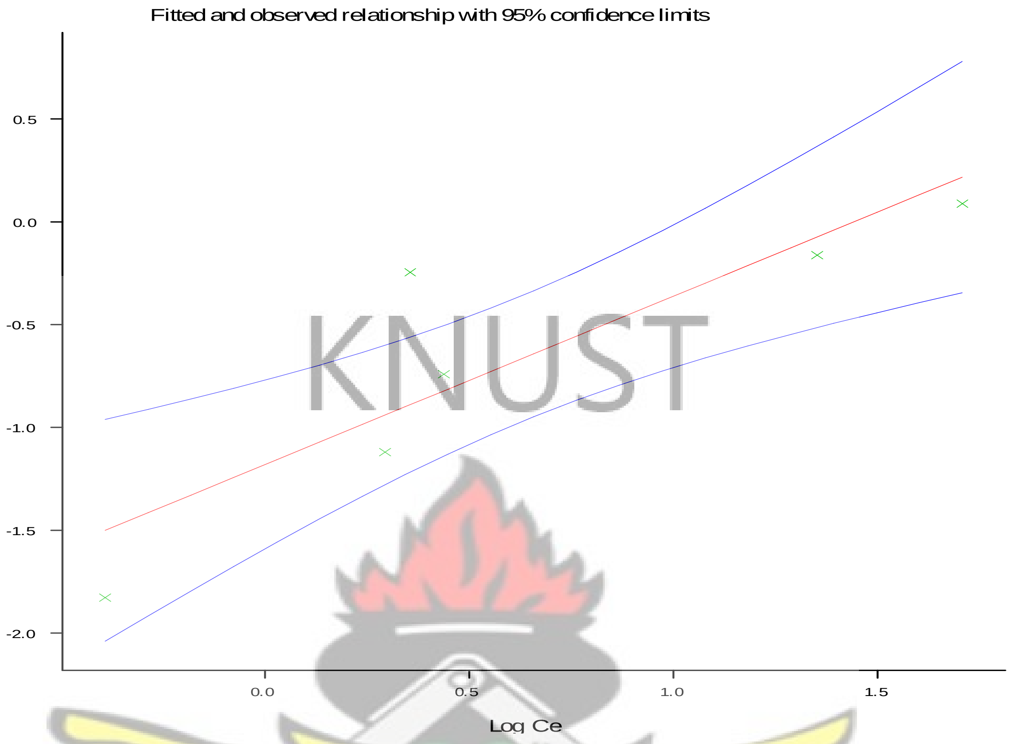


Fig. 17: The fitted Freundlich model for *Moringaoleifera* seeds.

