EXTRACTION OF COPPER USING CHICKEN DUNG AND CONCENTRATION OF TITANIUM USING BIOMASS FROM ORES IN MARAGWA LOCATION, THARAKA NITHI COUNTY

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DECLARATION

This thesis is my original work and has not been presented elsewhere for a degree or any other award.

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DEDICATION

This work is dedicated to my wife, Faith Kendi, my children, Loveyn Gatwiri, Edwin Mutuma and Ethan Murimi as well as my mother, Anastasia Mukwanjagi, for their immense support during the study.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
CNMC	China Nonferrous Metal Mining Corporation Ltd
EWS	Early Warning Systems
FTIR	Fourier-transform infrared spectroscopy
GDP	Gross Domestic Product
HMS	Heavy Media Separation
ICRAF	International Centre for Research in Agro forestry
KNBS	Kenya National Bureau of Statistics
Mt	Metric tonnes
MCA	Multichannel analyser
MS	Mass Spectrometry
NRF	National Research Fund
OCT	n-octyl alcohol
OPD	Optical Path Difference
PEA	Preliminary Economic Assessment
RBM	Richards Bay Minerals Company
SPA	Styryl phosphonic acid
SX/EW	Solvent Extraction and Electro-winning
UGM	Uganda Gold Mining
UNEP	United Nations Environmental Programme
USGS	United States Geological Survey
XRD	X-Ray Diffraction
XRFS	X-Ray Fluorescence Spectroscopy

ABSTRACT

Mineral data shows several deposits of copper and titanium minerals in Kenya yet the country continues to import copper and titanium products. In some regions of Tharaka Nithi County, occurs ores that are known to contain both copper and titanium minerals. These minerals have never been earmarked for extraction mainly because the common methods known for extraction are expensive. In addition, the hydrometallurgical or pyrometallurgical process used in copper extraction releases greenhouse gases into the environment. Titanium minerals, on the other hand, are relatively found free of iron minerals. However, titanium extraction from ores must be found mixed with iron minerals. The objective of this study was to extract copper from the ores using impure hydrazones derived from chicken dung and concentrating titanium using ore-laterite-carbonized biomass, carbonized biomass, and froth floatation. Samples were obtained from the selected ore deposits of Maragwa location in Tharaka Nithi County. The samples were obtained at 30 cm depth (level A) and further one-meter depth (level B). Samples obtained were dried at 105^{o}C for 9 hours and later ground to 60.0 meshes (250 microns) using a ball mill. Copper minerals were leached using hydrochloric acid. Titanium in the ore was concentrated using carbonized biomass, ore-laterite-carbonized biomass at 800-900°C, and froth floatation method. The analyses of the minerals for the mineralogical and chemical composition were done using X-ray Diffraction Spectroscopy (XRD), X-ray Fluorescence Spectroscopy (XRF) and Atomic Absorption Spectroscopy (AAS). The chicken dung was characterized using FTIR and MS methods. The copper mineral obtained was chalcopyrite. Copper composition was found to be 4.46%, with a mean of 4.47±0.70% at level A and 4.44±0.60% at level B. The mean rutile composition was found to be 0.92±0.11% with a mean of 0.77±0.16% at level A and 0.86±0.17% at level B. After concentration, rutile improved with a range of 1.0 to 2.5%. Reduction of copper using chlorinated chicken dung at pH above 11 produced copper with purity ranging from 57-85%. The use of iron electrode in acidic media during copper extraction produced Cu with purity ranging from 51-78%. It was found that the aluminium electrode was suitable for monitoring the reduction process of copper from the mixture of ore leachate and chlorinated chicken dung leachate. The copper composition in all deposits was found to be above the cut-off grade of 0.4 to 1.0 percent which is mined in other countries. The reduction of copper using chicken dung generated hydrazones was found to be a good method of copper extraction. This method of copper extraction does not require heavy capital investment since the chicken dung is locally available. The concentration of the ore - laterite using carbonized biomass was also found to be the best method of concentrating titanium from ores. The method is viable because laterite soils (heavily weathered material which is rich in iron oxides or alumina or both) are widely available while biomass is obtained from municipal waste. The experiments were done on the laboratory scale. The study, therefore, recommends a pilot study on large scale copper extraction and titanium concentration using the optimized values.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

In Kenya, about ninety-five percent of industries and manufacturing firms are micro and small firms, contributing about twenty percent of the sector's Gross Domestic Product (GDP) (Kippra, 2017). The exploitation of mineral resources will be key to boosting the growth of the Kenyan economy in addition to agriculture (Eyster, 2014; Habitat Planners, 2017). The major hindrance to the exploitation of the resources is a capital investment that is more reliant on technological requirements of the methodology of the resource extraction. There is a need therefore to explore alternative, affordable and locally viable methods of resources, extractions, and processing.

