

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

KUMASI

COLLEGE OF ENGINEERING

DEPARTMENT OF MATERIALS ENGINEERING

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ASSESSING THE POTENTIAL OF LATERITE IN ADSORBING CADMIUM
FROM MINE LEACHATE AND SURROGATE CADMIUM SOLUTIONS: A
CASE STUDY AT ANGLOGOLD ASHANTI IDUAPERIEM GOLD MINE LTD,
TARKWA

BY

SALAH ABIGAIL SEYRAM

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ENVIRONMENT.

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DECLARATION

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

SALAH ABIGAIL SEYRAM

(7685312)

Signature

Date

Student Name & ID

Certified by:

Mrs. Koomson Bennetta

Supervisor Name

Signature

Date

Certified by:

Prof. S. Kwofie

Head of Dept. Name

Signature

Date

ABSTRACT

Increased mining activities have resulted in the generation of huge stockpile of waste rocks. Subsequent heavy metal laden leachate emanate from these waste rocks. This has resulted in deleterious effects on adjacent water bodies and ecosystem thus posing issues of health and environmental concerns.

Waste rock samples were obtained from two active waste rock dump sites. The waste rocks were characterized using XRF and XRD. Leach test was then performed using US Geological Survey Field Leach Test (USGS FLT). Batch and columns test were conducted using United State Environmental Protection Agency (USEPA) batch type procedures for estimating soil adsorption of chemical elements (eg. heavy metals).

Cadmium level of 0.0505 mg/l obtained from the leach test exceeded WHO's guideline value of 0.03mg/l for potable water. Optimal time, pH, adsorbent dosage, temperature and initial concentration of 1hour, 9, 10 g, 20 °C and 10 mg/l respectively were obtained from the batch tests. Langmuir isotherm provided a better fit for the experimental data resulting in a maximum adsorption capacity of 10689.31mg/g. From the ΔG° values (-1027.98, -147.23, -249.63, -662.87, -1765.21) J, ΔS° value (36.9726) and ΔH° value (10432.36) J obtained from the thermodynamic study, it can be inferred that adsorption of cadmium onto laterite is feasible, spontaneous and endothermic.

Breakthrough time of 3 hours and exhaustion time of 11 hours were established from the column tests. Hence laterite proves as an appropriate adsorbent for cadmium.

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LIST OF SYMBOLS AND ACRONYMS

$q_{\max}$	Maximum adsorption capacity
C_0	Initial concentration
C_e	Equilibrium concentration
q_e	Amount adsorbed at equilibrium
AAS	Atomic Absorption Spectrometer
AMD/ARD	Acid Mine Drainage/ Acid Rock Drainage
USGS FLT	United State Geological Survey Field Leach Test
WHO	World Health Organization
EPA	Environmental Protection Agency
XRD	X-Ray Diffractometry
XRF	X-Ray Fluorescence
n, k	Freundlich constants
b	Langmuir constant
R^2	Regression Coefficient
K_c	Equilibrium constant
C_{ad}	Reduction of adsorbate concentration (mg/l) of the solution at equilibrium due to adsorption
ΔG^0	Gibb's free energy change
ΔH^0	Enthalpy change
ΔS^0	Entropy change
K_{sp}	Solubility product
Q_c	Ionic quotient
FAAs	Flame Atomic Adsorption Spectrometer
EMP	Environmental Management Plan

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Ghana is endowed with substantial mineral resources and has a well-established mining sector which has grown considerably in recent years to represent an important pillar of the Ghanaian economy. This notwithstanding mining is associated with some unavoidable environmental issues pertaining to water conservation and balance, waste streams or hazardous substances control, air pollution, etc. For example, mining of ore requires the striping of large volumes of waste rock, which can degrade through weathering producing leachate that are laden with toxic elements that can be mobilised into the geo-environment. A study by Addo (2001) revealed that waste rocks obtained from Pits I & 2 (AngloGold Ashanti Iduaperiem Mine, Tarkwa), showed the presence of pyrite, a potential source for ARD generation. Further investigations by Addo (2001) revealed that leachate emanating from Block I North Waste Dump (Pit 1) at the AngloGold Ashanti Iduaperiem Mine, Tarkwa had low pH and high metal ions concentration.

Generation of mine waste is an integral part of mining activities, thus, effects/problems from these geologic and anthropogenically derived materials remains issues of great environmental concern, therefore, necessitating the development of efficient and effective control measures. Amongst various metal removal techniques, adsorption is the preferred technique for heavy metal removal from wastewater because it offers flexibility in design and operation and, in many cases it will generate high-quality treated effluent. In addition, owing to the reversible nature of most adsorption processes, the adsorbents can be regenerated by suitable desorption processes for multiple use (Pan *et al.*, 2009). Attention has been focused on the

various adsorbents, which have high metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost. Because of their low cost and availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, coal, and oxides are classified as low-cost adsorbents. A few adsorbents that stand out for high adsorption capacities are chitosan (815, 273, 250, 222, 75 mg/g of Hg^{2+} , Cr^{6+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} , respectively), zeolites (175 and 137 mg/g of Pb^{2+} and Cd^{2+} , respectively), waste slurry (1030, 560, 640 mg/g of Pb^{2+} , Hg^{2+} , and Cr^{6+} , respectively), and lignin (1865 and 95 mg/g of Pb^{2+} and Zn^{2+} , respectively) (Babel & Kurniawan, 2004).

In summary, a mineral resource should be efficiently extracted to maximize its utilization and longevity. This can only be achieved if mineral resources are exploited in a sustainable manner by addressing the ensuing environmental and social problems. It is against this background that this work seeks to address the mobilisation of cadmium, which is toxic, in to the geo-environment by assessing the potential of laterite in attenuating its high concentration in leachate emanating from waste rock dumps in order to reduce adverse environmental impacts and promote post-mining beneficial land use.

1.2 Problem Statement

Population expansion and industrialization (all results of man's activities in his attempt to survive) create environmental conditions that are detrimental to his very survival. Amongst the environmental conditions is the release of heavy metal/trace metal content of mine waste effluents through exposure of sulphide bearing rocks through mining activities, producing acidic solutions which can cause metals in the geologic materials to dissolve. This effluent has the possibility of impairing the quality of surface water and underground water resources causing natural waters to

become unfit for use as potable water sources. Furthermore, contaminated leachate entering surrounding soil can result in sterilisation and degradation of ecosystems and limit the downstream beneficial uses of the receiving water (e.g. stock, recreation, fishing, aquaculture, irrigation). The ubiquitous nature of heavy metals, their toxicity even as trace quantities (for eg. Cd damages the kidneys, Pb adversely affects red blood cells, the nervous system and kidneys), their tendency for bioaccumulation in food chain, their non-biodegradability, their ability to undergo transformation, the economic impact and the stricter environmental regulation related to heavy metal discharges have prompted the development of processes for the removal of heavy metals from waste water and soils. (Babel & Kurniawan, 2004)

Studies by the following people are evident of the fact that most parts of the environment is fast undergoing environmental degradation and its immense economic value is diminishing from year to year, mainly due to mining activities. Armah *et al.*, (2010) and Akabzaa & Darimani (2001) documented heavy metal pollution in surface and groundwater and found high levels of arsenic in water and sediments near Prestea, while Tetteh *et al.*, (2010) found high levels of mercury and zinc content in the topsoil of towns (Teberebie, Mile 8) in Wassa West. The levels of concentration decrease with distance from mining sites, and extend beyond mining areas, probably due to the aerial dispersion of metals from mining areas (Akabzaa & Darimani, 2001).

The study therefore seeks to assess the potential of laterite for removing metals from leachate emanating from mine waste rocks.

1.3 Objectives

Main objective

To investigate the suitability of laterite in adsorbing cadmium from mine leachate.

Specific objectives are to:

- Characterize the mine waste (waste rock);
- Determine the levels of heavy metals (Fe, Mn, Cd, Zn and Cu) in the leachate;
- Determine the optimum time, pH, adsorbent dosage, temperature, initial metal concentration which will result in optimum adsorption of metals; and
- Determine thermodynamic parameters.

1.4 Justification of Objectives

The environment is the most important asset to man and the development of every nation depends largely on its well-managed environment. It is therefore prudent to protect it from pollution. In light of increasing environmental awareness of mining companies, understanding and controlling the potential environmental liabilities associated with mining sites has become increasingly important. Many of the residents in the Iduaperim and Teberebie in the Tarkwa Nseum District of Western Region depend on ground and surface waters for drinking and domestic purposes. However, leachate from the mining industry may pollute some of these water bodies and make them unsafe. It is imperative to treat this leachate before discharging them into the geo environment. The results of this work will be used to evaluate the existing environmental management plans (EMPs) and best management practices (BMPs) at the mine site. It will also add up to existing literature on Iduaperiem's operational impacts on the environment and also help to clear doubts or affirm that Iduaperim catchment communities have good sources of drinking water free from pollution.

The study is intended to assist mining companies in adopting sustainable environmental practices as regards their daily operations.

1.5 Scope of the Study

This thesis focuses on assessing the potential of laterite in removing heavy metals in leachate emanating from mine waste at the AngloGold Iduaperiem mine at Tarkwa in

the Western Region of Ghana. First, leach test (United State Geological Survey Field Leach Test) was conducted to ascertain the presence and amount of heavy metals as a potential threat from waste rock. Second, a series of batch experiments were performed to generate equilibrium isotherms using mine leachate and Cd stock solutions and optimal conditions obtained for column tests. Grapher 8 and Microsoft excel were used to draw all graphs.

1.6 Organisation of Study

The thesis work comprises five chapters each of which each addresses a principal heading. The first chapter gives an introduction to the subject matter, outlining the background of the research, the problem statement, objectives of the research, justification of objectives and scope of the study.

Chapter two presents a review of literature outlining the main fundamental theory behind the heavy metal removal methods. Included in this is the general overview of the environmental and health impacts of heavy metals.

Chapter three discusses the methodology used in conducting the thesis work.

Chapter four analyses the various graphs obtained from the adsorption tests. The chapter will also give interpretations to the results from the leach test, XRF tests.

The thesis ends with conclusions and recommendations for future works in Chapter five.

1.7 Methodology

The following will be carried out:

- X-Ray Diffractometry to ascertain the types of rocks present in the waste rock;
- X-Ray Fluorescence to find elemental constituents of the waste rock;

- United State Geological Survey Field Leach test to find mobilisation capacity;
- Atomic Absorption Spectrometry to determine elements in leachate;
- Batch experiments to obtain optimal conditions needed for maximum adsorption; and
- Column tests to obtain conditions needed for maximum adsorption in a field set up.

1.8 Limitations

Adsorption of cadmium was the only metal studied due to financial constraints. This however is not a true representation of the reality on the ground as adsorption is affected by the presence of other metals.



CHAPTER TWO

LITERATURE REVIEW

2.1 Mining and the Environment

Ghana is endowed with rich and diverse natural (timber, bauxite, manganese, fish, rubber, hydropower, petroleum, etc) and environmental (lithosphere, hydrosphere, atmosphere, biosphere) resources which are constantly exploited to meet the growing demands of the populace; however the uncontrolled manner of utilization of these resources results in reversible and irreversible changes within the environment.

The principal elements of the environment (i.e., land, water, air, plants and animals) have been severely affected by mining activities in Ghana (Amponsah-Tawiah & Dartey-Baah, 2011). In most parts of Tarkwa, and most mining communities the environment is undergoing rapid degradation and its immense economic value is diminishing from year to year, mainly due to the heavy concentration of mining activities in the area (Akabzaa & Darimani, 2001).

2.1.1 Impact of Mining on Land

Considerable degree of land alienation for farming activities have been acquired by mining companies for large scale surface mining operations. This action not only deprives mining communities of their source of livelihood but also continues to reduce the vegetation of the area to levels that are destructive to biological diversity. Erosion and land relocation is a major mining impact on land as mining produces large quantities of loosened exposed earthen materials. Erosion may cause significant loading of sediments (and any entrained chemical pollutants) to nearby water bodies, especially during severe storm events and high snow melt periods. “Sediment-laden

surface runoff typically originates as sheet flow and collects in rills, natural channels or gullies, or artificial conveyances. (Akabzaa & Darimani, 2001).

2.1.2 Impact of Mining on Water Systems

Chemical pollution of ground water and streams, siltation through increased sediment load, increased faecal matter and dewatering effects are the four main problems of water pollution that have been noticed in Tarkwa mining areas by Akabzaa and Darimani (2001).

On Tuesday, June 18th, 1996, between 2 and 3:00 pm, there was a cyanide spillage in the Angonaben stream, a main tributary of the Bonsa River. Following a heavy downpour, an enormous amount ($36,000\text{m}^3$) of gold pregnant cyanide solution with a cyanide concentration of 8-100 ppm was accidentally discharged from the contaminant facility within the premises of the Tarkwa Goldfields Limited (TGL's) operation. The spillage was reported to have affected up to nine villages along the banks of the river.

Samples taken from Awunabeng, a stream in the Teberebie village resettled by Tarkwa Goldfields Limited (TGL) showed augmented levels of faecal matter (126 counts/100 ml), suspended solids (16 mg/l), and low pH (5.11) confirming the community's fear that the stream might be polluted (Vinorkor and Syme, 2006).

Erosion and sedimentation processes cause build-up of thick layers of mineral fines and sediment within regional flood plains and alter aquatic habitat and result in loss of storage capacity within surface waters (Akabzaa & Darimani, 2001).

Mining has active dewatering effects. Apart from consuming huge amount of water, extensive excavation of large tracts of land and the piling of large mounds of earth along watercourses remove the source of water recharge for groundwater sources and

ultimately reverse the direction of flow of ground water, causing active dewatering. A number of boreholes, hand-dug wells and streams in the area have either become unproductive or provide less water with time. The same dewatering process reduces recharge to streams, especially during the dry season. For example mining activities have drawn huge amount of water from the Bonsa River, resulting in lower water flow levels in the Bonsa and the lower reaches of the Angonabeng River and lengthening patches of dryness during the dry season (Akabzaa and Darimani, 2001).

2.1.3 Impact of Mining on Air Quality

Mining activities and mining support companies release particulate matter (respirable dust, sulphur dioxide (SO₂), nitrogen dioxide (NO₂), carbon monoxide (CO) and black smoke) into the ambient air through activities such as site clearance, road building, open-pit drilling, blasting, vehicular movement, ore/waste rock handling and processing etc. In Prestea, values recorded for black smoke exceeded the tolerable levels of WHO guidelines and EPA standards. The highest value recorded was 207 gm⁻³ as against the tolerable levels of 85 gm⁻³ for WHO and 40 gm⁻³ for EPA-Ghana. Results of air quality monitoring for dust from the EPA monitoring station at the Tarkwa Government Hospital were as high as 199 gm⁻³, a value far above acceptable, detectable limits (70 gm⁻³ and 70 gm⁻³ for WHO and EPA respectively) for health safety (Akabzaa and Darimani, 2001). The continued viability of these elements to support the well-being and development of the rural populations in the Tarkwa and Ghana at large area is currently in doubt (Akabzaa and Darimani, 2001).

2.1.4 Impact of Mining on Plants and Animals

The most obvious mining impact on biodiversity from is the removal of vegetation, which in turn alters the availability of food and shelter for wildlife. For example, acid drainage and high metal concentrations generally result in an impoverished

environment thus altering conditions such as local climate, altitude, and other features of the local habitat which ensures the survival of wildlife species. For example, salmon species are particularly sensitive to increased concentrations of copper (Kelly, 1998). Mining can also impact on biodiversity by changing species composition and structure.