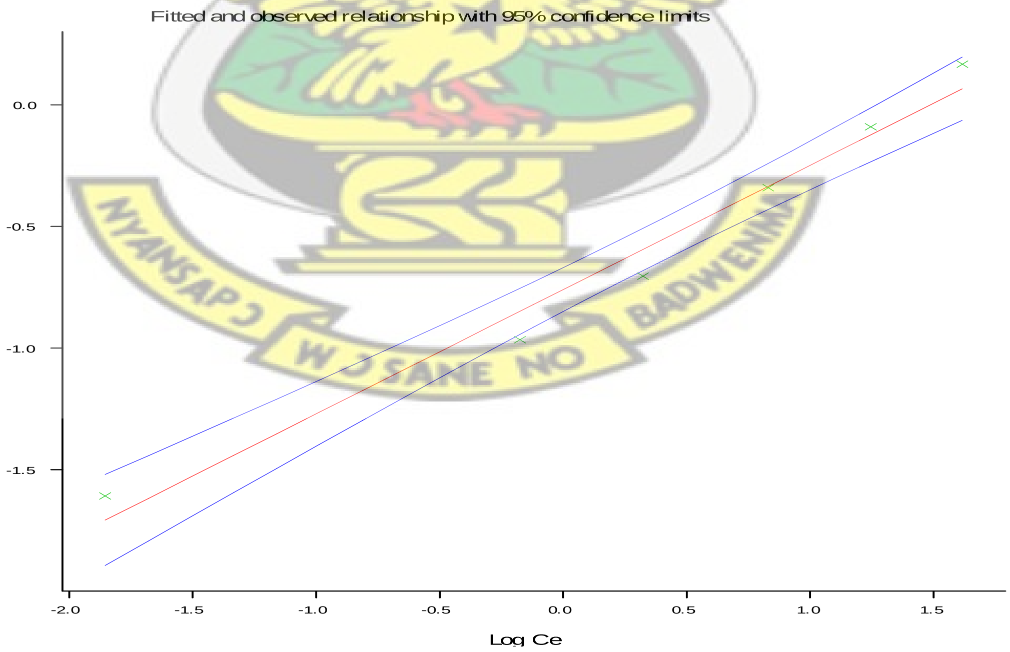


Fig. 18: Fitted Freundlich model when bauxite was used as sorbent

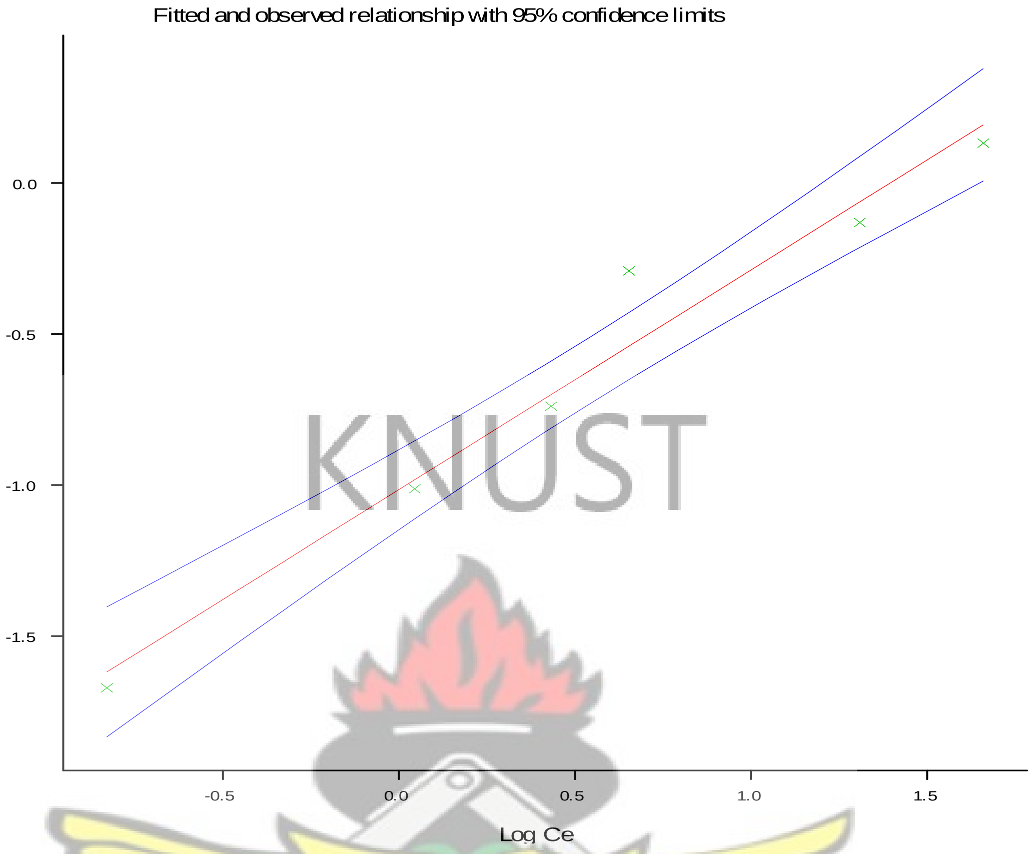


Fig. 19: **The fitted Freundlich model using Moringa-bauxite mixture.**

CHAPTER FIVE

5.0 DISCUSSIONS

The study shows that both *Moringa oleifera* seeds and the bauxite were good sorbents over the concentration range of arsenic solutions prepared. *Moringa oleifera* recorded a mean sorption of 90.94% at 25 mg/L (Fig. 10) and bauxite a sorption of 98.60% at 1 mg/L (Fig. 9). A combination of the two sorbents recorded a percentage sorption of 85.20% at 1 mg/L. Additionally, there was also a significant sorption of 82.00% at 25 mg/L when *Moringa oleifera* seeds were combined with bauxite (Fig. 11). Modelling these results along the Langmuir and Freundlich sorption isotherms, the latter provided a mathematical evidence that sorption was high for all the sorbents.