Copper deposits are usually found in varied mineralogical and elemental composition (Berger *et al.*, 2008). The minerals include chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), cuprite oxide (Cu_2O), and malachite ($Cu_2CO_3(OH)_2$) among many other minerals (Hoffman, 1996; British Geological Survey, 2007). Different copper deposits have a different mineralogical abundance (Long *et al.*, 2000). According to Long *et al.* (2000), in the United States of America, various copper deposits have varied mineral abundances. Such mineral abundances are as follows; malachite 36.1 percent, azurite 55.3 percent, covellite 79.8 percent, chalcocite 79.8, bonite 63.3 percent and chalcopyrite 34.5 percent. In China, about fifteen copper ores mined contains copper composition grading between 0.82 to 0.99 percent (Streicher-Porte *et al.,* 2010). In Mexico, the copper ores extracted contains average grades of 0.4 percent copper (Perez, 2013). Copper deposits in Chile and Peru country contain copper composition ranging from 1.0 to 2.0 percent (McCammon, 2003). Those in the Philippines and Canada contain copper composition ranging from 0.3 to 0.5 percent (Long *et al.,* 2000). The Democratic Republic of Congo, contain copper ores with mineral abundance ranging from 38.0 to 29.0 percent. (Nkuna *et al.,* 2016).

In African countries, copper ores mined contain mainly chalcopyrite and bornite minerals with an average copper composition of 0.5 to 2.3 percent (Haglund, 2013). In Botswana copper is extracted from chalcocite, bornite and copper sulfides grading between 1.3 and 1.5 percent copper (U.S. Geological Survey, 2012; Newman, 2013). In South Africa, copper reserves have been found to contain mainly chalcopyrite and bornite minerals grading between 0.49 to 0.71 percent (Heinrich, 1970). In Tanzania, the copper deposits grades at 0.3 to 0.14 percent from mainly azurite and malachite minerals (Yager, 2016). In Sudan, mineral deposits contain chalcopyrite grading at an average of 1.12 percent copper (Taib, 2014).

In Kenya, few copper deposits have been identified. For instance, in Macalder in South Nyanza and Kitere near Kisii, copper minerals occur as sheets, veins, and lenses. These minerals occur between layers of banded iron formation as sandstone, and metabasalts (Yager, 2012a). Copper sulfides minerals in these areas occur as quartz, sphalerite-pyrite, pyrrhotite-chalcopyrite, and copper carbonate. These minerals grade at 3.0 to 4.55 percent Cu. More copper minerals have been identified near Voi Hill and Mangu. (Saggerson, 1958). According to Saggerson (1958), the sample from the best-mineralized part of the outcrop assay at 8.2 percent Cu. In the Kanzugo region in Kitui County, green malachite and blue azurite minerals are found within the igneous rocks (Karuku, 2008). In Eastern Kenya, copper deposits have been studied in Maragwa location in Tharaka Nithi County. The minerals occur as chalcopyrite assaying 1.77 - 8.38 percent Cu. (Kugeria *et al.*, 2018). Despite the presence of such good copper deposits in Kenya, their extraction has not been exploited for economic growth. This is probably due to a lack of capital and technological requirements to establish industries in Kenya (Sampath, 2014).

Titanium is the ninth most common element in the earth's crust. It occurs in different mineralogical and chemical compositions averaging 0.9 percent (Hoffman, 1996). Titanium bearing minerals identified in Kenya comprise mainly of ilmenite ($FeTiO_3$), rutile (TiO_2), ilmenorutile ($(Ti, Nb, Fe)O_{26}$), titanite ($CaTiSiO_5$) and perovskite ($CaTiO_3$) (Contreras, *et al.*, 2017). Rutile is a mineral that naturally occurs as titanium dioxide polymorph (Meinhold, 2010). It is widely found in metamorphic and igneous rocks. Rutile is mostly available after erosion, transport, and deposition of rutile-bearing quartz along terraces, fluvial-alluvial and eluvial deposits (Kuşcu *et al.*, 2018). Titanium minerals found along Uyoma Peninsula in western Kenya are rich in Ilmenite with a composition averaging at 13.8 percent TiO_2 (Loupekine, 1968). The sand deposit found along Ras Ngomeni in Malindi contains 3 - 14 percent ilmenite and rutile (Ochola, 2011). Besides, the beach sands and dunes along the coast of Formosa Bay in Malindi contains less than 2 percent of ilmenite and rutile. Laterite soils in Mbeu in

Meru, Gitara Kianderi and Gitong’o in Tharaka Nithi County and Kaharate in Ruiru have been studied (Mutembei *et al.*, 2014; Warui *et al.*, 2015). The titanium minerals contain 3 - 6 percent rutile, 1.6 percent rutile and 5 - 8 percent respectively. Currently, sand containing rutile from Kwale County with a composition of about 5 - 6 percent Ti is mined by Base Titanium Limited (Yager, 2015; Ogola, 1987). Further studies were done on laterite in Kamahuha in Murang’a county was found to be rich in ilmenite minerals (Waithaka *et al.*, 2014). In general, titanium minerals in most parts of the country are rich in ilmenite.