2.2 Weathering of Rocks

Weathering is the breakdown and alteration of rocks and minerals at or near the surface of the earth into products that are in equilibrium with conditions found in the environment. Physical and chemical nature of materials formed in the earth crust are in disequilibrium with conditions occurring on the surface and because of the disequilibrium, materials occurring on the surface are easily detached, decomposed and eroded by various chemical and physical surface processes.

The process of weathering can result in three processes on rocks and minerals namely:

- Complete loss of particular atoms or compounds from the weathered surface;
- Addition of specific atoms or compounds to the weathered surface; and
- A breakdown of one mass into two or more masses with no chemical change in the mineral or rock (Piwdwimy, 2006).

There are three broad categories of mechanism for weathering: physical, chemical and biological weathering.

2.2.1 Physical Weathering

Physical weathering is the breakdown of rocks into pieces with no change in the chemical composition of the weathered material having the same properties as the original and this occurs mainly by temperature and pressure changes (Piwdwimy, 2006). There are several forms of physical weathering including abrasion, freezing

and thawing, thermal expansion and contraction of minerals, crystallization, action of organisms and plant roots.

2.2.2 Chemical Weathering

Chemical weathering is the breakdown of rocks by chemical reactions which utilize water, oxygen, carbon dioxide and organic acids. These reactions involve: hydrolysis, oxidation, carbonation, leaching and hydration (Goudie and Viles, 2008).

2.2.3 Biological Weathering

Biological weathering is the breakdown of rocks and minerals due to chemical and/or physical agents of an organism (Piwdwimy, 2006). The root of Plants and trees can wedge into crevices of rocks forcing it apart and ultimately causing it to fracture. When plants and animals decay, they release carbon dioxide into the air. When the carbon dioxide mixes with water, it forms carbonic acid which can chemically break down the minerals in the rocks. Worms, termites, gophers and prairie dogs, lichens can all be responsible for biologically weathering rocks (Thompson and Jonathan, 1998).

2.3 Leachate Formation from Waste Rocks

It is important to understand the mechanism of releasing metal elements from mining industries in order to predict or estimate migration of these contaminants in the environment. This will also help initiate necessary policy for pollution control and prevention in groundwater aquifer systems. Leachate is any liquid material that drains from land or stockpiled material and contains significantly elevated concentrations of undesirable material (Perkin, 1997). The production and flow of leachate from waste rock piles is controlled by wetting and drying cycles. The waste piles are intermittently wetted by water and seasonal run-off, dried by drainage and evaporation. The time taken to complete the entire wetting- drying cycle is dependent

upon porosity, permeability and climatic factors. A complete wetting-drying cycle for a waste rock pile located in a region of moderate to high rainfall with distinct seasons consist of four sequential stages;

- i. Sulphide oxidation and formation of secondary minerals;
- ii. Infiltration of water into dumps;
- iii. Drainage of water from dump; and
- iv. Evaporation of pore water

The first stage represents the atmospheric oxidation of sulphides which results in the decomposition of sulphides and the formation of secondary minerals. The reaction of pyrite with oxygen and water produces a solution of ferrous sulfate and sulfuric acid. Ferrous iron can further be oxidized producing additional acidity. Iron and sulfur oxidizing bacteria are known to catalyse these reactions at low pH thereby increasing the rate of reaction by several orders of magnitude (Nordstrom and Southam 1997). In undisturbed natural systems, this oxidation process occurs at slow rates over geologic time periods. When pyrite is exposed to oxygen and water it is oxidized, resulting in hydrogen ion release, acidity, sulfate ions, and soluble metal ions. The acidity of water is typically expressed as pH or the logarithmic concentration of hydrogen ion concentration in water such that a pH of 6 has ten times the hydrogen ion content of neutral pH 7 water (Jennings *et al.*, 2008). The dissolution of iron sulfide minerals leads to acid production by mine wastes. The second stage is the infiltration of meteoric water and seasonal run-off. Pores are wetted to the extent that weathering of minerals occurs. The third stage involves drainage of water from the pore spaces. Solutes dissolved in the pore water are transported to the water table or are channeled to surface seepages. Air replaces the pore water during drainage and a thin pore water film is left behind coating individual grains. The fourth stage is the evaporation of the water film during the drying cycle. Drying results in the precipitation of secondary

minerals that may coat the sulphide mineral surfaces. If drying continues, some of these minerals may dehydrate, crack and fall from the sulphide surfaces exposing fresh sulphides to atmospheric oxygen (Perkin, 1997).

The position of water table in mine waste has an important role in influencing the composition of drainage water. This is because the water table elevation fluctuates in response to seasonal conditions forming zones of cyclic wetting and drying. Such fluctuations provide optimal conditions for the oxidation of sulphides and associated secondary weathering products (Perkin, 1997).

The abundance and distribution of acid producing and acid buffering minerals vary from one particle to another. Waste parcels with abundant pyrite, free movement of air and impeded movement of water are expected to develop higher acidities than equal volumes that contain less pyrite or that are completely saturated with water. Physical and chemical conditions within waste rock dumps vary even on a microscopic scale. The resulting drainage water is a mixture of fluids from a variety of dynamic micro-environments within the dump. Consequently the water quality in different parts of waste dumps exhibits spatial and temporal variations (Lottermoser, 2010).

2.4 Changes in Waste Dump Seepage

When mine waste is exposed to weathering processes some soluble minerals go readily into solution whereas other minerals weather at different rates. Kinetic and static equilibrium weathering and dissolution of different minerals within mine waste also plays an important role on the chemistry of mine waters. Kinetic weathering processes in particular determine changes to mine water chemistries over time because acid producing and acid neutralizing minerals have different reaction rates. The drainage water chemistry of a dump or tailings evolves with time as different

parts of the material starts to contribute to the overall chemical load. Generally the chemical load reaches a peak after which the load decreases slowly with time. When altered, weathered or oxidized wastes are subjected to rinsing and flushing, the pore water will be flushed first from the waste. Then easily soluble alteration minerals, weathering and oxidation products and secondary efflorescence will dissolve and determine early rates of metal release and seepage chemistry, in particular, the soluble and reactive minerals will contribute to equilibrium dissolution at an early stage. Finally weathering kinetics of sulphides and other acid neutralizing minerals will take over and determine the drainage chemistry (Lottermoser, 2010).

Mine drainage quality prediction cannot be based on the assumption that the waste material experiences uniform contact with water. Water moving through an unsaturated portion of waste contacts waste briefly whereas water of the saturated zone has a longer contact time with the waste. In addition some material may have a very low permeability allowing very little ground water to flow through it. These waste portions contribute little to the chemistry of drainage waters. In order to understand the chemistry of drainage waters emanating from waste rock dumps, it is important to determine what waste portions are contacted by water and what the nature of this contact is (Hawkins, 1998).

2.5 Environmental Impacts of Leachate from Mine Waste

Drainage water from tailings dam, mine waste dumps, heap leach pads and ore stockpiles may contain suspended solids and dissolved contaminants such as acids, salts, heavy metals, metalloids and sulphate. The uncontrolled discharge of mine waters with elevated contaminant concentration into the environment may impact on surrounding surface waters, aquatic life, soil, sediments and ground waters. Therefore

such waters should not be released from a mine site without prior treatment. The environmental impacts of leachate from mine waters are discussed as follows:

2.5.1 Surface Water Contamination

The release of AMD waters with their high metal and salt concentration impact on waters for fishing, irrigation and drinking water supplies (Seal *et al.*, 2008). Irrigation of crops with stream water that is affected by AMD effluents may be inappropriate if the impacted stream has metals and metalloid concentrations above threshold values that are considered to be phytotoxic to crops. For example, the results of a study by Akabzaa *et al.*, (2007) showed that past and present large scale and illegal small-scale mining activities have affected water resources in Obuasi and its satellite communities resulting in stream water being significantly polluted by As, Hg, Fe, and, to some extent, Cu, Ni and Zn. Microprobe mapping of sulphide grains in rock samples showed a variety of Cu, As, Ni and Zn bearing sulphides as possible sources of augmented concentrations of these pollutants in water (Akabzaa *et al.*, 2007). Poor water quality also limits its reuse as process water at the mine site and may cause corrosion to and encrustation of the process circuit (Lottermoser, 2010). Studies by Akabzaa and Darimani (2001) produced startling results of very high abnormal content of faecal chloroform, suspended solids, chloride, colour and manganese content, particularly in the Angbenabe River at Nkwantakrom for water samples obtained from boreholes, wells and streams within Tarkwa area. In general the severity of surface water contamination decreases downstream of the contamination source due to mixing with non-contaminated stream which causes the dilution of elements, compounds and the neutralization of acidity. Mineral precipitation, adsorption and coprecipitation may also remove elements from solution leading to lower dissolved contaminant concentrations in impacted waterways.

2.5.2 Impact on Aquatic Life

Photosynthetic aquatic organisms use bicarbonate as their inorganic carbon source. However, high acidic waters can however destroy the natural bicarbonate buffer system which keeps the pH of natural waters within a distinct pH range. The destruction of the bicarbonate system by excessive hydrogen ions will result in the conversion of bicarbonate to carbonic acid and then to water and carbon dioxide thus decreasing the pH to less than 4.3 making survival of the organisms difficult (Brown *et al.*, 1991). In summary, the impact of contaminated waters and sediments containing high concentrations of metals and metalloids on aquatic ecosystem and downstream plant and animals can be a reduction of biodiversity, changes in species, depletion of numbers of sensitive species, or even fish kills and death of other species (Lottermoser, 2010). Some incidents related to heavy metal impact on aquatic water includes: In 1998, a mine flood incident in Spain deposited some 6 million m³ of acid water over the banks of the Guadiamar River with metal and sulfide rich sediments. The U.S. EPA described 66 incidents in which environmental injuries from mining activities are detailed (EPA, 1995). Nordstrom and Alpers (1999) reported that millions, perhaps billions, of fish have been killed from mining activities in the U.S. during the past century.

2.5.3 Sediment Contamination

Improper disposal of contaminated water from mining, mineral processing and metallurgical operations releases contaminants into the environment (Herr and Gray, 1997). Precipitation of dissolved constituents may result in abundant colourful mineral coatings in stream channels. Consequently metals and metalloids may be contained in various sediment fractions (Lottermoser, 2010). Contaminated sediments may be transported further and deposited in downstream environments. Also change

in water chemistry may cause the contaminated sediment to become a source of metals and metalloids in the stream water (Butler, 2009).

2.5.4 Ground Water Contamination

Mining derived contaminants may enter waters of the unsaturated or saturated zone or become attenuated at the ground water – surface water interface (Gandy *et al.*, 2007). Contaminated water may migrate from waste source into aquifers, especially if the waste repository is uncapped, unlined and permeable at its base or if the lining of the waste source has been breached. Again, the flooding of underground workings may impact on the chemistry of mine waters and local ground water. Significant concentrations of sulphate, metals, metalloids and other contaminants have been found in ground water plumes migrating from mine workings and waste repositories and impoundments at metal sulphide mines (Lottermoser, 2010).

Conservative contaminants move at ground water velocities, however, reactive contaminants move more slowly than the ground water velocity and a series of different pH zones may be present in the contaminant plume. The occurrence of these zones is attributed to the successive weathering of different pH buffering phases in the aquifer. Such attenuation processes in the aquifer including pH changes can reduce the constituent concentrations to background levels in the pathway of the subsurface drainage. Neutralizing minerals such as carbonates may be contained in the aquifers and these minerals buffer acidic ground waters.

Depending on the neutralizing property of the aquifer through which the water moves, it could take many years before significant impact on ground and surface water quality is detected. In the worst case, when the neutralizing minerals are completely consumed then the acidic ground water plume will migrate down gradient and can eventually discharge to the surface (Lottermoser, 2010). Table 2.1 shows General

Wastewater Quality Guidelines for Discharges into Water Bodies or Water Courses adopted by EPA in 1992.

Table 2.1 General Wastewater Quality Guidelines for Discharges into Water Bodies or Water Courses

PARAMETER/DESCRIPTION	PERMISSIBLE LEVEL
pH	6 – 9
Temperature	<3°C above ambient
Colour (TCU)	100
Oil and Grease (mg/l)	5
Oil (mg/l)	No visible floating oil
BOD (mg/l)	50
COD (mg/l)	250
Total Dissolved Solids (mg/l)	1000
Total Suspended Solids (mg/l)	50
Turbidity (NTU)	75
Conductivity (µS/cm)	1500
Total Coliforms (MPN/100ml)	400
E. Coli (MPN/100ml)	10
Ammonia as N (mg/l)	1.0
Nitrate (mg/l)	50
Flouride (mg/l)	20
Phenol (mg/l)	1.0
Sulphide (mg/l)	1.5
Total phosphorus (mg/l)	2.0
Total Cyanide (mg/l)	1.0
Free Cyanide (mg/l)	0.2
Cyanide as Weak Acid Dissociable (mg/l)	0.6
Total Arsenic (mg/l)	0.5
Soluble Arsenic (mg/l)	0.1
Cadmium (mg/l)	<0.1
Chromium (+6) mg/l	0.1
Total chromium (mg/l)	0.5
Copper (mg/l)	2.5
Lead (mg/l)	0.1

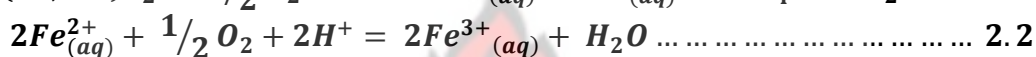
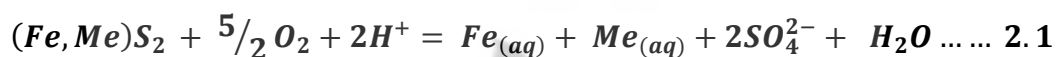
Source EPA, 1992

2.6 Heavy Metals and Mining

Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter (Barakat, 2010). Heavy metals occur as natural components of the

earth and some are required in varying amounts by living organisms; the threat however arises, when these metals are mobilized in excessive, detrimental volumes by high concentrations of sulphuric acid generated from the mass oxidation of sulphide-bearing minerals (pyrite) through weathering resulting in tolerance levels being exceeded (Akabzaa *et al.*, 2001).

According to Plumlee *et al.*, (1999), schematically, the Equations 1& 2 represent reactions that can take place to generate metal ions under typical sulphide surface weathering conditions:



There are three basic ways of metal exposure to human being from mining wastes:

- Firstly, through the dispersion of toxic dust from the surface of mine waste dumps or tailing impoundment located close to settlements;
- Secondly by mobilisation of metal ions into a water stream used as a source of water; and
- Thirdly with food through a food chain.

Toxic metals are easily transported and accumulated in organisms, increasing in levels of concentration up the food chain over time; and are able to mimic other metals that are crucial for enzymatic processes, resulting in metabolic interference in the cells as essential metals are displaced by toxic metals (Ewart, 2011).

A study by Armah *et al.*, (2010) revealed that most of the water bodies in Tarkwa (within which the study area, AngloGold Ashanti Iduaperiem mine forms part) have mean levels of arsenic, iron, mercury, zinc and lead which are above WHO and GEPA guideline values. Barakat (2010) lists Arsenic, Cadmium, Chromium, Copper, Nickel, Zinc, Lead as metals of relevance in the environmental context.

2.6.1 Arsenic (As)

Arsenic is mostly found in iron ores and in sulphide form, the most common ores being, among others, arsenopyrite (FeAsS) and realgar (AsS). (Young *et al.*, 2007). Arsenic in the environment occurs in soil and minerals and it may enter air, water and land through wind-blown dust and water runoff. The principal exposure pathway is inhalation, although ingestion and dermal exposure are also possible. It cannot be destroyed once it has entered the environment and can cause health effects to humans and animals. Groundwater may contain a higher concentration of arsenic that originated from geological materials. Data obtained by researchers on As levels in top soils of some mining areas in Ghana indicated values above 300 ppm in some cases (Tetteh *et al.*, 2004). Long term drinking water exposure causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea. The WHO provisional guideline of 10 ppb has been adopted as the drinking water standard (Mohan & Pittman, 2007).