Pushpa *et al.* (2005), attributes the sorption capacity of *Moringa oleifera* seeds to the electrostatic force of attraction between the negatively charged arsenate (AsO_4^{-3}) and the positively charged amino acid groups (NH_3^+) which constitutes the protein in the *Moringa oleifera* seeds. It is reported that an aqueous solution of the *Moringa* seed is a heterogeneous complex mixture, having cationic polypeptides with various functional groups, especially low molecular weight amino acids. Amino acids have been reported as efficient phytochelators (Samuel, 2002) that work even at low concentrations and having the tendency to interact with metal ions significantly. The amino acids, depending on the pH, possess both the negatively and positively charged ends and are, thus, capable of generating the appropriate atmosphere for attracting the anionic or cationic species of the metal ions (Sharma *et al.*, 2007). This could possibly be the underlining factor in the measurement of the optimum sorption at the solution concentration of 25 mg/L. The right amount of H^+ yielded from dissociation of H_3AsO_4 (Afidenyo, 2011; Hunter *et al*., 1993), might have contributed enormously to the right pH, as pH coupled with concentration play an important role in the sorption capacity of a sorbent.

The high sorption capacity of *Moringa oleifera* for arsenic is not an isolated study as an earlier work by Pushpa *et al*., (2005) suggests a slightly lower sorption (85.60%) as against the sorption achieved in the present study (90.94%). The slight variation in the sorption might have arisen from slight difference in the pH and volume of test solution. The consistency of high sorption of *Moringa oleifera* seeds is not with arsenic alone but also with cadmium (85.10%), (Sharma *et al*., 2005), thus confirming the ability of the biomass to sorb both anionic and cationic species. The sorption recorded in this study is also consistent with sorption by *Lessonia nigrescens* (Hansen *et al*., 2006).However, work done in the Slovak Republic by Cernasky *et al*., (2007) suggests a very low sorption of arsenic by another biosorbent, *Aspergillus clavatus* (14.4%). This, they attributed to repulse electrostatic interactions between negatively charged surface of biomass and the arsenate (AsO_4^{3-}).

The sorption capacity of *Moringa oleifera* in the current study does not represent an exceptional performance as Pandey *et al.* (2009), reported 88% sorption of trivalent arsenic using *Momordica charantia,* vis-a-vis the consistent reports by Pushpa *et al.*

(2005) and Mohan (2006) that removal of trivalent arsenic in aqueous solution is much more difficult than pentavalent arsenic.

The sorption capacity of bauxite is attributed to the presence of oxides of iron (Fe_2O_3 and Fe_3O_4), TiO_2, silica (SiO_2) and hydrated aluminium oxide ($Al_2O_3.XH_2O$);these compounds have numerous pore sites which provide electrostatic attraction between the ionic species of the metal (arsenic) and these surfaces (Dube *et al.*, 2000; Mohan and Pitman, 2006). Sutherland *et al.*, (2001) has also suggested that oxides of iron, aluminium and titanium have been used as sequestration agents for arsenic in the treatment of water in Bangladesh. In addition to electrostatic interactions, the sorption capacity of bauxite may also be due to adsorption by covalent bonding (Westergren, 2006).

A study by Bhakat *et al.* (2006), Ayoob *et al.* (2007) and Wang *et al.* 2008, on sorption using calcined bauxite found out that the sorption capacity was 99.20% 99.98%, 99.93% respectively as compared to the 98.60 % in the present study when raw bauxite was used. This was due to the fact that calcination increases the sorption capacity of the material by increasing the pore spaces and binding sites. The sorption capacity of bauxite in the present study, though numerically lower, it is economical. This is because the calcination of bauxite comes with a huge cost because of the provision of energy. The sorption by the Moringa-bauxite is possibly based on the mechanism of sorption by individual components of the mixture; bauxite and *Moringa oleifera* seeds. The recording of the optimum sorption at 1 mg/L and another good sorption at 25 mg/L affirm the dependence of sorption on pH and concentration of the test solution.

Sorption capacity of the mixture for arsenic in this study provides a new dimension for the sequestration of heavy metals (arsenic) as existing works combined either two materials of organic (Guibal, 2004) or inorganic (Apak *et al.*, 1998) origin, contrary to the focus of this study which is the combination of an organic (*Moringa oleifera* seeds) and an inorganic (bauxite) material. Nevertheless, on the basis of combination of sorbents (neglecting focus on either organic or inorganic), then the study is not in isolation. The sorption capacity of the mixture is consistent with that provided by Apak *et al.* (1998).

In the present study, sorption models were used to mathematically evaluate the effectiveness of the sorbents, thus bauxite, *Moringa oleifera* and the *Moringa*-bauxite mixture. Sorption models take into account sorption levels at all concentrations and do not solely depend on the optimum sorption. Therefore a very high optimum sorption does not guarantee a very good model. Similarly, an experimental data from sorption can fit well both sorption isotherms.