The concentration of titanium from laterite soils from the Tunyai Division, in Tharaka Nithi County, has been investigated using charcoal (Mutembei, 2013). From his studies, rutile composition increased from 1-2 percent to above 5 percent. This composition is suitable for commercial extraction. The concentration of laterite containing rutile using biomass has been done (Warui *et al.,* 2015). The mixture of biomass and ore in the ratio of 1:10 respectively was reduced in the environment of 500 - 800 °C. The heated mixture was later separated using a strong magnet and the rutile composition increased from 1.6 - 4.2 to 4.43 - 8.5 percent. The concentration techniques used the advantage of the iron present in the mineral. Exploring methods of concentrating titanium in iron-poor content ores is important hence this study.

Several methods have been used in the extraction of copper, which includes bioleaching techniques, solution mining and froth flotation methods (Ochromowicz & Chmielewski, 2011). Displacement of copper from solution using scrap iron is one of the oldest technologies (Habashi, 2005). According to Habashi (2009), the reduced copper was impure with 85 - 90 percent copper, 0.2 - 2 percent iron, and traces of silica and alumina. Impurities like iron and cobalt are known to increases the softening temperature of rolled copper products. Similarly, the presence of impurities like Se, Te, S, and O_2 in Cu_2X compounds generally makes them brittle. The presence of such impurities also reduces the conductivity of copper metal (Habashi, 2013). The hydrometallurgical process of copper extraction is one of the methods of obtaining copper from ores (David & Jones, 1994). The method involves the leaching of low-grade ore in an elevated temperature and pressure conditions. The leaching also takes place in the environment containing oxygen and in acidic chloride lixiviate solution. Copper is then obtained from the leachate through the solvent extraction process.

Pyrometallurgy process is another method of copper extraction (Allen *et al.*, 1998). The method involves the concentration of sulfide ore and then smelting the concentrate using furnaces to remove sulfur and other impurities. The copper is then obtained by electrolysis of the melt as a pure copper cathode product. The two methods involve the use of high temperatures. Processes that use high temperatures are expensive and environmentally unfriendly.

Previous studies done by Mutembei *et al.* (2014) have shown that iron-containing laterite is widely found distributed in some parts of Tharaka Nithi County. According to the study, laterite is rich in iron with a composition of about 15 - 45 percent. Furthermore, iron minerals in laterite can be reduced to more magnetic mineral - magnetite using charcoal or biomass (Mutembei *et al.*, 2014; Waithaka, 2014). Because of the abundance of laterite materials, the use of iron obtained from concentrated laterite for extraction of copper was also investigated in this study.

1.2 Statement of the Problem

Rich copper deposits with the composition of about 4 percent and titanium reserves of about 1 - 6 percent have been identified and mapped in Kenya. These minerals have minimal exploration due to heavy capital investment requirements and lack of local technology. The leaching process of copper extraction would be commercially viable if affordable reducing agents are used. Chicken dung is available in large quantities in Kenya. The dung is a potential source of impure hydrazones that may form an important input as a reducing agent. The concentration of titanium pauses the major hindrance. A viable method of concentrating the mineral has been locally established but the method requires the mineral to be found in the mix with iron ore. Where the mineral is found in relatively high abundance in Kenya, the titanium ore is free of appreciable iron ore content. This study therefore investigated and established alternative and viable methods of concentration of titanium and extraction of copper.

1.3 Justification of the Study

Kenya has several copper and titanium deposits which are not exploited because of lack of capital, and basic exploration techniques (Davies & Osano, 2005; Habitat Planners, 2017; Kugeria *et al.*, 2018). For instance, there are copper deposits rich in copper minerals at Macalder in South Nyanza and Kitere region in Kisii (Yager, 2012).

Another deposit had been identified at Voi and Maungu with a concentration of 8.2 percent copper (Saggerson, 1958). In Kitui County there are copper deposits found at the Kanzugo region rich in malachite and blue azurite minerals (Karuku, 2008).

In Maragwa location in Tharaka Nithi County, copper deposits have been found occurring as chalcopyrite minerals (Kugeria *et al.,* 2018). These ores have higher copper composition than those mined in Uganda and other developed countries (Nyakairu & Koeberl, 2001). Despite the presence of such good copper deposits, they are yet to be exploited for economic growth. This is probably due to a lack of capital and technology to establish industries in Kenya (Sampath, 2014; Kugeria *et al.*, 2018). Besides this, the country continues to import electrical wires and transformers and other heavy machinery and goods made of copper and titanium metals (Olivares *et al.*, 2010; U.S. Geological Survey, 2014). The availability of mineral deposits and their exploitation can promote industrial development for any nation if appropriate technology is put into place. Most of the developed countries invest heavily in the capital, skilled manpower, and expensive machinery since they adopt imported technology. This reduces the net gain on any exploitation of natural resources. There is a need, therefore, to investigate locally viable methods, and improve on the technology to maximally reap from the exploitation of natural resources.

In Kenya, the extraction of valuable minerals like copper and titanium is probably hampered by high capital and technological investment requirements. This study focuses on developing a new technique that can be used in the extraction of copper. The study also investigates on extracting copper by reduction of copper ions using iron metal in acidic media of the ore leachate. The study further investigates on the extraction of copper using *in-situ* prepared hydrazones from the chicken dung. This is in the effort of developing local environmentally sustainable technology (Kugeria *et al.,* 2018; Kugeria *et al.,* 2019).