2.6.2 Cadmium (Cd)

Cadmium can be found as greenocktite (cadmium sulphate CdS) and otavite (cadmium carbonate, CdCO_3) and is often associated with zinc, lead and copper in sulphide form (Young *et al.*, 2007). Food is the main source of cadmium intake (Nurlan, 1999). Cadmium enters the environment through disposal of wastewater from households or industries as well as weathering of rocks.

Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate (Baysal *et al.*, 2013). Cadmium is strongly adsorbed by organic matter in soils. Soils that are acidified enhance the cadmium

uptake by plants. When cadmium concentrations in soils are high they can also influence soil processes of microorganisms and pose as a threat to the whole soil ecosystem (ATSDR, 2001).

Cadmium derives its toxicological properties from chemical similarities to Zinc an essential micronutrient for plant, animals and human. Cadmium replaces Zinc in some enzymes, altering the stereostructure of the enzymes and impairing its catalytic activities thereby resulting in stomach pains, vomiting and diarrhoea. The adverse effects resulting from a long term exposure to cadmium include: kidney damage, chronic obstructive pulmonary disease (inhalation only), chronic renal failure, kidney stones, liver damage (rare), lung cancer, osteomalacia, possible hypertension, and proteinuria. Results of some animal studies show that animals given cadmium-contaminated food and water show high blood pressure, iron-poor blood, liver disease, nerve damage or brain damage. These effects have not been observed in humans. The U.S. Department of Health and Human Services determined that cadmium and certain suspected carcinogens (substances that cause cancer) (ATSDR, 1989).

A guideline value for cadmium is up to 0.003 mg/l drinking-water (WHO, 1996).

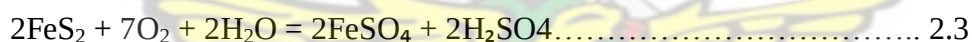
2.6.3 Lead (Pb)

Lead is in nature found in sulphide minerals (galena, PbS and anglesite, PbSO_4), oxide minerals (massicot, PbO) and carbonate minerals (cerrusite, PbCO_3) (Young *et al.*, 2007). In the environment, lead binds strongly to particles, such as soil, sediment and sewage sludge and its associated with relatively low mobility and bioavailability but can accumulate in biota feeding primarily on particles, e.g. mussels and worms (Bhatnagar *et al.*, 2012). The central nervous system, kidneys and the reproduction systems can be affected by inhalation and ingestion of lead (Nilsson & Randhem,

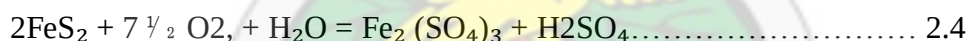
2008). A provisional tolerable daily intake is set to 3.5 µg of lead per kg of body weight for infants lead to a calculated guideline value of 0.01 mg/l (WHO 1996).

2.6.4. Iron

The iron content of environmental samples is as result of leachate form acid mine drainage and iron product from industrial waste. Iron may be found in solution, colloidal state (subjected to organic matter), inorganic or organic iron compounds, or suspended forms (OMOE, 2008). Iron is essential to humans as it a major constituent of haemoglobin. However, Iron has negative impacts such as: Iron gradually oxidises in the presence of oxygen and water, forming compounds giving it its distinct orange colour, these compounds gradually precipitate out to the floor of waterways, essentially smothering all forms of life (Kilic *et al.*, 2010). The reactions that occur include the oxidation of the sulphide to sulphate solubilises, forming ferrous ion,



which is subsequently oxidised to ferric ion:



Iron may cause conjunctivitis, choroiditis, and retinitis. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis (OMOE, 2008)

2.6.5. Manganese

Manganese is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Manganese occurs principally as pyrolusite (MnO₂) (Gouli, 2009).

Manganese intake can bring forth a variety of serious toxic responses upon prolonged exposure to elevated concentrations either orally or by inhalation. The uptake of manganese by humans mainly takes place through food, such as spinach, tea and

herbs. High concentrations of manganese lead to anorexia and asthenia which comes with characteristic manganese psychosis, with unaccountable laughter, euphoria, impulsiveness and insomnia followed by overpowering somnolence. It proceeds with headache, leg cramps and sexual excitement, followed by lethargy. Finally, speech disturbances, general clumsiness in movement and micrographia occur (Hoekman, 2008). Manganese concentrations above 0.1 mg/l impart an undesirable taste to drinking water. At about 0.02 mg/l, manganese will form coatings on piping that may later slough as a black precipitate (Asklund & Eldvall, 2005). Manganese is believed to have a neurotoxic effect; a provisional health-based guideline value of 0.5 mg/l is proposed to protect public health (WHO 1996).

2.6.6. Copper

Copper is a trace element that is essential for human health which can be found in many kinds of food (nuts, mushrooms, avocados, oysters etc), in drinking water and in air. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions (Baysal *et al.*, 2013).

2.6.7. Zinc

Zinc is mostly found as zinc compounds, in combination with oxides, sulphides and carbonates, of which the sulphide form is probably the most common one. Although zinc is not so toxic, it derives some toxicity from its close association with cadmium (Young *et al.*, 2007). Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of

taste and smell, slow wound healing and skin sores. Although humans can handle proportionally large concentrations of Zn, too much Zn can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can also damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis (Gundogdu *et al.*, 2009).

2.6.8. Chromium (Cr)

Chromium occurs in a number of oxidation states, but Cr (III) (trivalent chromium) and Cr (VI) (hexavalent chromium) are those of biological relevance with toxicological properties being the difference between the two. Chromium is in general not bioaccumulated and there is no increase in concentration of the metal in food chains. Cr (III) is an essential nutrient for man in amounts of 50 - 200 µg/day. Chromium is necessary for the metabolism of insulin. It is also essential for animals. In general, Cr (III) is considerably less toxic than Cr (VI). Cr (VI) has been demonstrated to have a number of adverse effects ranging from causing irritation to cancer. High concentrations of chromium can damage and/or accumulate in various fish tissues and in invertebrates such as snails and worms. The lethal chromium level for several aquatic and terrestrial invertebrates has been reported to be 0.05 mg/litre (Baysal *et al.*, 2013).

2.7 Methods of Removing Heavy Metals

Heavy metals exhibit high solubility in aquatic environments depending on the pH and can easily be absorbed by living organisms once they enter the food chain, with the tendency to accumulate causing serious health disorders once tolerable levels are exceeded (Babel & Kurniawan, 2004). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Many techniques can be employed for the treatment of wastewater laden with heavy metals including

conventional treatment processes such as chemical precipitation, ion exchange, electrochemical removal etc. These processes have significant disadvantages, which are, for instance, incomplete metal removal, high-energy requirements, production of toxic sludge, expensive equipment and monitoring systems, high reagent or energy requirements (Eccles, 1999).

Important parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economics parameter such as the capital investment and operational costs influence the selection of the most suitable treatment for metal-contaminated wastewater (Bhatnagar, 2012).

2.7.1 Ion-Exchange

An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials (Baysal *et al.*, 2013). Ion exchange is feasible when an exchanger has a high selectivity for the metal to be removed and the concentrations of competing ions are low. The metal of interest may then be recovered by incinerating or adsorbing the metal-saturated resin. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. Though it is relatively expensive as compared to adsorption, precipitation, it has the ability to achieve high removal levels. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to the pH of the solution. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view (Barakat, 2010).

2.7.2 Electrowinning

In Electrowinning or electro recovery, current obtained from electricity is passed through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions move to the negatively charged cathodes and are reduced to a metal and deposited on a cathode (Barakat, 2010). A noticeable disadvantage is corrosion could become a significant limiting factor, and electrodes would frequently have to be replaced (Kurniawan et al., 2006)

2.7.3 Coagulation

Coagulation process involves adding iron or aluminum salts, such as aluminum sulphate, ferric sulphate, ferric chloride or polymers, to the water. These chemicals are called coagulants, and have a positive charge. The positive charge of the coagulant neutralizes the negative charge of dissolved and suspended particles in the water. When this reaction occurs, the particles bind together or coagulate (this process is sometimes also called flocculation). The larger particles, or floc, are heavy and quickly settle to the bottom of the water supply. This settling process is called sedimentation (Barakat, 2010).

Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. The contaminants present in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form. Electro-coagulation system is effective in removing suspended solids, dissolved metals, tannins and dyes (Baysal et al, 2013)

EPA (1995) investigated the use of lime softening and alum coagulation (using ferric sulfate or alum) for the removal of such heavy metals as Pb, Cd, Cr, etc. While lime

softening achieved removals of greater than 98% in the pH range of 8.5-11.3 for cadmium, cadmium removals by ferric sulphate and alum coagulation were lower than that of lime softening and were shown to depend on pH. Cadmium removals increased with increasing pH. Ferric sulfate coagulation of a river water containing 0.3 mg/l Cd showed removal to increase from 20% at pH 7.2 to above 90% at pH $\geq$ 8. Alum coagulation results also increased with increasing pH; however above pH 8, removals may depend on the raw water turbidity. Both ferric sulphate and alum coagulation achieved greater than 97% removal of lead from a river water containing 0.15 mg/l Pb in the pH range of 6-10. Experiments on well waters under similar conditions had removal rates by ferric sulphate and alum coagulation of > 97% and 80-90%, respectively. When the lead concentration was increased to 10mg/l, ferric sulphate coagulation again achieved removals in excess of 95% whereas alum coagulation achieved only 80% removal. Using Cr waters, ferric sulphate achieved the best results, removing 35% at pH 6.5 on a river water containing 0.15 mg/l Cr (Peters & Ku, 1985).

2.7.4 Reverse Osmosis

Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated (Baysal *et al.*, 2013).

2.7.5 Cementation

Cementation is a type of precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe (0) to ferrous Fe(II) to replace a metal having a

lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner (Baysal *et al.*, 2013).

2.7.6 Precipitation

Chemical precipitation is the most widely used method for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Eq. (1) Wang *et al.*, (2004)



where M^{2+} and OH represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide. Adjustment of pH to the basic conditions (pH 9–11) is the major parameter that significantly improves heavy metal removal by chemical precipitation. Lime and limestone are the most commonly employed precipitant agents due to their availability and low-cost in most countries (Mirbagherp and Hosseini, 2004).

Precipitation is best explained in terms of solubility product (K_{sp}) and ionic quotient (Q_c) The solubility quotient (often called the ion product) has the same form as the solubility constant expression, but the concentrations of the substances are not necessarily equilibrium values. Rather, they are the concentrations at the start of the reaction. A comparison of K_{sp} with Q_c provides a prediction of the direction of the reaction.

If $Q_c < K_{sp}$, the reaction will go in the forward direction (the solution is unsaturated)

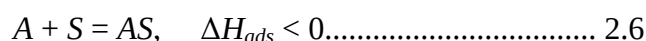
If $Q_c = K_{sp}$, the reaction mixture is at equilibrium.

If $Q_c > K_{sp}$, the reaction should go in the reverse direction (precipitation occurs) (Wang *et al.*, 2004)

Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive (Barakat,2010).

2.7.7 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption technologies are superior to other treatment processes (ion exchange, electrowinning) due to their low initial cost, flexibility, ease of design and ease of operation. In addition, they are not subjected to toxic contaminations and do not create harmful substances (Bhatnagar, 2012). Adsorption is a consequence of surface energy. When a molecule approaches a surface, it encounters a net attractive potential that is similar to the potential between two molecules and arises for the same reasons. However, a gas or solid molecule near a surface is attracted not by a single molecule but by several closely spaced surface atoms. The adsorption of a molecule on a solid surface is always an exothermic process. If we represent the gas or solid molecule, the adsorbate, by A and the adsorption site on the surface by S, the process of adsorption can be represented as a chemical reaction:



The surface of an atomic solid has about 10^{15} atoms/cm² of surface. If we assume that one molecule adsorbs on each atom of the solid surface, then there are 10^{15} sites on which molecules can adsorb. When one molecule is adsorbed on each site, the surface is said to be covered with a **monolayer**. (Renge *et al.*, 2012)

Adsorption is usually described through isotherms (Freundlich isotherm, Langmuir isotherm, BET isotherm), that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid) (Renge *et al.*, 2012). In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle.

Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent (Barakat, 2010). In spite of the abundant usage of activated carbon its application is sometimes restricted due to its higher cost. Attention has therefore, shifted towards the use of non-conventional naturally occurring materials, agricultural and industrial waste products as low-cost adsorbents for water remediation (Bhatnagar, 2012). Adsorption offers significant advantages like the low-cost, availability, profitability, ease of operation and efficiency (Demirbas, 2008).

2.8 Types of Adsorption

Two main types of adsorption exist namely:

2.8.1 Physisorption

Physical adsorption (physisorption) is relatively non-specific and is due to the operation of weak forces between molecules. In this process, the adsorbed molecule is not affixed to a particular site on the solid surface; it is free to move over the surface (Sawyer *et al.*, 1994). The physical interactions among molecules, based on electrostatic forces, include dipole-dipole interactions, dispersion interactions and hydrogen bonding. When there is a net separation of positive and negative charges within a molecule, it is said to have a dipole moment. Molecules such as H₂O and N₂

have permanent dipoles because of the configuration of atoms and electrons within them. Hydrogen bonding is a special case of dipole-dipole interaction and hydrogen atom in a molecule has a partial positive charge. Positively charged hydrogen atom attracts an atom on another molecule which has a partial negative charge. When two neutral molecules which have no permanent dipoles approach each other, a weak polarization is induced because of interactions between the molecules, known as the dispersion interaction (Montgomery, 1985).

2.8.2 Chemisorption

In this adsorption process an actual chemical bond, usually covalent, is formed between the molecule and surface atoms. A molecule undergoing chemisorption may lose its identity as the atoms are rearranged, forming new compounds at the demand of the unsatisfied valences of the surface atoms.

Chemical adsorption, (chemisorption) is also based on electrostatic forces, but much stronger forces act as a major role on this process (Sawyer *et al.*, 1994). In chemisorption, the attraction between adsorbent and adsorbate is a covalent or electrostatic chemical bond between atoms, with shorter bond length and higher bond energy (Montgomery, 1985).

The enthalpy of chemisorption is very much greater than that for physisorption, and typical values are in the region of 200 kJ/mol and about 20 kJ/mol for physisorption (Atkins, 1994).

2.9 Adsorption models

Isotherm adsorption models have been used in waste stream treatment to predict the 'When a mass of adsorbent and waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. Adsorption data for wide range of adsorbate

concentrations are most conveniently described by adsorption isotherms, such as the Langmuir or Freundlich isotherms.

2.9.1 Langmuir isotherms

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism.

It is based on four hypotheses:

- (i) The surface of the adsorbent is uniform, that is, all the adsorption sites are equal;
- (ii) Adsorbed molecules do not interact;
- (iii) All adsorption occurs through the same mechanism; and
- (iv) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent (Langmuir, 1916).

The general Langmuir model (Demirbas, 2008) is defined below:

$$\frac{X}{M} = \frac{K_L C_e}{1 + a_L C_e} \dots\dots\dots 2.7$$

which can be linearized to:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b \cdot q_{max}} \cdot \frac{1}{c_e} \dots\dots\dots 2.8$$

where K_L and a_L are the isotherm constants. K_L and a_L values can be determined using linear regression

2.9.2 Freundlich Isotherms

The general Freundlich equation (Demirbas, 2008) is defined as:

$$\frac{X}{M} = K_F (C_e)^{1/n} \dots\dots\dots 2.9$$

Which can be linearized to:

$$\ln\left(\frac{X}{M}\right) = \ln K_F + \frac{1}{n} \ln C_e \dots\dots\dots 2.10$$

where K_F and n are adsorption capacity and affinity, respectively.