Langmuir sorption model was not well-followed by the experimental data for all the sorbents (Fig. 14, 15 and 16) even though optimum sorption was high. This is was because the points were not very close to the fitted model. This observation was contrary to the model shown in the work by Pushpa *et al.* (2005) and Wang *et al.* (2008) but is consistent with the model provided by Sharma *et al.* (2005). However, the Freundlich sorption model was well followed by all sorbents, exhibiting high linearity of the points plot (Fig. 17, 18 and 19). The high level of linearity recorded with the Freundlich model is consistent with those of Pushpa *et al.* (2005), Ayoob *et al.* (2007) and Sharma *et al.* (2005)

CHAPTER SIX

6.0 RECOMMENDATIONS AND CONCLUSION

6.1 Conclusion

The study can conclude that Bauxite was a better sorbent at extreme concentrations of arsenic whiles at intermediate concentrations, *Moringa oleifera* was a better sorbent. When *Moringa oleifera* was mixed with bauxite, the sorption capacity combined the trends of *Moringa oleifera* and bauxite.

Moringa oleifera seeds can sorb 90.94% of arsenic in an aqueous solution at 25mg/L and the worst sorption of 49.05% at 100 mg/L. Bauxite had a peak sorption of 98.60% at 1mg/L and worst sorption of 58.65% at 100mg/L. Moringa-bauxite mixture recorded an optimum sorption of 85.20% at 1 mg/L and worst sorption of 54.75% at 100 mg/L.

6.2 Recommendations

- It was observed during the filtration that *Moringa oleifera* produced a soapy filtrate which indicates the presence of saponins (Agyente-Badu and Lowor, 2009). Moringa seeds, therefore needs drying in the oven predictably, a temperature of 60-65^{o}C to reduce the sudsy and soapy nature of the seeds.
- It is also recommended that *Moringa*-bauxite mixture must be used ahead of bauxite alone or *Moringa* seeds alone. This is because bauxite in itself is the ore from which aluminium is obtained. Should there be a heavy investment in that field then there will be a problem with available quantity for sorption. The choice is also to reduce the sudsy, foamy and soapy nature of the *Moringa* seeds.

- Different species of *Moringa* should be assessed for potential metallic sequestration.
- pH modification over the concentrations with the highest mean sorption should be considered so as to further investigate the effect of pH on these concentrations.
- Another area of worth-consideration is the X-Ray Diffraction (XRD) of the arsenic standards in terms of native and exhausted sorbents.
- Possibility of desorption through acid elution of arsenic and subsequent sorbents reuse is another good area which can be considered for studies.

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APPENDIX

Calculations involved in the preparation of arsenic solutions.

Concentration of stock solution= 3.0973 g/L

Preparation of 100 mg/L arsenic standard

Dilution formula: $C_1V_1=C_2V_2$, where C_1= Initial concentration, V_1= Initial Volume, C_2=Final concentration and V_2= Final volume.

C_1= 3097.3 mg/L, V_1=? C_2= 100 mg/L and V_2= 200 mL

3097.3 mg/L x V_1= 100 mg/L x 200 mL

$V_1= (100\ mg/L)/(3097.3\ \text{mg/L}\ ) \times 200\ mL$

$V_1=(100\ \ )/(3097.3\ \ ) \times 200\ mL$

V_1= 6.45 mL

Therefore 6.45 mL of the 3097.3 mg/L stock solution of arsenic was taken and diluted to 200 mL with distilled water. 50 mL of this solution was measured into an Erlenmeyer flask.

Preparation of 50 mg/L arsenic standard.

C_1= 100 mg/L, V_1=?, C_2= 50 mg/L and V_2= 200 mL

100 mg/L x V_1= 50 mg/L x 200 mL

$V_1= (50\ mg/L)/(100\ \text{mg/L}\ ) \times 200\ mL$

$V_1=(50\ \ )/(100\ ) \times 200\ mL$

V_1= 100 mL

Therefore 100 mL of the excess 100 mg/L stock solution of arsenic was taken and diluted to 200 mL with distilled water. 50 mL of this solution was measured into an Erlenmeyer flask.

Preparation of 25 mg/L arsenic standard

C_1= 50 mg/L, V_1=? C_2= 25 mg/L and V_2= 200 mL

50 mg/L x V_1= 2_5 mg/L x 200 mL

$V_1 = (25mg/L)/(50\ \text{mg/L}\ ) \times 200\ mL$

$V_1 = (25\ )/(50\ ) \times 200\ mL$

V_1= 100 mL

Therefore 100 mL of the excess 50 mg/L stock solution of arsenic was taken and diluted to 200 mL with distilled water. 50 mL of this solution was measured into an Erlenmeyer flask.