The study has also focused on the concentration of rutile from ores that have poor iron-ore content. The technique is expected to concentrate titanium using biomass and ore-laterite mixture using biomass. The invention is to investigate the possible concentration of titanium using the iron- ore and investigate whether iron content will also be concentrated in iron ores with poor iron content. Biomass is an environmental menace especially in major cities like Nairobi (United Nations Environmental

Programme report (UNEP, 2012)). This challenge will continue increasing as population and urbanization increases. Burning of the biomass from municipal waste in limited air produces reducing gases like CO, H_2, and CH_4. These are greenhouse gases. The waste can be used in the concentration of titanium from ores (Waithaka *et al.,* 2014; Warui *et al.,* 2015; Kugeria *et al.,* 2018)). This would make organic waste as an alternative source of energy for industrial development.

The use of laterite in the concentration of titanium would offer an alternative technique for obtaining rutile from titanium ores. The use of treated chicken dung leachate in copper extraction would also offer a new mining technique for copper. The results of this study would offer an alternative method of extracting copper and concentrate titanium from ores. The techniques if successful would help in the development of copper and titanium extraction industries. This would help the country to earn foreign exchange by exporting copper and titanium rather than importing the same products. Most of the minerals are found in rural areas. The establishment of these industries would attract the establishment of other service industries such as transport and communication. This would provide job opportunities to many Kenyans, thus boosting the countries revenue. Moreover, the decentralization of industries to rural areas will encourage urban to rural migration as people look for jobs and better business opportunities. This will promote urbanization and the development of rural areas. This will culminate in the promotion of attainment of the vision 2030 and manufacturing as envisaged in agenda four of the Kenyan Government.

1.4 Research Questions

i. What is the chemical and mineralogical composition of minerals found in Maragwa Location in Tharaka Nithi County?

ii. Can titanium be concentrated from ores by reduction using biomass, biomass-laterite mix and froth floatation?

iii. Can electrochemical reduction of copper using iron, aluminum, and impure hydrazones from chicken dung be used for copper extraction?

iv. Can electrochemical reduction of copper from a mixture of ore leachate and chlorinated chicken dung leachate be monitored using an aluminum electrode as an indicator?

1.5 Objectives of the Study

1.5.1 General Objective

To investigate an alternative and viable method for extraction of copper and concentration of titanium from mineral ores obtained from Maragwa Location in Tharaka Nithi County.

1.5.2 Specific Objectives

The specific objectives of the study are to;

i. Evaluate mineralogical and chemical composition of ores from Maragwa location and laterite from Tunyai location in Tharaka Nithi County.
ii. Concentrate titanium in the ores using biomass, biomass-laterite mix vis a vis froth floatation.
iii. Extract copper from the ores using iron in acidic media, and hydrazones obtained from chicken dung.
iv. Assess the use of aluminium electrode as an indicator in copper extraction from the mixture of copper leachate and chlorinated chicken dung leachate

1.6 Scope and Limitations of the Study

Mineral ores for this study were obtained from selected sites in Maragwa Location in Tharaka Nithi County. The scope of this study was;

i. To concentrate titanium using froth floatation, biomass, and laterite materials on a laboratory scale,
ii. To reduce copper from ores using aluminium, iron, and use of chlorine-treated chicken dung leachate on a laboratory scale.
iii. The minerals investigated were obtained from 30 cm depth and further one-meter depth.

During the concentration of titanium and copper reduction, the following were the limitations for the study;

i. The tuning of concentration equipment was not done and the study investigated chemical transformation in the ores at the temperature range of 800 - 900 °C.
ii. The concentration of titanium from the ores was investigated on the amount of titanium in the concentrate. The final recovery extends in terms of total

concentrated titanium as a ratio of initial titanium in the ore was not investigated.

iii. The concentration of titanium using the froth floatation method was done using oleic acid, Aeroflot, 2-butoxyethanol and UCON R-22 as frother chemicals. The collector chemicals used in the study were polyacrylamide, bromoformium, tetrabutylether, and tri cresyl phosphate.

iv. During copper reduction using chlorinated chicken dung leachate, investigations were only done on optimization of pH, time and temperature parameters. Investigations on the effects of different sources of animal dung, including broilers as opposed to layers, among other animals were not done.

v. During copper reduction using chlorinated chicken dung leachate, aluminium electrode was used to monitor change in potential against the concentration of copper ions.

vi. In the reduction of copper ions using an iron electrode in acidic media, hydrochloric acid was used. During the process, reduction time and temperatures were optimized.

CHAPTER TWO

LITERATURE REVIEW

2.1 Mineralogical and Chemical Composition of Various Copper Ores

The mineralogical and chemical composition of various copper deposits differs depending on the geology of a particular region (Berger *et al.,* 2008). Copper ores may consist of one or more copper minerals with varied chemical composition. Such copper minerals include malachite, cuprite oxide, covellite, chalcopyrite, bornite and chalcocite (Hoffman, 1996; British Geological Survey, 2007). Different countries have copper deposits with varied elemental and chemical compositions (Berger *et al.*, 2008). The exploitation of mineral resources in developing countries is either lacking or where it is done, the economic gain to the country is limited due to heavy per capital investment and low returns.