2.10 Factors Affecting Adsorption

Adsorption is a process which involves reactions between the adsorbate and adsorbent thus varying certain conditions may improve or exacerbate the rate and amount of adsorption. These conditions include pH levels, initial concentration of metal solution, concentration of adsorbent, temperature, agitation speed, and contact time. All of these conditions produce different results once changed; however, the magnitude and significance of change alters between the different conditions as each has a different effect on the adsorption process. (Kaakani, 2012).

2.10.1 pH

pH affects adsorption reactions through H^+ and OH^- ions that are emitted into the solution. A more acidic pH releases more H^+ ions that may react with the adsorbent or adsorbate, hence affecting results. Likewise, an alkaline pH solution releases OH^- which may also react with the adsorbent or adsorbate. Unfortunately, a universal pH value cannot be determined and set due to the different types of adsorbents used and their chemical constitutions. Hence, tests need to be performed to determine the most efficient value of pH (Kaakani, 2012).

2.10.2 Adsorbent dosage

An increase in adsorbent dosage can result in increased adsorption of metals due to increased adsorption surface area. One way to reduce the quantity of adsorbent is to increase the surface area. This can be achieved by using very small diameters of the adsorbent. Larger surface areas are a lot more successful in adsorption, and hence, the same adsorbent may require smaller dosages once ground compared to its larger counterpart (Kaakani, 2012).

2.10.3 Contact time

The greater the contact time, the greater the possibility that equilibrium has been reached, and hence, adsorption has reached its maximum. Not allowing for enough contact time will not effectively complete the adsorption process (Kaakani, 2012).

2.10.4 Agitation Speed

Adsorption is highest at a certain speed that needs to be determined through experimentation. Agitation either speeds up or slows down adsorption. However, a higher agitation speed does not necessarily mean a higher rate of adsorption (Kaakani, 2012).

2.10.5 Initial Metal Concentration

Usually the lower the concentration of the metal, the better the adsorption, as there is less adsorbate for the adsorbent to remove. However, some adsorbents perform extremely well in high initial concentrations of adsorbate, and hence, have a higher adsorption capacity. These adsorbents are thus favourable due to their capacity (Kaakani, 2012).

2.10.6 Temperature

According to Le-chatlier's Principle, the magnitude of adsorption should increase with decrease in temperature. In fact, it is found to be so in case of physical adsorption because Vanderwaal's forces are strong at low temperatures. However, the chemisorption first increases with rise in temperature and then starts decreasing. The initial increase shows that like chemical reactions, chemisorption also needs activation energy.

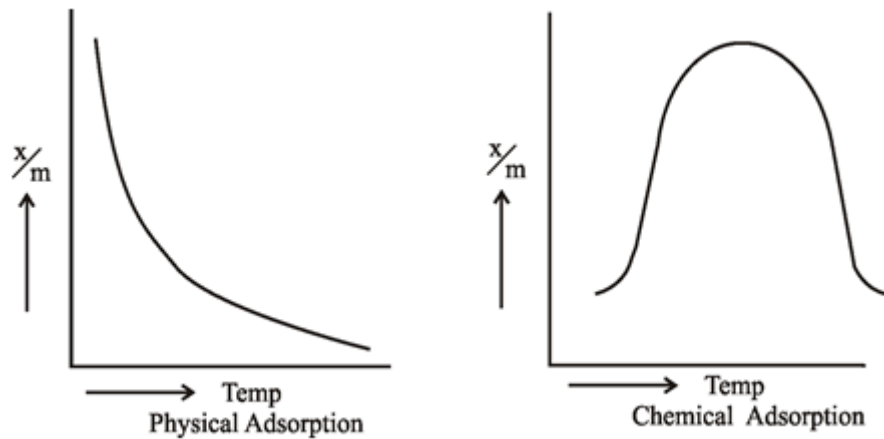


Fig 2.1 Plot of Adsorption against Temperature

A plot of amount adsorbed (x/m) against temperature drawn at constant equilibrium pressure as shown in Fig. 2.1 produces a curve showing regular decrease in adsorption with temperature rise for physical adsorption and increased adsorption and gradual decrease for chemisorption. Such curves are known as Adsorption Isobars (Kelly, 1998).

2.11 Adsorption Using Low Cost Adsorbents

Major disadvantage with conventional treatment technologies is the production of toxic chemical sludge whose disposal/treatment is not eco-friendly. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals. In general, an adsorbent can be assumed as “low-cost” if it requires a little bit processing, is abundant in nature, or is a by-product or a waste from an industry thus some natural material or certain industrial waste qualify as resources for low cost adsorbents. According to Mohan and Pittman (2007) generally these materials are locally and easily available in large quantities and are therefore inexpensive and have little economic value. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. In light of the above, natural, biological, organic, zeolites, industrial by products, agricultural wastes, biomass, and polymeric materials (Kurniawan *et al.*,

2005) have emerged as an economic and eco-friendly option. Some of the reported low-cost sorbents are bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool and modified cotton (Renge *et al.*, 2012). The Table 2.2 shows adsorption of various heavy metals using laterite. Table 2.3 shows Ghana EPA and WHO Permissible levels for heavy metals concentrations, pH, Turbidity, electrical conductivity and total dissolved solids in aquatic environments.



Table 2.2 Experiments on Adsorption using laterite

Heavy Metal	Adsorbent	Type of Test	Experimental Variable	Experimental Conditions	Results	Reference
Arsenic (As)	Laterite concretions	Batch test	pH, temperature, ionic strength	25°C, 35°C, 45°C and 60°C in a temperature controlled bath. 0.1 to 2.0mg/L As (III) and As (V) concentrations 0.25g of ground Prestea LC	Sorption capacity for both arsenite and arsenate increases with temperature. Arsenic (III) sorption on both Prestea and Awaso LC exhibits decreasing sorption with increasing ionic strength. Arsenic (V) sorption on Prestea and Awaso LC increases with increasing solution ionic strength	Frederick Kenneh Partey
Arsenic (As)	Heat treated laterite	Batch and column test	Laterite dosage, agitation speeds and initial Arsenic concentrations.	355-710 µm laterite particle size. initial arsenic concentrations- 0.3163, 0.5654, 0.8484, 1.0086 mg L ⁻¹) laterite dose -5 g L ⁻¹) agitation speed-400 (±5) rpm. 298 K, 308 K, 318 K	The removal rate was dependent on the initial arsenic concentrations and adsorption equilibrium data indicates favorable adsorption of arsenic onto laterite.	Rahman et al
Pb, Zn, Ni, and Mn	Laterite	Batch tests	pH	0-100 ppm of Pb, Zn, Ni, and Mn (single or multiple component solutions) 50 ml to 1-g of laterite sample.	sorption behavior of Pb, Mn, Zn, and Ni in laterite soil is significantly affected by the coexistence of other metals and the environmental factors including soil moisture	A. Putthividhya

Phosphorus	Laterite	Batch tests	contact time, pH , optimum dosage	particle size 2 mm and 4 mm, influent flowrate (Q) 10 ml/minute, and bed depth (H) 25 cm were studied. Break through curve of 4 mm particle size is slightly higher than 2 mm particle size.	contents Optimum dose was found to be 15 mg/l. Removal efficiency of optimum contact time was about 120 minute. Adsorption of phosphorus increases with decrease in pH of solution. Langmuir isotherm is fit for adsorption of phosphorus. Percent removal of phosphorus reaches up to 89 %.	Patil Mansing R.
Zinc	laterite		effects of pH, dosage of the lateritic soil, contact time	Contact time of 10,30,60,120,180 mins, Adsorbent dosage of 5,10,15,20,25 mg/l Zinc concentration of 50,100,150,200,250 ppm pH of 2,3,4,5,6	Maximum percentage removal of 88% obtained at contact time of 10 mins, 250 ppm Zn concentration, pH of 6	Nabilah et al

Table 2.3: Ghana EPA and WHO Permissible levels for heavy metals concentrations, pH, Turbidity, electrical conductivity and total dissolved solids in aquatic environments

Parameter(mg/l)	GEPA	WHO
Manganese	-	0.4
Lead	0.1	0.01
Copper	-	2.0
Arsenic	1.0	0.01
Zinc	10	3.0
Mercury	0.2	0.01
Iron	-	0.3
Cadmium	-	0.003
pH	6.5-8.5	6.5-8.5
Turbidity	(NTU)	5
Electrical Conductivity(μ S/cm)	-	-
Colour	15	15
Total dissolved solids (mg/l)	1000	1000

2.12 Laterite

Laterite soil is a red-colored clay-rich soil found in the tropics and subtropics. It needs the high temperatures and the abundant rainfalls of the tropics to form. The water washes out the bases and the silic acid, and enriches it with aluminium, silicates, aluminium hydrosilicates, iron-oxide and iron hydroxides. Especially the iron leads to the typical red color (Maji *et al.*, 2007)

2.12.1 Classification and characteristics of laterite

Laterite may be classified as follows:

- Residual laterite formed in place under free drainage conditions. In these conditions of extreme oxidation the iron alone remains at the surface and the aluminum moves downward;

- ii. Laterite formed by accumulation of iron oxide. Such laterite can also be formed by oblique leaching. The areas from which the iron has been leached are enriched with gibbsite;
- iii. Transported laterite. This is the remolded product of old indurate layers that have been broken up;
- iv. Ground-water laterite, which is developed over a permanent water table near the surface; and
- v. Fossil laterite, which may be secondary formations, in particular, from the addition of silica or carbonate.

Table 2.4 Summary of Aluminous and Ferruginous laterite

Characteristics	Aluminous laterite	Ferruginous laterite
Induration	Slight to moderate	Moderate to very heavy
Colour	Whitish-rose to red	Rust to red brown
Density	Low	High
Structure	Basically scoriaceous	Extremely varied: pistolic, alveolar, lamellar etc.
Chemical composition	Strongly hydrated, $\geq 20\%$ Little insoluble material	Slightly hydrated (10%) Plenty insoluble material
Mineralogical constituents	Principally gibbsite, goethite, little kaolinite, little or no quartz	Principally variable amounts of gibbsite, kaolinite, goethite, quartz are present. Gibbsite is often absent.

(Maignen, 1958)

2.13 Study Area

2.13.1 Location

The research was conducted within the AngloGold Iduaperiem Mine, an open pit gold mining operation located 10 km southwest of the town of Tarkwa, the capital of the Wassa West District in the Western Region of Ghana.

2.13.2 Mining Activity

AngloGold Iduaperiem's mining concession covers an area of 100 km² of which 15 km² (14%) is occupied by current mining and mineral processing operations and related infrastructure. There are four active waste rock dump sites, two of which were selected for this research.

2.13.3 Geology

Geologically, Iduaperiem is situated in the Birimian Shield, a regional metallogenic province formed of Palaeoproterozoic age volcanic and metasedimentary rocks hosting numerous gold districts (Konongo, Tarkwa, Obuasi, Prestea and Axim).

2.13.4 Climate

Iduaperiem falls within the southwestern equatorial zone. Annual average rainfall is 1,718 mm (Schlumberger, 2012). The area is very humid and warm with temperatures between 26-30 °C. Mean annual pan evaporation is 1,081mm (Dickson & Benneh, 1980).

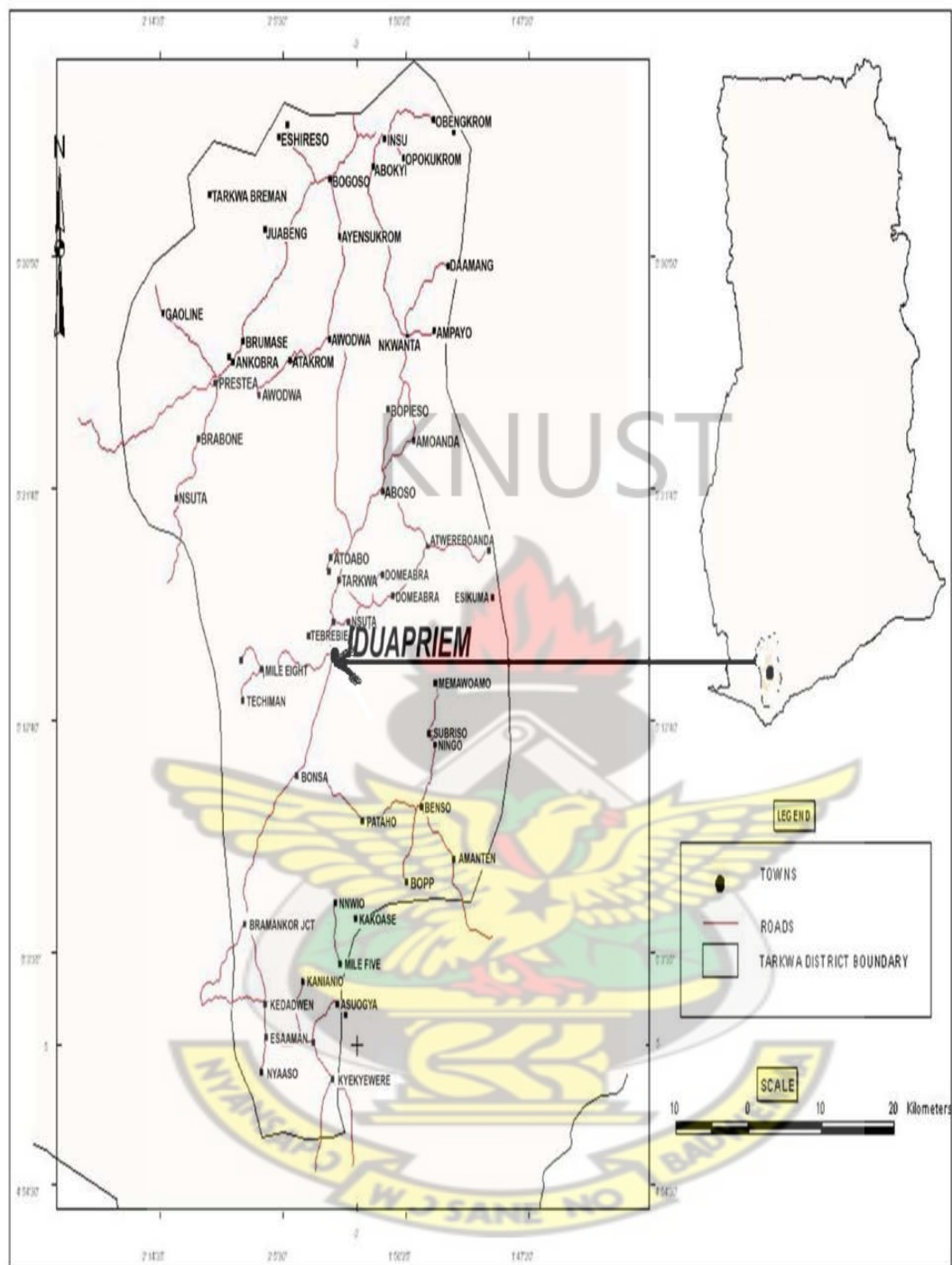


Fig. 3.1: Map of Tarkwa Showing Location of AngloGold Iduapriem Mine
Source: (RMSC, 2010)

CHAPTER THREE

3.0 MATERIALS AND METHODS

The research was conducted in two parts namely:

- i. Field work
- ii. Laboratory work

3.1 Field Work

3.1.1 Sample Collection

Waste rocks labelled A and B were collected from waste rock dumps four and ten respectively was done using the non-grid composite sampling method as employed by Smith et al (2000) and Hageman (2007). In previous studies by Addo (2001), waste rock dumps four were established to have reactive rocks forming the basis for their selection. See appendix A for detailed procedure.