Preparation of 10 mg/L arsenic standard

C_1= 25 mg/L, V_1=? C_2= 10 mg/L and V_2= 200 mL

25 mg/L x V_1= 10 mg/L x 200 mL

$V_1 = (10mg/L)/(25\ \text{mg/L}\ ) \times 200\ mL$

$V_1 = (10\ )/(25\ ) \times 200\ mL$

V_1= 80 mL

Therefore 80 mL of the excess 25 mg/L stock solution of arsenic was taken and diluted to 200 mL with distilled water. 50 mL of this solution was measured into an Erlenmeyer flask.

Preparation of 5 mg/L arsenic standard

C_1= 10 mg/L, V_1=? C_2= 5 mg/L and V_2= 200 mL

10 mg/L x V_1= 5 mg/L x 200 mL

$V_1 = (5mg/L)/(10\ \text{mg/L}\ ) \times 200\ mL$

$V_1 = (5\ )/(10\ ) \times 200\ mL$

V1= 100 mL

Therefore 100 mL of the excess 10 mg/L stock solution of arsenic was taken and diluted to 200 mL with distilled water. 50 mL of this solution was measured into an Erlenmeyer flask.

Preparation of 1 mg/L arsenic standard

C1= 5 mg/L, V1=?, C2= 1 mg/L and V2= 100 mL

5 mg/L x V1= 1 mg/L x 100 mL

$V1= (1\text{mg/L})/(5\text{ mg/L}) \times 100\ mL$

$V1=(1)/(5) \times 100\ mL$

V1= 20 mL

Therefore 20 mL of the excess 5 mg/L stock solution of arsenic was taken and diluted to 100 mL with distilled water. 50 mL of this solution was measured into an Erlenmeyer flask.

Statistics generated using Genstat Discovery (Edition 4).

Analysis of variance

Variate: Final Conc

```
Source of variation              d.f.        s.s.         m.s.       v.r.    F pr.
Initial Conc                        5   1.454E+04    2.909E+03 1.704E+05    <.001
Type of sorbent                     2   4.561E+01    2.281E+01   1336.21    <.001
Initial Conc.Type of sorbent
                                   10   1.677E+02    1.677E+01    982.46    <.001
Residual                           36   6.144E-01    1.707E-02
Total                              53   1.476E+04
```

Tables of effects

Variate: Final Concentration

Initial Conc effects, e.s.e. 0.0435, rep. 9

```
   Initial Conc          1          5         10         25         50        100
                   -12.334    -11.249     -9.594     -7.981      7.646     33.512
```

Type of sorbent effects, e.s.e. 0.0308, rep. 18

```
   Type of sorbent          B1         C1         M1
                        -1.084     -0.079      1.163
```

Initial Conc.Type of sorbent effects, e.s.e. 0.0754, rep. 3

```
   Initial Conc    Type of sorbent          B1         C1         M1
              1                          0.936     -0.013     -0.923
              5                          0.506     -0.061     -0.445
             10                          0.287     -0.119     -0.168
             25                          3.338      0.074     -3.412
             50                         -1.489      0.318      1.170
            100                         -3.578     -0.200      3.777
```

Tables of means

Variate: Final Conc

Grand mean 12.497

```
   Initial Conc          1          5         10         25         50        100
                     0.163      1.247      2.903      4.515     20.143     46.009

   Type of sorbent          B1         C1         M1
                        11.413     12.418     13.660

   Initial_Conc    Type_of_sorbent          B1         C1         M1
```

```
      1                      0.014     0.071     0.403
      5                      0.669     1.108     1.965
     10                      2.106     2.705     3.898
     25                      6.769     4.511     2.266
     50                     17.570    20.382    22.476
    100                     41.347    45.731    50.949
```

Standard errors of means

```
Table            Initial_ConcType_of_sorbent
                                          Initial_Conc
                                       Type_of_sorbent
rep.                     9          18             3
d.f.                    36          36            36
e.s.e.              0.0435      0.0308        0.0754
```

Standard errors of differences of means

```
Table            Initial_ConcType_of_sorbent
                                          Initial_Conc
                                       Type_of_sorbent
rep.                     9          18             3
d.f.                    36          36            36
s.e.d.              0.0616      0.0435        0.1067
```

Least significant differences of means (5% level)

```
Table            Initial_ConcType_of_sorbent
                                          Initial_Conc
                                       Type_of_sorbent
rep.                     9          18             3
d.f.                    36          36            36
l.s.d.              0.1249      0.0883        0.2163
```

Stratum standard errors and coefficients of variation

Variate: Final_Conc

```
d.f.              s.e.        cv%
 36             0.1306        1.0
```