In 1998, assessment of world resources estimated 550 million tons of copper which was contained in identified and undiscovered resources in the United States (Hammarstrom *et al.,* 2013; McCammon, 1997). A global assessment of porphyry copper deposits has shown a total of about 1.8 billion tons of copper reserves some of which has already been extracted. By the end of the year 2013, undiscovered copper resources estimated 3.1 billion tons. Chile is the largest copper producer in the world (Kuck, 2014). According to Kuck (2014), most of its copper is extracted from mines that contain 0.4 - 1.0 per cent copper.

In Nigeria, copper deposits are not yet explored despite identified possible potential copper deposit at Azara (Oyeladun, 2015). In Zambia, there occur several copper deposits with the mineralogy changing from chalcopyrite to chalcopyrite-bornite in most deposits (Haglund, 2013). Such ores include; Mufulira, Nkana, Chambishi, Kitwe, Mopani, Konkala, Lubambe and Sentinel Mines. Further studies by Haglund (2013) have shown that Mopani mines which are found in Kitwe produce sulfide mineral. Rokana mine is another deposit rich in carrollite, chalcopyrite, bornite, pyrite and chalcocite minerals (Loyd, 2013). Zambia’s copper mines have an average copper composition of 0.5 to 2.3 percent, with Lubambe copper mine grading at 2.3 percent copper (Haglund, 2013). In 2013, Blackthorn Resources Limited explored the Kitumba mine in Zambia (First Quantum Minerals Limited, 2016). The company discovered mineral reserves of about 108.9 million metric tonnes (Mt) of copper which were grading at 1.09 percent. Kalumbila copper mine was later discovered with resources estimating at 1.03 billion Mt of ore grading at 0.51 percent copper (First Quantum Minerals Limited, 2016).

In Botswana, the Boseto copper mines contain copper ores mainly in the form of chalcocite, bornite and copper sulfides (U.S. Geological Survey, 2012). Other minerals like malachite and chrysocolla are also found at shallow depths. Most copper ores have copper composition averaging between 1.3 and 1.5 percent (Discovery Metals Limited, 2012). Some of the copper deposits in Botswana are Boseto, Selebi-Phikwe, Zeta and Plutus mines. The Boseto mine contained approximately 20.5 million metric tonnes **(**Mt) of copper grading at 1.5 percent. Besides, the inferred resources from the same mine were estimated at 94.8 metric tonnes grading at 1.3 percent Copper. Plutus mine is a deposit which has mineral reserves of 13.3 million Mt grading at 1.3 percent copper in the year 2012.

In South Africa, the Phalaborwa Complex Mines are the leading copper-producing ores rich in chalcopyrite, bornite and various silicates minerals (Heinrich, 1970; Coakley & Dolley, 1996; Yager, 2014b). According to Yager (2014b), open-pit mining started at Palabora in 1964 and ended in the year 2002. The ore had an estimated reserve of 225 million Mt and an additional unexplored reserve of 16 million Mt grading 0.49 percent copper. By the end of 2005, proven and probable reserves totaled to 112 million Mt grading at 0.56 percent copper.

The Kamoa deposit in the Democratic Republic of Congo is predominated by copper sulfide minerals (Nkuna *et al.,* 2016). In their analysis, Nkuna *et al.* (2016) found out that other copper ores consisted of predominantly bornite, chalcopyrite, and chalcocite minerals. Some of these copper deposit includes Ruashi mine, Kinsenda Mine, Musonoi mine and Kamoa Mines (Yager, 2012b). The inferred copper reserve was amounting to 13.1 million Mt grading at 2.68 percent copper (Yager, 2013; Yager, 2014a). Kinsenda mine, for instance, had copper reserves amount to 6.1 million Mt grading at 4.8 percent copper. A feasibility study on a new copper mine at the Musonoi region was done by Jinchuan Company in the year 2013. The copper reserves obtained estimated at 31.7 million Mt grading at 2.96 percent copper (Yager, 2012b).

In East Africa**,** copper mining has been going on in Uganda since 1950s to 1980s (Cox, 1993). According to Cox (1993), there are several localities identified with copper deposit but the only commercially significant deposit to date has been at Kilembe, Boboong, Lokapeliethe and Loyolo in Karamoja region, and Kampono and Kitaka in Mbarara District. Between 1957 and 1979, a total of 16.29 million tons of the ore averaging 1.95 per cent Cu were mined and treated to yield 217,000 tons of blister copper. Copper deposits with as low as 0.48 - 2 per cent Cu is what was used in extraction of copper in Uganda (Tuhumwire, 1995). Recently, Uganda Gold Mining (UGM) Company has provided an update on drilling activities at the Kilembe copper project in Uganda (Tuhumwire, 2002). At the Bukangama West, target drill hole UGM-011 intersected 9.99 m of the ore grading 0.72 per cent Cu and drill hole UGM-010 intersected 14.48 m of the ore grading 0.48 per cent Cu. Currently, Tibet Hima Industry Company Ltd. of China and its joint-venture partners planned to reopen the Kilembe mines near the border of the Democratic Republic of the Congo. The companies planned to start mining copper in May 2015 and to complete a new copper smelter by August 2015. Initial planned production was 550,000 metric tons per year (t/yr) of ore (Zambian Mining Magazine, 2013; Khisa, 2015).