Laterite labelled Sample C was obtained from Balungo in the Northern Region of Ghana. Fig 3.1 shows a map Of AngloGold Iduaperiem Mine with Waste Rock Sampling locations. See Appendix B for details

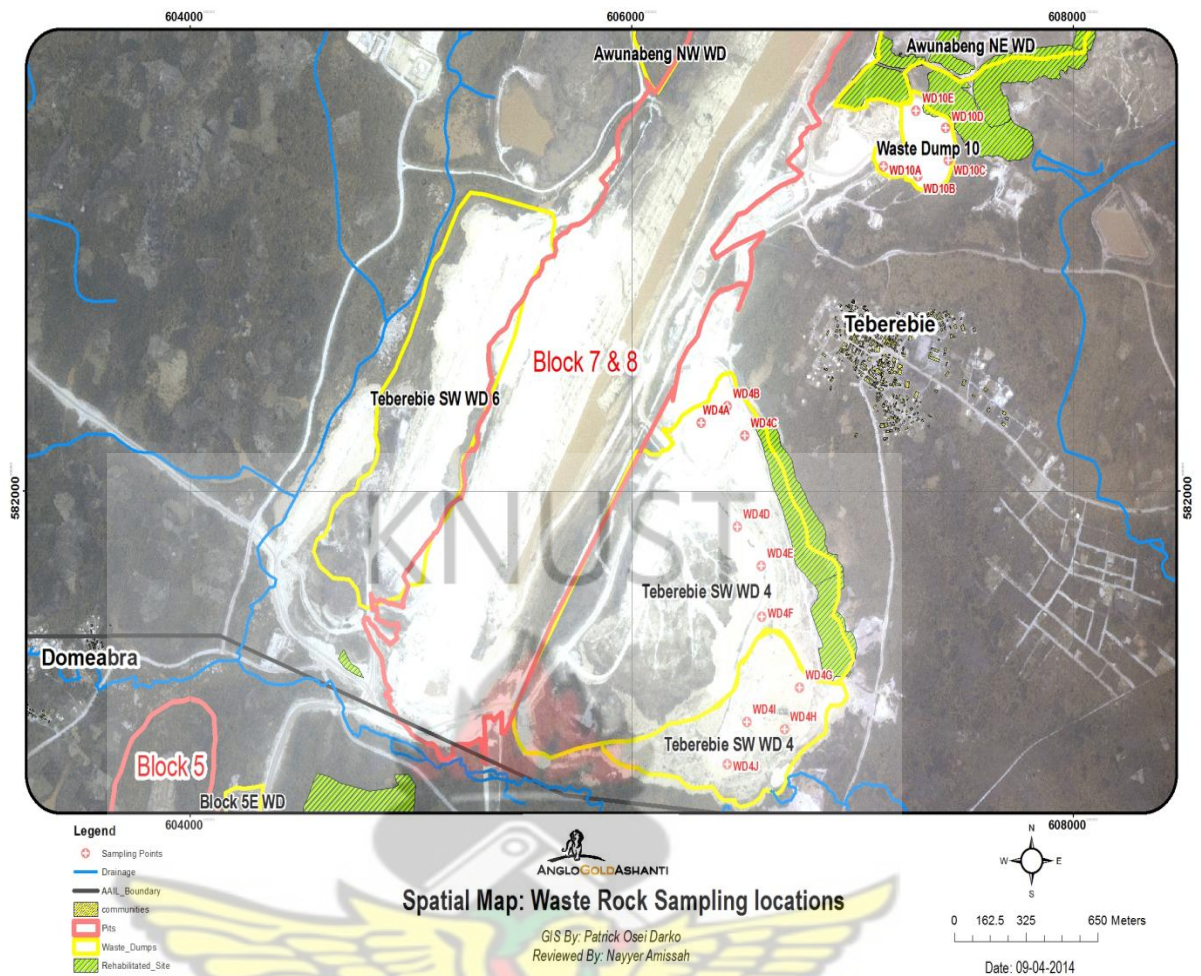


Fig 3.1 Map Of Iduaperiem AngloGold Mine Showing Waste Rock Sampling Locations

3.2 Laboratory Work

Laboratory analysis performed included:

X-Ray Diffractometry (XRD) Test

X-Ray Fluorescence (XRF) Test

Leach Test

pH

Batch Tests

Column Tests

3.2.1 Sample preparation

Waste rock and laterite samples

Waste rock and laterite samples were air dried and pulverized to obtain 600 μm , < 2 mm for waste rock samples and < 90 μm and 120 μm for laterite.

100 g each of the 3 sieved samples were placed in re-sealable bags and sent for elemental and compound analysis (XRF) and mineralogical analysis (XRD).

Standard solution

Standard solutions of 2, 4, 6, 8, 10 mg/l were prepared by dilution of 1000 g/l stock solution of cadmium. Five 1L bottom flasks were washed and rinsed with distilled water. With the help of a pipette the flasks were filled with 1ml of the stock solution and diluted to the 1L mark using distilled water thus obtaining a cadmium concentration of 1000 mg/l. Further dilutions were done to obtain the desired concentrations needed for each experimental run.

3.2.2 X-Ray Powder Diffraction (XRD) Test

Ten grams each of sample A, B and C were placed in a ceramic bowl and ground into powder with the aid of a pestle. The homogenized samples were placed in the XRD machine (model type- SIEMENS D 5000) where X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. When the geometry of the

incident X-rays impinging the sample satisfies the Bragg Equation ($n\lambda=2d \sin \theta$), constructive interference occurs and a peak in intensity occurs with each specific wavelength being characteristic of target metals (Clark and Dutrow, 2013; Moore and Reynolds, 1997).

3.2.3 XRF Test

4 grams of waste rock material was weighed onto the electric weighing balance and mixed with 0.9 g of powdered wax (licowax) which served as a binder and a dilution factor. The weighed sample was put in a decontaminated sample cap and placed in a homogenizer with the time and frequency set at 3 mins and 15 hertz respectively. The mixed sample was then molded into a circular pellet using a caster and a hydraulic press. The prepared samples (pellets) were put in a disc and then placed in the disc plate inside the XRF machine. Each sample was analyzed separately using the geological method due to the nature of the samples.

3.2.4 Properties of lateritic soil

pH

pH was determined by a 1:2.5 suspension of soil: water ratio using a pH meter (pH 211 microprocessor).

3.2.5 Leach Test

Leach test was performed according to the protocol of U.S Geological Survey Field Leach Test developed by Hageman (2007). See Appendix D detailed procedure.

3.2.6 Batch Tests

All experimental runs were undertaken using USEPA batch type procedures for estimating soil adsorption of chemicals and OECD guideline for the testing of

chemicals in duplicate with a constant solid to liquid ratio of 1:10 as recommended by USEPA (USEPA, 1987).

Batch tests were conducted in three different stages namely:

- Kinetic study
- Increasing initial concentration of Cd study
- Increasing adsorbent dosage study
- thermodynamic study

See Appendix E for detailed procedure for batch tests, equations used to calculate isotherm and thermodynamic parameters.

3.2.7 Column Tests

Description of columns

Column tests were performed using micro columns having a diameter and depth of 4.5 cm and 20 cm respectively. Cotton wool was placed at the base of the column to prevent loss of adsorbent/wastewater. Tubes were then inserted into the bottom of the five gallon container containing the wastewater and passed through the opening of the cover of the column. The tank containing the untreated wastewater (waste rock + distilled water) was placed at a higher elevation so that the wastewater could be introduced into the column by gravitational flow.

Procedure for column test

200 g of the adsorbent (laterite) was weighed and placed in the column. To prevent channeling distilled water was first passed through the column. Untreated wastewater (waste rock leachate) having an initial cadmium concentration of 0.0505 mg/l and its pH adjusted to 9 was fed upward into the column. The pH was measured and recorded at both the influent and effluent and adjusted when necessary. The effluent water is

collected at different time intervals using 14 ml graduated polypropylene tubes and the effluent samples were analysed for residual Cd concentrations. From the data obtained. Blanks tests were run alongside the experimental run.

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CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Mineralogy

Result of the XRD for laterite soil is shown in Figure 4.1.

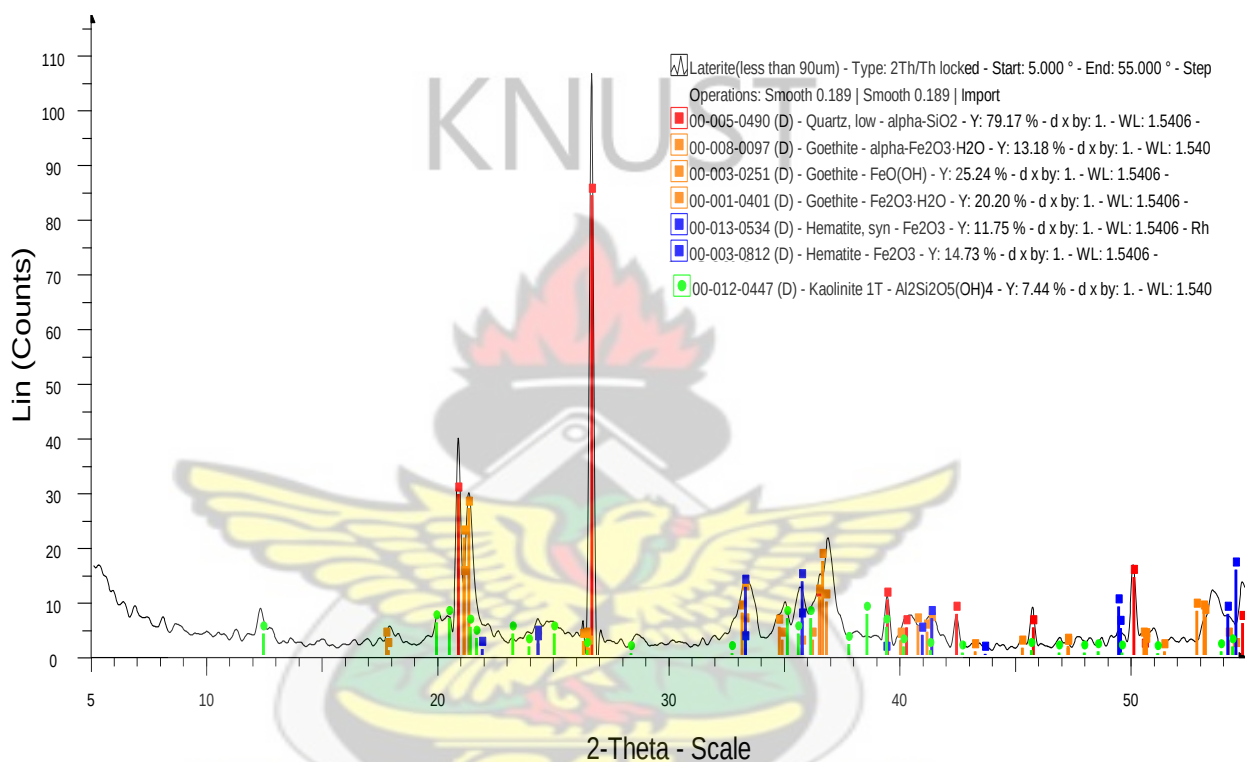


Fig 4.1 Diffractogram of Laterite soil

The dominant compound phases identified for laterite included Quartz, Goethite, Kaolinite and Hematite. Quartz with a value of 79.17% represented the highest compound phase.

Results of the XRD for waste rocks are shown in Figure 4.2 and 4.3

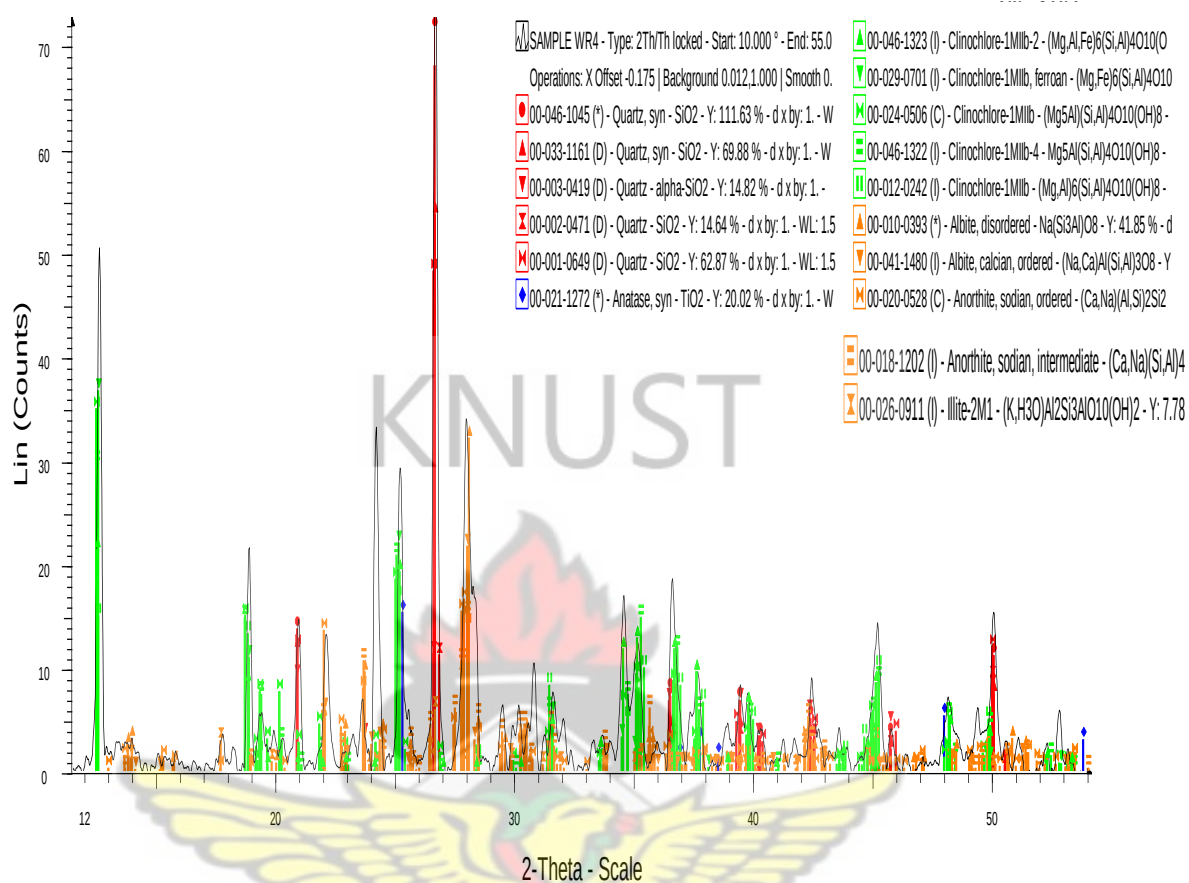


Fig 4.2 Diffractogram of Waste Rock from Dump Four

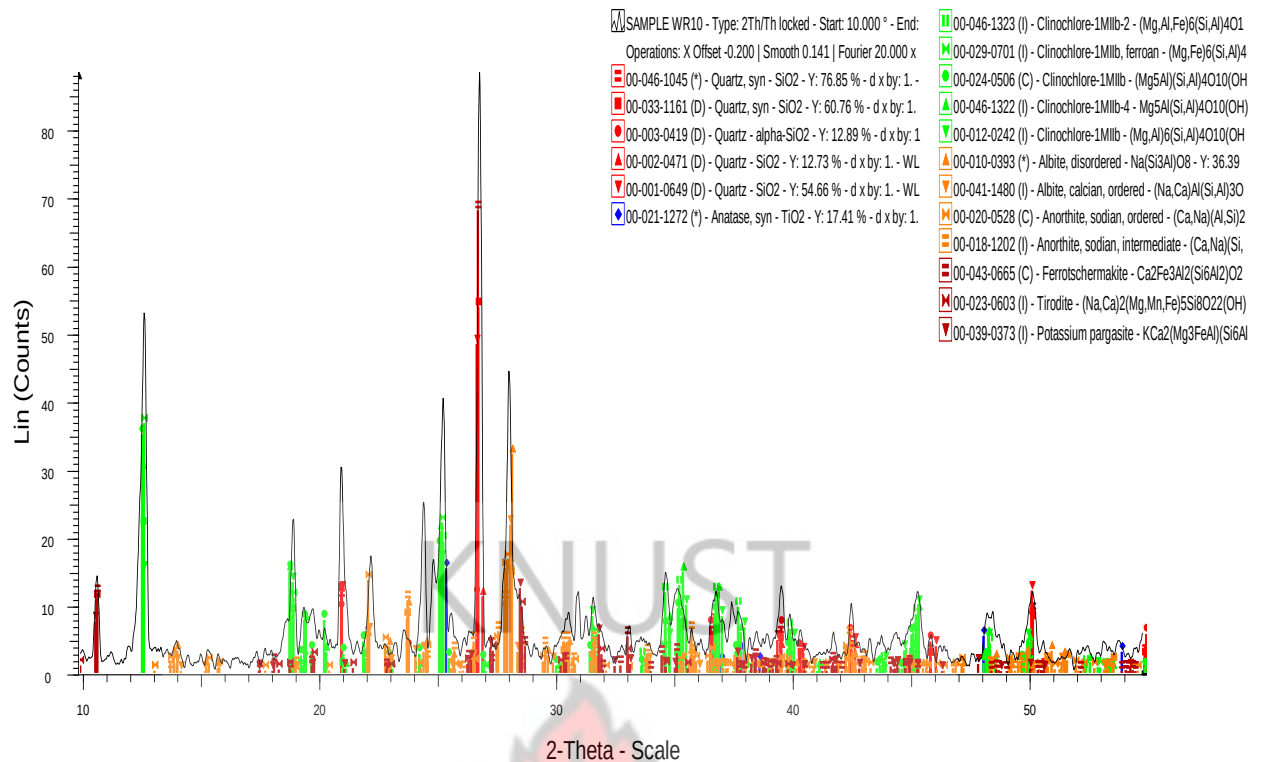


Fig 4.3 Diffractogram of Waste Rock from Dump Ten

The dominant compound phases identified for sample A and B included Quartz, Anatase, Anorthite, Clinocllore, Albite. Quartz with a value of 79.17% represented the highest compound phase. The absence of acid forming sulphidic ores is noticed indicating that the generation of Acid Mine Drainage (AMD) is unlikely.

4.2 Physical properties of Laterite

Table 4.1 summarizes the results of the test conducted to determine physical properties of laterite.

Table 4.1 Properties of Laterite Soil

Characteristic	Value
pH _{ZPC}	3.5-4.0
pH	6.75

Attributing to the fact that adsorption of cation is favored at pH > pH_{ZPC}, while the adsorption of anion is favored at pH < pH_{ZPC} (Das and Mondal, 2011), laterite will have a negatively charged surface above a pH of 4 thus becoming favorable to adsorb positive cadmium ions.

Laterite soil is slightly acidic (pH 6.75).

4.3 Elements in Waste Rocks

XRF results of the two waste rock samples as given by the Geological Survey Department laboratory are shown on Table 4.2

Table 4.2 XRF Results for Sample A and B

Element	Sample A %	Sample B %	Key	location
Na ₂ O	1.64	2.33	Sample A	Waste rock
MgO	18.35	16.18		from
Al ₂ O ₃	19.15	20.48		dump ten
SiO ₂	50.14	49.89	Sample B	Waste rock
P ₂ O ₅	0.09	0.13		from
SO ₃	<0.0019	0.02		dump four
K ₂ O	<0.012	0.75		
CaO	3.20	5.68		
TiO ₂	0.343	0.350		
MnO	0.11	0.15		
Fe ₂ O ₃	10.53	9.39		
Total	103.54	105.34		

Generally most elements recorded a low value for sample A as compared to sample B.

The highest recorded major element is SiO₂ showing percentage values of 50.14% and 48.89% for samples A and B respectively. The percentage of Sulfur trioxide

(SO₃) in the samples is <0.0019% and 0.02% for samples A and B respectively. Based on the XRF results for the major oxides, percentage concentrations for Sulfur trioxide (SO₃) is lowest in Sample A and this can be attributed to its long exposure to the environment and therefore undergoing the greatest oxidation as compared to Samples B. Sample B being the least exposed to the environment recorded the highest SO₃ percentage concentration.

4.4 Leach Test

Results of Pre-filtration pH and Specific Conductance (SC) of the leachate are given in Table 4.3. Results of heavy metal analysis are presented in Fig.4.4 (See Appendix F for details).

Table 4.3: Pre-filtration pH, specific conductance (SC) and Alkalinity

Sample	pH	SC/ μ m	Alkalinity(CaCO ₃ mg/l)
A	8.6	203.9	400
B	9.31	97	550

The pH of the leachates were basic with Sample B from waste dump four showing the highest pH and alkalinity of 9.31 and 550 CaCO₃mg/l. This trend can be attributed to the presence of mostly basic oxide such as Na₂O and MgO in the waste rock samples as indicated in the XRF analysis. The source of the basic nature of the samples can be inferred from the XRD results. Sample A contains more water soluble constituents than sample B, consequently it can be inferred that Sample A is more weathered than Sample B.

The lowest specific conductance value obtained was for leachate from sample B. Higher concentration of electrically charged metal ions in the leachate leads to higher

specific conductance. This explains why leachate from sample B recorded the least specific conductance. This can be attributed to the lower concentration of metal ions in the waste rock samples from dump four. This analysis is based on the results obtained from the metal analysis using the Flame Atomic Adsorption Spectrometer (FAAS).

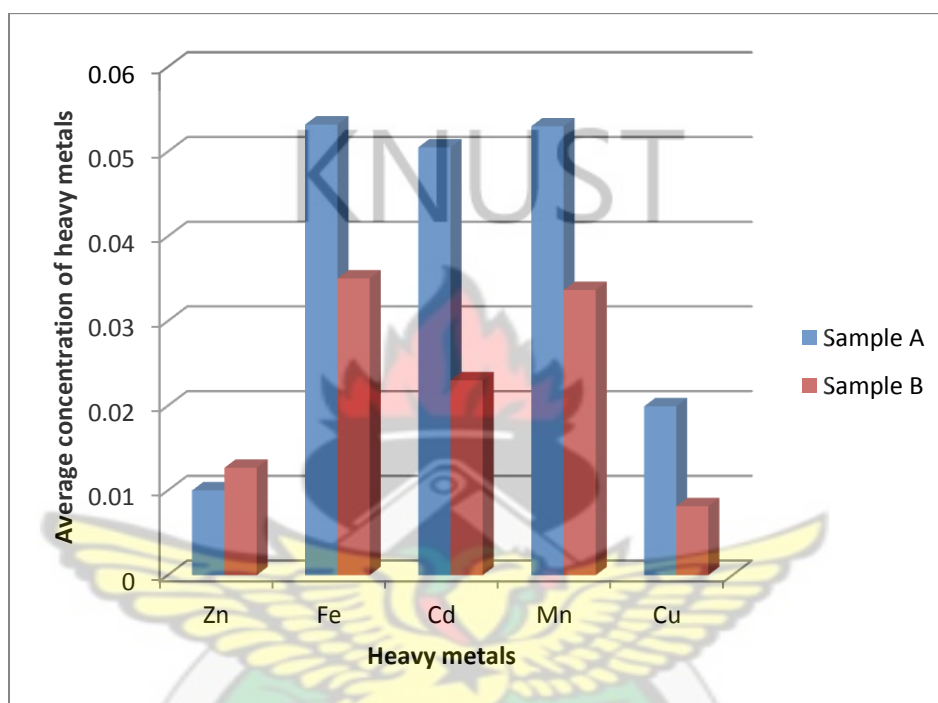


Fig.4.4 Bar Chart For Metal Analysis of Post Filtration Leachate For Sample A and B

The concentration of heavy metals in post-filtration leachate of all 2 samples analyzed using FAAS showed relatively lower levels of Zinc, Manganese, Copper and Iron as shown in Appendix F and Figure 4.4. The lowest concentration of all the heavy metals was recorded in Sample B which represents waste rock from dump four. This could be as a result of its short exposure to the environment as compared to waste rock from dump ten and as such being the least oxidized through chemical weathering. The levels of heavy metals found in the filtrates were below the EPA acceptable standards for potable water in all 2 filtrate samples. Levels of heavy metals were below the WHO guideline for potable water except for cadmium which recorded a value of

0.0505 mg/l slightly above the WHO guideline value (0.03 mg/l) for potable water. Even though the levels of heavy metals recorded in the filtrate were below the WHO guidelines and EPA acceptable standards for potable water, one must take into consideration the ability of these heavy metals like cadmium and lead to accumulate in living tissue of organisms once exposed to sources containing them. This can cause several health problems (kidney stones, lung cancer, osteomalacia, possible hypertension, proteinuria etc) (ATSDR, 1989).

4.5 Batch Test Results

4.5.1 Kinetic Test Results

Results of the uptake of cadmium (II) ion as a function of contact time are presented in Figures 4.5 and 4.6. See Appendix G & H for details.

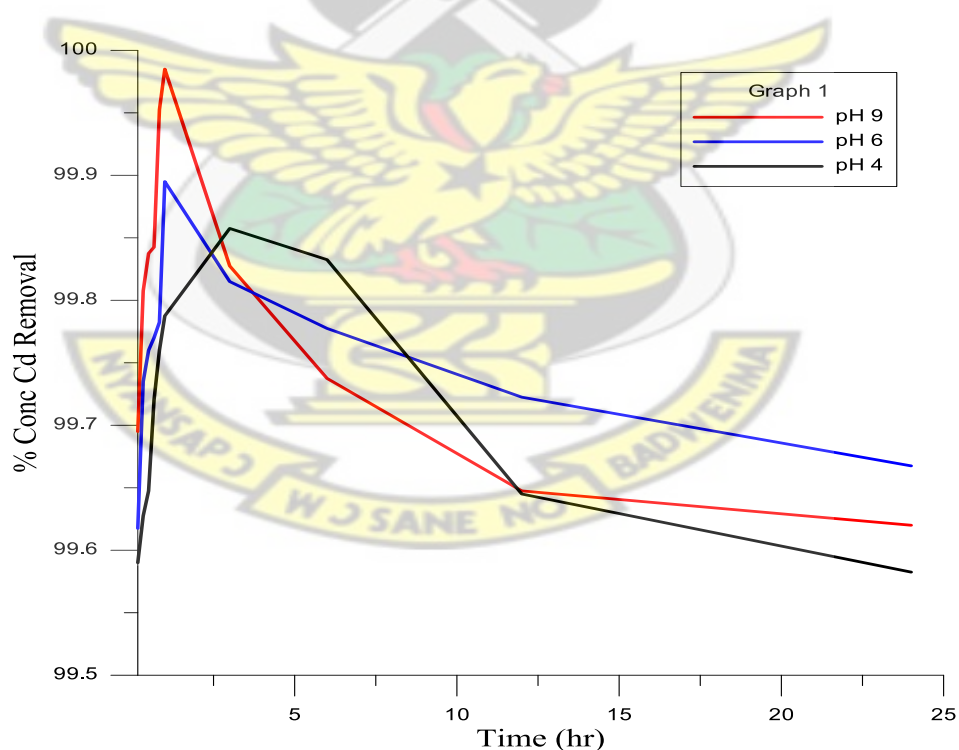


Fig 4.5 Kinetic Tests for 2mg/l Cd Stock Solution, 2g Adsorbent Dosage

Effect of time

The removal rate of cadmium was initially rapid in the first ten minutes leading to a 99.70%, 99.59%, 99.62% removal for pH 9, 6 and 4 respectively. Adsorption peaked after an hour at a maximum removal of 99.99% and 99.90% for pH 9 and 6. For pH 4 maximum removal of 99.65% was obtained after 3 hours. Cadmium desorbed into solution after equilibrium was attained as shown in Figure 4.5 implying that the rate of desorption was higher than the rate of adsorption after equilibrium.

The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurred controlled by the diffusion process from the bulk to the surface. In the later stage leading to equilibrium, the sorption is likely an attachment-controlled process due to less available sorption sites. Similar findings for adsorption of phosphorus and zinc onto laterite have been reported by other investigators (Patil, 2013).

Effect of pH

Sorption rate is lower in acidic medium. Attributing to the fact that, at low pH, there is electrostatic repulsion resulting in lower rate of adsorption due to high positive charge density (Bhattacharya et al, 2006). With increasing pH, electrostatic repulsions decrease due to reduction of positive charge density on sorption sites of adsorbent resulting in increase in rate of adsorption. pH of 9 is used in all further work as optimal adsorption is obtained at pH 9.0 and it falls within the EPA's pH guideline range for effluent discharge.

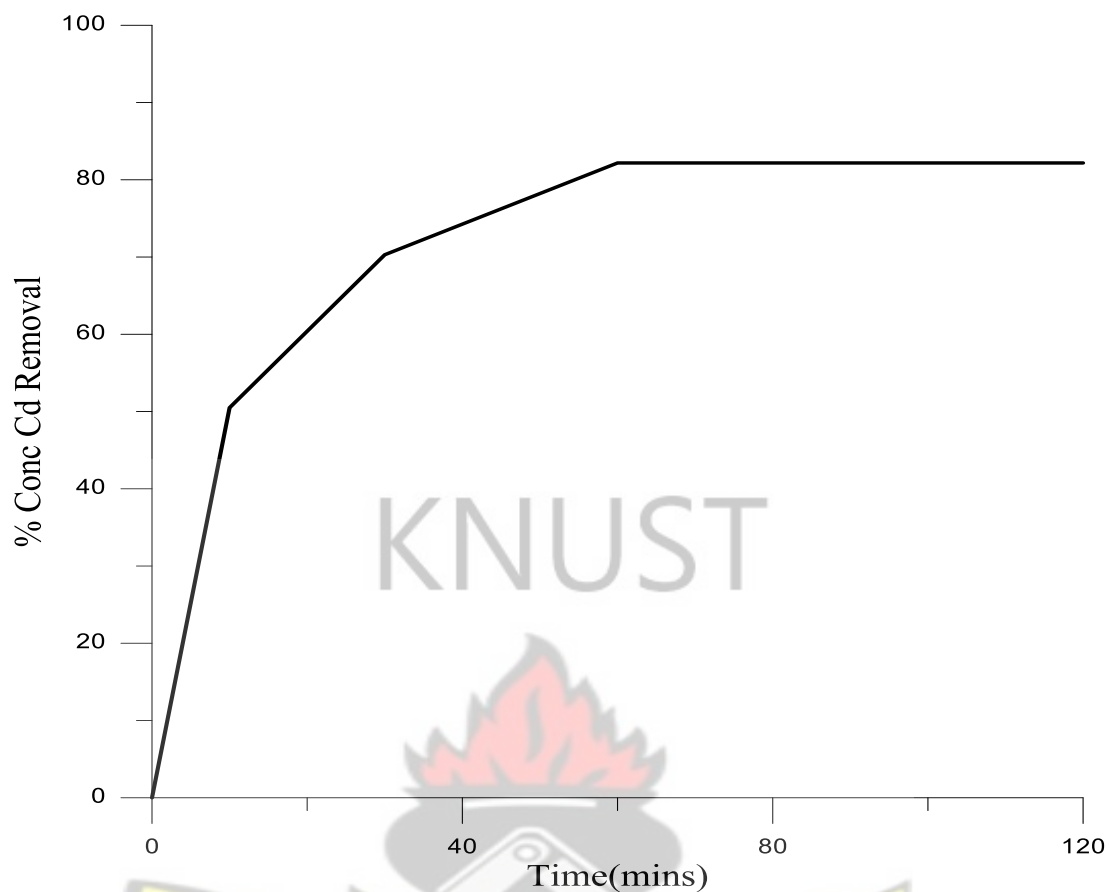


Fig 4.6 Kinetic Test for Leachate (Experimental Conditions- 0.505mg/L Cd Solution, 2g Adsorbent Dosage)

Maximum percentage removal of 82.1782 was obtained after an hour from kinetic leach test as shown in figure 4.4 above.