In Kenya, studies on copper mineralogy in the Kanzugo region, in the northern parts of Kitui County shows the presence of green malachite, bornite and blue azurite minerals (Karuku, 2008). The minerals are found scattered over a width of about seven kilometers and with chemical composition ranging from 3 to 8 percent copper. Further studies on the geology of the Kasigau-Kurase area have shown that minerals found around Voi hill and Maungu-Nyangala ridge are rich in malachite and rare azurite mineral. These minerals assay between 1.5 and 8.2 percent copper (Saggerson, 1958). In some parts of Tharaka Nithi County, copper deposits have been documented to have chalcopyrite and few traces of covellite minerals (Dubois and Walsh, 1970). Further studies in Maragwa Location in Tharaka South Sub-County have shown copper reserves rich in chalcopyrite minerals that assay at 2 - 8 percent copper (Kugeria *et al.*, 2018).

2.2 Methods of Copper Extraction Used in Various Countries

Different or the same methods are used in different countries to concentrate and extract copper depending on the ore mineralogy (Wills, B. A. 2011). In Zambia, China

Nonferrous Metal Mining Corporation Ltd. (CNMC) used heap leaching method to obtain copper in concentrate at Baluba Center Mine which produced 28,069 metric tons (t). The same method was used at Chambishi West Mines and continued with the development of the southeast Chambishi ore body. The southeast ore body project, which was expected to be completed in 2016, was designed to produce 63,000 t/yr of copper in concentrate. At Mufulira, Bwana Mkubwa, and Kansanshi mines solvent extraction and electrowinning (SX-EW) plants were established in 2006 while at Konkola mine (SX-EW) plants were established by 2007(China Nonferrous Metal Mining Corporation Ltd., 2014; Loyd, 2016).

In Democratic Republic of Congo (DRC), SX-EW methods are used to mine copper at Kolwezi Tailings project and the Mutoshi Mine from 2008, and at the KOV Mine in 2009 (Yager, 2013; Engineering & Mining Journal, 2014). In 2013, Mutanda Mining SPRL Company established SX-EW plant at the Mutanda Mine in Congo DRC. The output at Mutanda amounted to about 150,600 t of refined copper. (Hack, 2013; Glencore Xstrata plc, 2014; Kibawa, 2014). Other copper deposits which used SX-EW methods in Congo DRC are; Mukondo Mountain Mine, Luita mine, Comide mine, Kinsevere Mine, Kipoi Central deposit, Ruashi Mine and Etoile Mine (Kitumba, 2013; Eurasian Natural Resources Corp. Ltd., 2014; Kibawa, 2014; Anvil Mining Ltd., 2012).

In Uganda, bioleaching and SX-EW process was used to extract copper metal from a cobalt-rich pyrite deposit from the Kilembe copper mine tailings near Kasese. However, the production in 2013 decreased to 376 metric tons (t) from 556 t produced in 2012 because of depletion of the stockpile (Kasese Cobalt Company Ltd., 2007). In Kenya, as noted earlier there are several copper deposits with varied elemental and mineralogical composition. These minerals have not been exploited because the methods available are expensive. In Tharaka Nithi County, copper deposits have been documented to assay 0.35 - 5 per cent   (Dubois and Walsh, 1970). In the study, alternative and affordable methods of extraction of copper were investigated. This was to enable extraction of available minerals for economic development.

2.3 Mineralogical and Chemical Composition of Various Titanium Ores

Titanium the ninth most abundant element in the Earth's crust, and found in most rocks and soils. Titanium minerals occur in many forms, such as titanium oxides, titanate, and silico-titanate (Gambogi, 2018). According to Gambogi (2018), the titanium-bearing minerals that have economic importance are ilmenite, leucoxene, and rutile. In India, titanium minerals are the largest and richest grades in the world (Murty *et al.*, 2007). Indian deposits are rich, in ilmenite grading at 50-53 percent TiO_2. The Chavra deposit of Kerala and Ratangiri deposit of Maharastra contains the mineralogical composition of 60 percent of TiO_2 (Gambogi, 2018). The beach sand found in the Chavara deposit contains minerals which grade at 60 percent TiO_2 (Babu, Vasumathi, & Rao, 2009). According to Babu *et al.* (2009), Orissa sand deposit grades at 48 percent TiO_2. Manavalakurichi deposit has minerals grading at 50 percent TiO_2.