4.6 Adsorption Isotherms

Equations 2.7, 2.9, 2.10 shown in Appendix E were employed to generate the sorption data shown in Appendix I and J and then fitted to Langmuir, and Freundlich isotherms as shown in Figures 4.7-4.10.

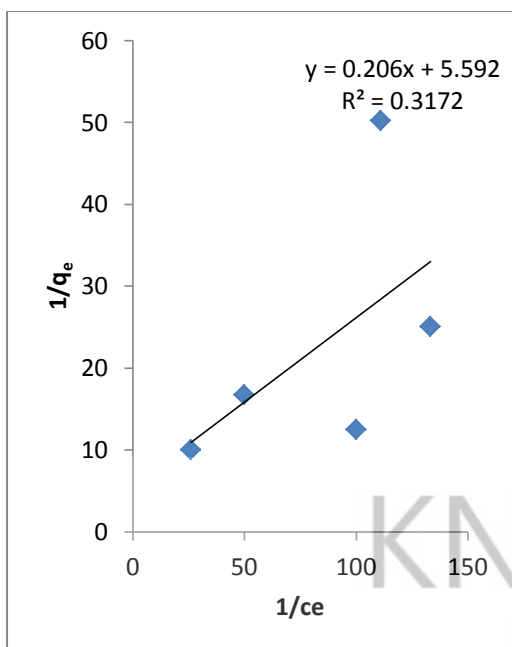


Fig 4.7 Langmuir Plot for Increasing Cd Concentration

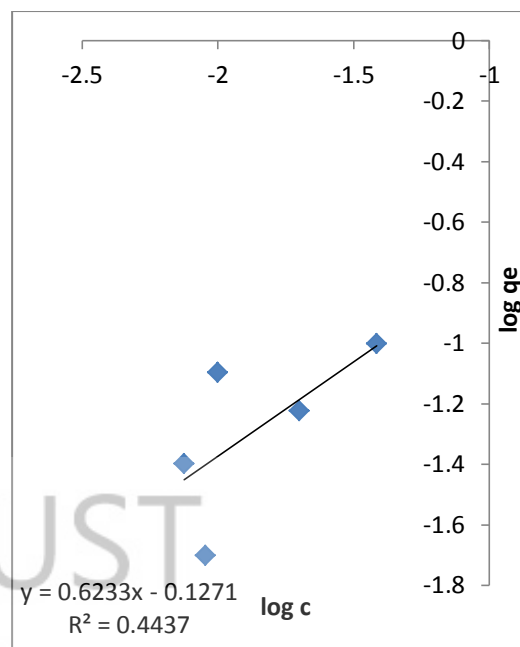


Fig 4.8 Freundlich Plot for Increasing Cd Concentration

4.6.1 Effect of increasing initial cadmium concentration

The uptake of the Cadmium increased as the initial metal concentration was increased. When the initial Cd^{2+} cations concentration increased from 2 to 10 mg/l, the uptake capacity of laterite increased from 0.039925 mg/g to 0.09985 mg/g as shown in Figures 4.7 and 4.8. A higher initial concentration provided an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases thus increased the uptake (Mobasherpour et al, 2013).

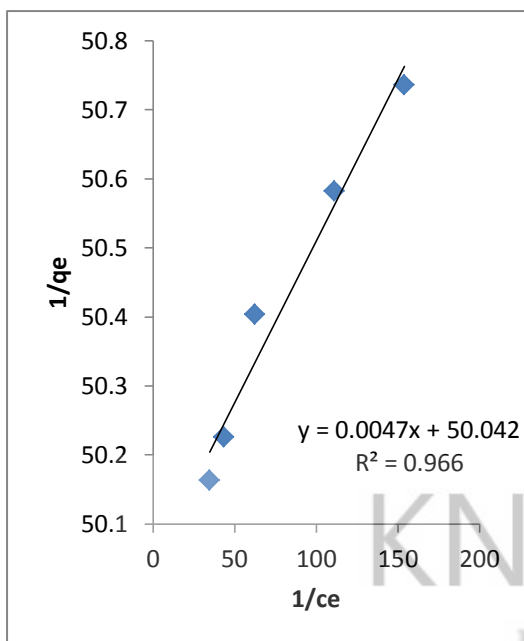


Fig 4.9 Langmuir Isotherm for Increasing Adsorbent Dosage

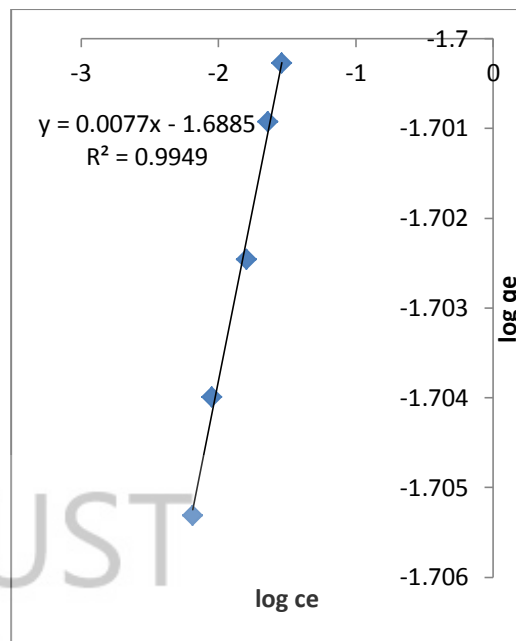


Fig 4.10 Freundlich Isotherm for Increasing Adsorbent Dosage

4.6.2 Effect of Adsorbent Dosage

It was observed that percentage of cadmium removed increased with increasing adsorbent dosage. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent (Patil, 2013). As the adsorbent dosage increased from 2 to 10 g, the adsorption capacity increased from 0.01971 to 0.01984 mg g⁻¹. This may be due to the increase in total adsorption surface area available to cadmium ion. Thus, with increasing the adsorbent mass, the amount of cadmium ion adsorbed onto unit mass of adsorbent gets increases, thus causing an increase in q_e value. This concurs with Patil (2013) findings.

4.6.3 Adsorption model parameters

Adsorption isotherm model parameters, R^2 , K , n obtained from Langmuir and Freundlich plots are tabulated in Table 4.4

Table 4.4 Isotherm models for Cadmium (II) using laterite (experimental conditions: initial concentration- 0.0505 mg/l, pH -9)

Treatment	Langmuir			Freundlich		
	Q _{max} (mg/g)	K	R ²	n	K	R ²
Increasing initial Cd concentration	27.15054	0.178828	0.3712	1.6044	0.7462	0.4437
Increasing adsorbent dosage	10689.31	0.019983	0.966	130.548	0.0205	0.9949

From the correlation coefficients, it is clear that the Langmuir isotherm ($R^2=0.966$) and Freundlich ($R^2=0.9948$) isotherm both fit the data with Freundlich being the best fit due to its higher correlation co-efficient value (0.9948). This concurs with the fact that cadmium adsorbed more onto laterite in the case of increasing adsorbent dosage as compared to the other scenerios with the indicator being the highest $q_{\max}$ value 10689.31mg/g. Moreover binding affinity coefficient, K of cd was also high in the same treatment.

4.7 Thermodynamic study

The thermodynamic parameters (K_c , ΔG° , ΔH° , ΔS°) for the adsorption of cadmium ions onto laterite calculated using Eqns 4.2-4.4 shown in Appendix E are presented in Table 4.5. See Appendix L for details.

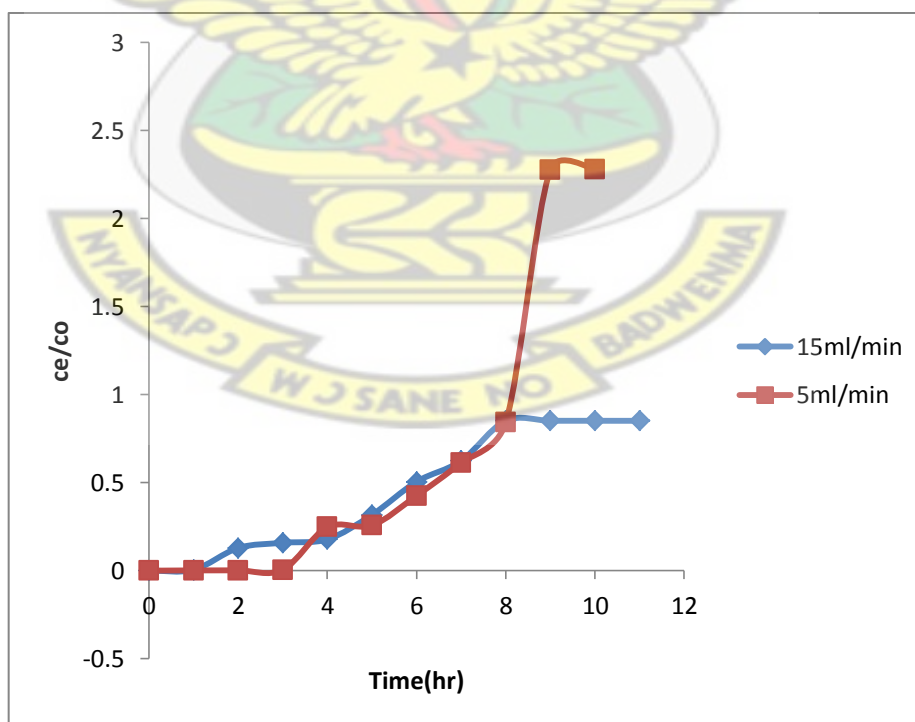
Table 4.5 Thermodynamic parameters for adsorption of cadmium onto laterite

Temperature(K)	k_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)
293	1.525	-1027.98	10432.3629	36.9726
298	1.061224	-147.226		
303	1.104167	-249.624		
308	1.295455	-662.87		
313	1.970588	-1765.21		

The negative ΔG^0 values confirm feasibility of the cadmium adsorption on the laterite surface and the positive value of ΔS^0 indicates the spontaneity of adsorption process. Positive value of ΔH^0 indicates that the adsorption is the endothermic in nature. Similar results were obtained by Maiti et al (2007) and Das & Mondal (2011).

4.8 Column Test Results

The results of the column test for two flow rates (5ml/min and 15ml/min) are shown in Fig 4.9. See Appendix K for details.

**Fig 4.11 Breakthrough Curves For 5ml/Min and 15ml/Min**

(Experimental conditions: Initial volume of leachate- 5L, cadmium concentration - 0.0505mg/l, influent pH – 9)

Increasing flowrate decreases the breakthrough time from 3hours to 1hour as seen from corresponding $\frac{C_e}{C_o}$ values of 0.0051 and 0.0049 for 5 ml/min and 15 ml/min respectively. Longer breakthrough ensures that the metal has enough contact with the adsorbent resulting in high cadmium adsorption. Exhaustion time of ten hours and eleven hours for 5ml/min and 15ml/min flowrates were obtained.



CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

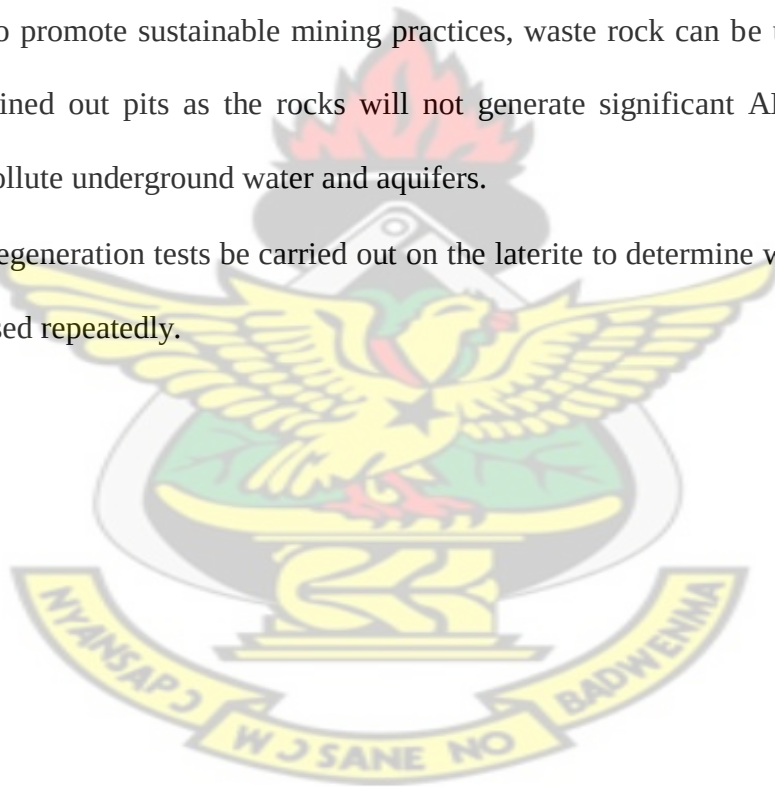
From the results and discussions, it can be concluded that:

- The dominant compound phase present in the 2 waste rock samples was Quartz (SiO_2), a non-acid forming compound.
- Concentration of heavy metals was low except cadmium whose concentration was 0.0505 mg/l exceeding WHO's guideline value of 0.03mg/l for potable water.
- Optimal time, pH, adsorbent dosage, temperature and initial concentration of 1 hour, 9, 10 g, 20⁰C and 10 mg/l respectively were obtained from the batch tests.
- Freundlich isotherm best fitted the equilibrium adsorption data.
- ΔG° , ΔS and ΔH° values of (-1027.98, -147.23, -249.63, -662.87, -1765.21), 36.9726 and 10432.36 were obtained from the thermodynamic study indicating that adsorption of cadmium onto laterite is feasible, spontaneous and endothermic.
- Increasing flow rate decreases the breakthrough time from 3hours to 1hour.
- Laterite proves as an ideal low cost adsorbent for adsorbing cadmium from wastewater.

5.2 RECOMMENDATIONS

It is therefore recommended that:

- The adsorption efficiency of laterite and other metals or varying combinations of metals be studied.
- A model to allow future researchers to predict the adsorption efficiency of laterite on heavy metals should be developed.
- Waste rock dumps should be sited far away from water bodies to avoid contamination of the water bodies by run-off water from the waste rock pile.
- To promote sustainable mining practices, waste rock can be used to back-fill mined out pits as the rocks will not generate significant AMD products to pollute underground water and aquifers.
- Regeneration tests be carried out on the laterite to determine whether it can be used repeatedly.



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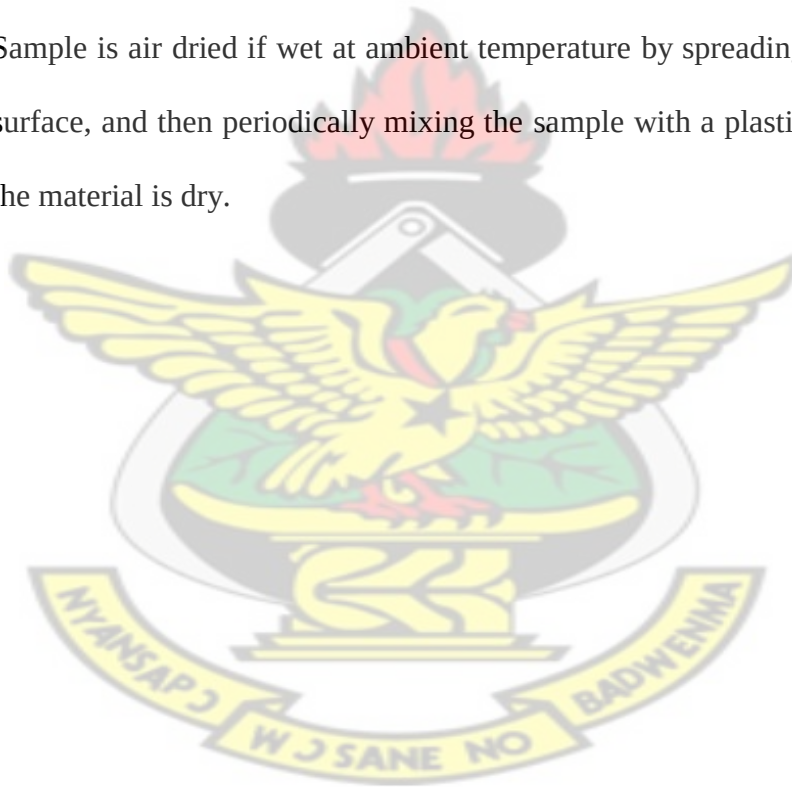
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APPENDICES

APPENDIX A

Procedure for collecting and preparation of waste rock samples using the non-grid sampling strategy

1. Composite sample weighing at least 1 kg is collected from a depth of up to 10cm by randomly walking back and forth across the entire mine waste pile and collecting a minimum of 30 increments at every ten paces taken using a stainless steel or plastic shovel and plastic bucket.
2. Sample is air dried if wet at ambient temperature by spreading it out on a flat surface, and then periodically mixing the sample with a plastic scoop until all the material is dry.



APPENDIX B

Table showing coordinates of waste rock sampling points

	EASTERNS (X)	NORTHERNS (Y)
WD10A	607142.0364	583274.9336
WD10B	607297.2053	583237.4791
WD10C	607434.5386	583299.0115
WD10D	607423.8373	583426.5354
WD10E	607289.1793	583495.2021
WD4A	606316.4277	582266.2006
WD4B	606433.2615	582331.6275
WD4C	606512.7085	582217.1304
WD4D	606479.995	581857.2822
WD4E	606587.4821	581703.0615
WD4F	606589.8188	581504.4441
WD4G	606760.3962	581224.0429
WD4H	606692.6326	581060.4755
WD4I	606522.0552	581090.8523
WD4J	606433.2615	580924.9483
	COORDINATE SYSTEM	UTM/WGS84

APPENDIX C

Physical properties of laterite

pH

10 g of air-dried soil was weighed into a beaker and 25mL of deionized water was added. The soil to solution ratio is 1:2.5. A duplicate quality control of samples is also prepared. The solution was stirred for 30 minutes and then let to settle for 24 hour. pH meter was immersed into the supernatant and pH measurements are recorded.



APPENDIX D

Procedure for Leach Test using the US Geological Field Leach Test

1. 50.0 g of prepared sample is weighed using a small field balance or a laboratory balance, and carefully added to a 1.0-L wide-mouth, plastic bottle.
2. 1.0-L deionized water is measured in 1,000-mL clean graduated cylinder and slowly added to the bottle so that no dust is lost. (NOTE: Depending upon the amount of solid material available, other leaching volumes can be used as long as the 20:1 water-to-solid ratio is maintained.)
3. The bottle is tightly capped and vigorously hand shaken for 5 minutes. Alternatively, the sample can be shaken on a bench-top horizontal shaker for 5 minutes.
4. After shaking, the bottles are turned upright and the contents are allowed to settle for 10 minutes.
5. After settling, unfiltered subsamples of the leachate are dispensed into disposable plastic beakers and measured for pH, specific conductance, alkalinity, and other characteristics.
6. A portion of leachate is filtered using a 60-cm² Leur Lock syringe and a 0.45- μ m pore-size nitrocellulose filter. If filtration is difficult, a 0.70- μ m glass fiber pre-filter can be used in conjunction with the 45- μ m filter in a serial manner. Subsamples of the filtrate are collected and preserved for analysis.

APPENDIX E

Parallel method for batch tests from the OECD guideline

Samples with the same soil/solution ratio are prepared, as many as the time intervals at which it is desired to study the adsorption kinetics.

After centrifugation and if so wished filtration, the aqueous phase of the first tube is recovered as completely as possible and is measured after, for example, 4 h, that of the second tube after 8 h, that of the third after 24 h, etc.

Methods for obtaining adsorption data to construct adsorption isotherm

Method 1

Mix a batch of solutions, each with the same volume but containing several dilutions of the initial solute concentrations, with a fixed mass of adsorbent in each reaction vessel

Method 2

Mix a batch of solutions, each with the same volume and initial concentration to the solute, with different amounts of the adsorbent.

In both methods, the change in solute concentration after apportioned contact time provides the basis for the construction of adsorption isotherms.

Equations used in obtaining parameters for Langmuir & Freundlich isotherm, thermodynamics of adsorption

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b \cdot q_{max}} \cdot \frac{1}{c_e} \dots \text{Eqn 2.7}$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \dots \text{Eqn 2.9}$$

$$q = \frac{(C_0 - C_t)v}{m} \dots \text{Eqn 2.10}$$

$$K_c = \frac{c_{ad}}{c_e} \dots \text{Eqn 4.2}$$

$$\Delta G^\circ = -RT \ln K_c \dots \text{Eqn 4.3}$$

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots \text{Eqn 4.4}$$

APPENDIX F

Leach Test Results

Metal analysis on post-filtration leachate for sample A and B

Sample A

Sample/metal	Zn	Fe	Cd	Mn	cu
Set 1	0.011	0.0503	0.032	0.050	0.027
Set2	0.009	0.060	0.029	0.060	0.0180
Set 3	0.010	0.0493	0.04	0.049	0.0148
Average	0.01	0.0532	0.03367	0.053	0.019933

Sample B

Set 1	0.011	0.0456	0.03	0.040	0.0130
Set 2	0.013	0.0331	0.021	0.032	0.0060
Set 3	0.014	0.0264	0.018	0.0054	0.0054
Average	0.012667	0.035033	0.023	0.008133	0.008133

APPENDIX G

Kinetic Test Results

Kinetic Test Results Cadmium Stock Solution at Ph 9

Time (hr)	Set 1 Cd(mg/l)	Set 2 Cd(mg/l)	Average residual conc of cd (mg/l)	Conc of cd adsorbed (mg/l)	Amount of cd adsorbed, q_e (mg/g)	% conc of cd adsorbed
0.167	0.006	0.0062	0.0061	1.9939	0.019939	99.695
0.334	0.0039	0.0038	0.00385	1.99615	0.0199615	99.8075
0.5	0.0034	0.0031	0.00325	1.99675	0.0199675	99.8375
0.667	0.0032	0.0031	0.00315	1.99685	0.0199685	99.8423
0.834	0.001	0.0009	0.00095	1.99905	0.0199905	99.9525
1	0.0004	0.0002	0.0003	1.9997	0.019997	99.985
3	0.0035	0.0034	0.00345	1.99655	0.0199655	99.8275
6	0.0054	0.0051	0.00525	1.99475	0.0199475	99.7375
12	0.0071	0.0071	0.00705	1.99295	0.0199295	99.6475
24	0.0077	0.0075	0.0076	1.9924	0.019924	99.62

Batch Kinetic Test Results Cadmium Stock Solution at Ph 6

Time (hr)	Set 1 Cd(mg/l)	Set 2 Cd(mg/l)	Average residual conc of cd	Conc of cd adsorbed	Amount cd adsorbed, q_e (mg/g)	of % conc of cd adsorbed
0.167	0.0078	0.0075	0.00765	1.99235	0.019924	99.6175
0.334	0.0053	0.0053	0.0053	1.9947	0.019947	99.735
0.5	0.0049	0.0047	0.0048	1.9952	0.019952	99.76
0.667	0.0046	0.0046	0.0046	1.9954	0.019954	99.77
0.834	0.0044	0.0043	0.00435	1.99565	0.019957	99.7825
1	0.0022	0.002	0.0021	1.9979	0.019979	99.895
3	0.0038	0.0036	0.0037	1.9963	0.019963	99.815
6	0.0045	0.0044	0.00445	1.99555	0.019956	99.7775
12	0.0056	0.0055	0.00555	1.99445	0.019945	99.7225
24	0.0067	0.0066	0.00665	1.99335	0.019934	99.6675

Batch Kinetic Test Results Cadmium Stock Solution at Ph 4

Time (hr)	Set 1 Cd(mg/l)	Set 2 Cd(mg/l)	Average residual conc of cd	Conc of cd adsorbed	Amount of cd adsorbed, q_e (mg/g)	% of cd adsorbed
0.167	0.0083	0.0081	0.0082	1.9918	0.019918	99.59
0.334	0.0075	0.0074	0.00745	1.99255	0.019926	99.6275
0.5	0.0071	0.007	0.00705	1.99295	0.01993	99.6475
0.667	0.0058	0.0054	0.0056	1.9944	0.019944	99.72
0.834	0.0048	0.0048	0.0048	1.9952	0.019952	99.76
1	0.0043	0.0042	0.00425	1.99575	0.019958	99.7875
3	0.0029	0.0028	0.00285	1.99715	0.019972	99.8575
6	0.0033	0.0034	0.00335	1.99665	0.019967	99.8325
12	0.0071	0.0071	0.0071	1.9929	0.019929	99.645
24	0.0083	0.0084	0.00835	1.99165	0.019917	99.5825

APPENDIX H

Leachate Kinetic Test Results

Kinetic Test Results for Leachate

Time (mins)	Set 1 Cd (mg/l)	Set 2 Cd (mg/l)	Average Cd(mg/l)	Conc of cd adsorbed	Amount of adsorbed, q_e (mg/g)	% conc of Cd adsorbed
0	0.0505	0.0505		0	0	0
10	0.025	0.025	0.025	0.0255	0.000255	50.495
30	0.013	0.017	0.015	0.0355	0.000355	70.297
60	0.007	0.011	0.009	0.0415	0.000415	82.1782
360	0.008	0.01	0.009	0.0415	0.000415	82.1782

APPENDIX I

Determination of Isotherms

Effect of Increasing Cadmium Concentration

sample	Initial conc of Cd (mg/l)	Final Conc, C_e (mg/l)	Conc adsorbe d (mg/l)	Amount adsorbe d, X	q_e , X/M	$1/C_e$	$1/q_e$	Log C	Log q_e
1	2	0.0075	3.9925	0.07985	0.039925	133.33333	25.0469631	-2.1249	-1.39876
2	4	0.009	1.991	0.03982	0.01991	111.1111	50.2260171	-2.0458	-1.70093
3	6	0.01	7.99	0.1598	0.0799	100	12.5156446	-2	-1.09745
4	8	0.02	5.98	0.1196	0.0598	50	16.7224080	-1.6989	-1.2233
5	10	0.0385	9.9615	0.19923	0.099615	25.974026	10.0386488	-1.4145	-1.00168

APPENDIX J

Determination of Isotherms

Effect of Increasing Adsorbent Dosage

sample	Mass of adsorbent (mg)	Final Conc, C_e (mg/l)	Conc adsorbed (mg/l)	Amount adsorbed, X	q_e , X/M	$1/C_e$	$1/q_e$	Log C	Log q_e
1	2	0.0065	1.971	0.15768	0.01971	153.846	50.7357	- 2.1871	- 1.7053
2	4	0.009	1.977	0.07908	0.01977	111.111	50.5817	- 2.0456	- 1.7040
3	6	0.016	1.984	0.1984	0.01984	62.5	50.4032	- 1.7959	- 1.7024
4	8	0.023	1.991	0.03982	0.01991	43.4783	50.226	- 1.6383	- 1.7010
5	10	0.029	1.984	0.1984	0.01984	34.4828	50.163	- 1.5376	- 1.7003

APPENDIX K

Column Test for 5ml/Min and 15ml/Min

15ml/min	15ml/min	5ml/min
Time (hr)	Ce/Co	Ce/Co
0	0	0
1	0.0051	0.0015
2	0.128713	0.002
3	0.158416	0.0049
4	0.178218	0.247525
5	0.316832	0.257426
6	0.50495	0.425743
7	0.623762	0.613861
8	0.851485	0.841584
9	0.851232	2.277228
10	0.851124	2.2776
12	0.85111	

APPENDIX L

Parameters for Thermodynamic Plot

Temperature(T)	Ce (mg/l)	C _{ad}	K _c	1/T	lnK _c
293	0.02	0.0305	1.525	0.003413	0.421994
298	0.0245	0.026	1.061224	0.003356	0.059423
303	0.024	0.0265	1.104167	0.0033	0.099091
308	0.022	0.0285	1.295455	0.003247	0.258862
313	0.017	0.0335	1.970588	0.003195	0.678332



APPENDIX M

XRF Results for waste rock

GEOLOGICAL SURVEY DEPARTMENT X-RAY FLUORESCENCE LABORATORY RESULTS

DATE: 15/4/2014

Minor Elements	Dimension	4	10
Na	%	1.730	1.210
Mg	%	9.755	11.060
Al	%	10.840	10.140
Si	%	23.320	23.440
P	%	0.056	0.038
S	%	0.007	< 0.00078
K	%	0.622	< 0.0099
Ca	%	4.058	2.284
Ti	%	0.210	0.206
V	ppm	75.300	63.700
Cr	ppm	688.000	652.000
Mn	%	0.117	0.083
Fe	%	6.567	7.367
Co	ppm	62.000	75.000
Ni	ppm	118.200	280.100
Cu	ppm	15.000	22.000
Zn	ppm	56.100	48.500
Ga	ppm	13.200	12.000
Ge	ppm	1.000	1.400
As	ppm	1.400	5.100
Rb	ppm	11.100	0.600
Sr	ppm	348.300	204.200
Zr	ppm	99.000	63.400
Ba	ppm	286.000	50.100
Ce	ppm	30.000	36.000
Th	ppm	0.800	1.900

Major Oxides	Dimension	4	10
Na2O	%	2.33	1.64
MgO	%	16.18	18.35
Al2O3	%	20.48	19.15
SiO2	%	49.89	50.14
P2O5	%	0.13	0.09
SO3	%	0.02	< 0.0019
K2O	%	0.75	< 0.012
CaO	%	5.68	3.20
TiO2	%	0.350	0.343
MnO	%	0.15	0.11
Fe2O3	%	9.39	10.53
TOTAL	%	105.34	103.54

ATT:MS ABIGAIL SEYRAM SALAH - KNUST
DEPT. OF MATERIALS ENGINEERING

ANALYSIS BY: MR. MOHAMMED AWAN
P. O. (ASSISTANT CHEMIST)
For Dr. Daniel Boamah
Head of Geochemistry and Laboratories