In Eastern Quebec of Canada, the titanium ores present are Magpie titano-magnetite deposits grading at 12 percent TiO_2 (Heinz *et al.*, 2005). Further studies done at the Atlantic Coastal plain of the South-Eastern United States show that titanium occurs in coastal sand in form of minerals ilmenite ($FeTiO_3$), rutile (TiO_2), or leucoxene (Ellefsen & Bradley, 2018). In their study, Ellefsen & Bradley (2018) found that the titanium content in the sands graded at about 55 to 65 percent TiO_2. In Tanzania, Liganga titanium ore deposits contain rutile minerals grading at 13 percent (Yager, 2016).

In Kenya, titanium ores are found in the form of ilmenite containing 13.8 percent TiO_2 in western Kenya, and 3 - 14 percent ilmenite and rutile in Ras Ngomeni (Ogola, 1987). Another study done on river sand along the river Tiva in Kitui county reported ilmenite grading at 4.09 percent (Kennedy, 2016). Studies done on laterite in Tunyai Location in Tharaka Nithi County showed that ilmenite composition ranged between 1 - 5 percent (Mutembei, 2013). Recent studies on lateritic soils in Mbeu in Meru reported 3 - 6 percent rutile, while those in Gitara Kianderi and Gitong'o region in Tharaka Nithi County reported 1.6 and 2 percent rutile (Mutembei *et al.*, 2014; Warui *et al.*, 2015). Besides, a study at Kaharate in Ruiru shows 5 - 8 percent rutile and 5 - 6 percent Ti from rutile minerals from Kwale County (Yager, 2015; USGS, 2014; Warui *et al.*, 2015).

2.4 Concentration of the Titanium Ore Using Froth Flotation

Froth flotation is a process used for selectively separating hydrophobic concentrates from hydrophilic gangue during mineral processing (Florida institute of phosphate research, 2008). The process is used for the separation of a large range of sulfides, carbonates, and oxides of copper before further refinement (Bulatovic, 2007; Grobler *et al.*, 2009). The froth flotation process involves pulverizing the ore into a fine powder to increase surface area and mixing it with water to form a slurry. The mineral is made hydrophobic by adding suitable collector chemicals. Examples of anionic collectors are sodium oleate and fatty acids which occur in polar groups such as $RCOO^-$, $ROSO_3^-$, RSO_3^-, $ROCS_2^-$ and $R_2O_2PS_2$· The slurry formed which is hydrophilic gangue and hydrophobic mineral is then introduced to the frothing machine which is aerated to create bubbles (Kawatra, 1985) The air bubbles produced to support the mineral particles by reducing their density. This forms a stable froth which is then skimmed to another container. In the case of mineral with no sulfur element, chemicals are known as frothing agents are used (Grobler *et al.*, 2009).

Froth flotation is the standard method used to concentrate about 75 percent of all copper produced from copper industries in United States of America (U.S.EPA, 1994). The percentage composition of copper contained in the ores concentrated by froth flotation are; chalcopyrite 34.5, bornite 63.3, chalcocite 79.8, covellite 66.4, azurite 55.3, malachite 57.4 and chwsocolla 36.1 (Klein and Hurlbut, 1966). One of the advantages of flotation method in United States of America is the recovery of molybdenum [as molybdenite (MoS_2)] and other precious metals in the copper concentrate. Such recovery provides a significant portion of a mine's revenue (U.S.EPA, 1994). Titanium dioxide obtained from iron titanate is used as commercial grades and it ranges from 45 to 65.8 per cent. This grade is regarded as a huge resource for rutile. Extraction of titanium from this mineral has been, and still is very expensive. Therefore there is need for more cost effective methods of concentrating the ore to improve the concentration of titanium (Zhang *et al.*, 2011). According to Zhang *et al.* (2011), the commonly used process for low grade titanium ores is sulphate process. In this process, ilmenite is reacted with sulphuric acid at 150 to 180 ˚C, as shown in the equation 2.1.

$$FeTiO_{3(s)} + 5H_2O_{(l)} + 2H_2SO_{4(aq)} \xrightarrow{150\ -\ 180^{o}C} FeSO_4.7H_2O_{(aq)} + TiOSO_{4(aq)} \quad 2.1$$

Titanyl sulphate ($TiOSO_4$) hydrolyzes at 90˚C to Titanyl hydroxide ($TiO(OH)_2$) as shown in equation 2.2 (Baba *et al.,* 2013).

$$TiOSO_{4(aq)} + 2H_2O_{(l)} \xrightarrow{90^{o}C} TiO(OH)_{2(s)} + H_2SO_{4(aq)} \qquad 2.2$$

Titanyl hydroxide ($TiO(OH)_2$) is then calcined at 1000°C to rutile (TiO_2) as in equation 2.3.

$$TiO(OH)_{2(s)} \xrightarrow{1000\ ^{o}C} TiO_{2(s)} + H_2O_{(g)} \qquad 2.3$$

The concentration of titanium from ores containing titanomagnetite has been investigated (Zhang *et al.*, 2011). In their study, Zhang, *et al.* (2011), involved two steps. First, titanomagnetite concentration using the high-intensity magnet. The second step involved removing the remaining titanomagnetite in the tailing by froth floatation. It was observed that titanomagnetite had more optimal floatability compared to ilmenite mineral. The concentration of rutile from eclogite tailings has been investigated (Shaoxian *et al*., 2017). In their study, lead ion was used as the activator while sodium fluorosilicate was used as the depressant. The styryl phosphonic acid and n-octyl alcohol were used as collector chemicals. The feed ore grade used was off 4.5 percent TiO_2. After concentration, the concentrate obtained was grading at 84.47 percent TiO_2 with the recovery of 61.5 percent.

A closed-circuit flotation is another procedure that was developed by Shaoxian *et al.* (2017). The procedure involved a one-stage rougher flotation followed by two-stage scavenger flotation and lastly two-stage cleaner flotation. The process eventually obtained a concentrate of 92 percent TiO_2 with a final recovery of 70 percent. Extraction of titanium from such low-grade ores using froth flotation is very expensive and therefore there is a need for more cost-effective methods of concentrating titanium. Studies done on concentration of iron from laterites using froth flotation, has shown that the same technique could be applied in concentration of titanium (Mutembei *et al*., 2013). Further studies have also been done on laterites using the same technique to concentrate titanium in Mbeu, Gitong'o, Gitara Kianderi and Kaharate (Warui *et al.*, 2015). Therefore, in this study the method was applied on copper ores to concentrate titanium.

2.5 Concentration of Titanium Using Biomass

Studies done on the concentration of iron from laterite using biomass has shown that the same technique could be applied in a concentration of titanium (Mutembei *et al.*, 2013). Further studies have also been done on laterite using the same technique to concentrate titanium in Mbeu, Gitong'o, Gitara Kianderi and Kaharate (Warui *et al.*, 2015). The concentration of titanium in low-grade titanium-containing laterite soils was done using biomass (Warui, 2015). The mixture of laterite and biomass in the ratio of 1:10 respectively was thermally treated at between 500 and 800 °C in closed ceramic crucibles. The concentrate obtained was mainly rich in maghemite and titanium minerals. Further reduction of maghemite at temperatures above 800 °C led to the increase of the rutile in the tailing with more than 5 percent.

The X-ray diffraction spectra of the ore containing ilmenite before and after reduction using biomass is given by figures 2.1 and 2.2 below (Warui *et al.,* 2005). From the spectra the ilmenite peak was found present in both samples. This shows that temperatures of 500 – 700 ˚C were not appropriate for the reduction of ilmenite.

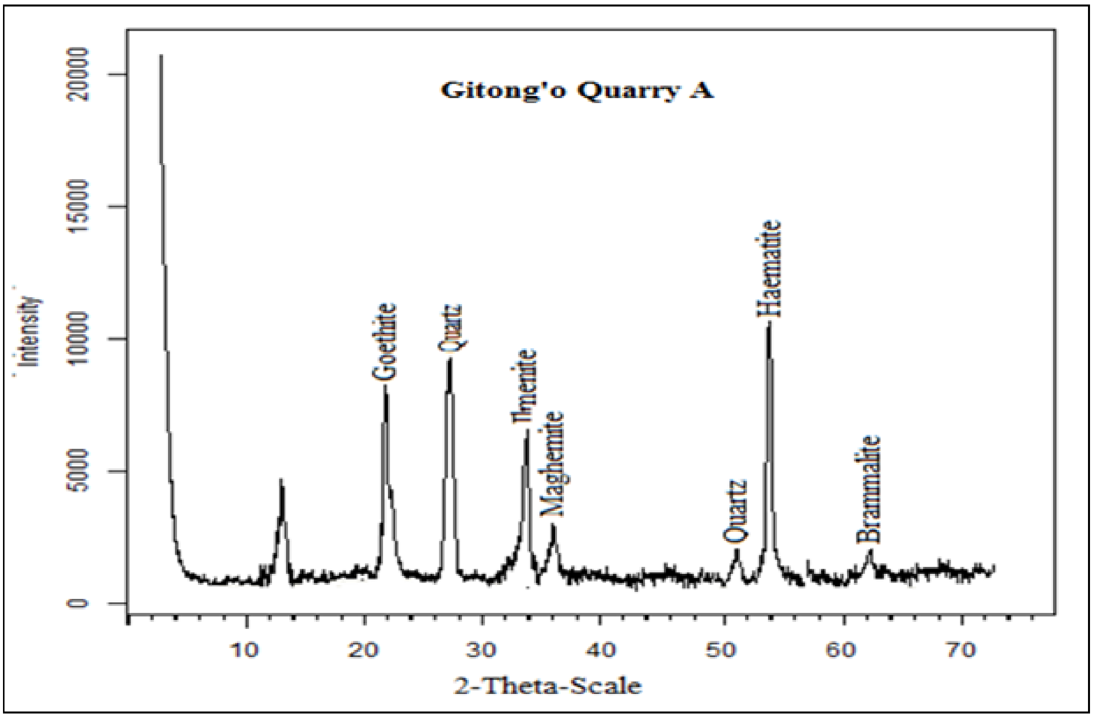

Figure 2.1: Spectra for raw laterites before heat treatment
Source: Warui *et al.,* 2005

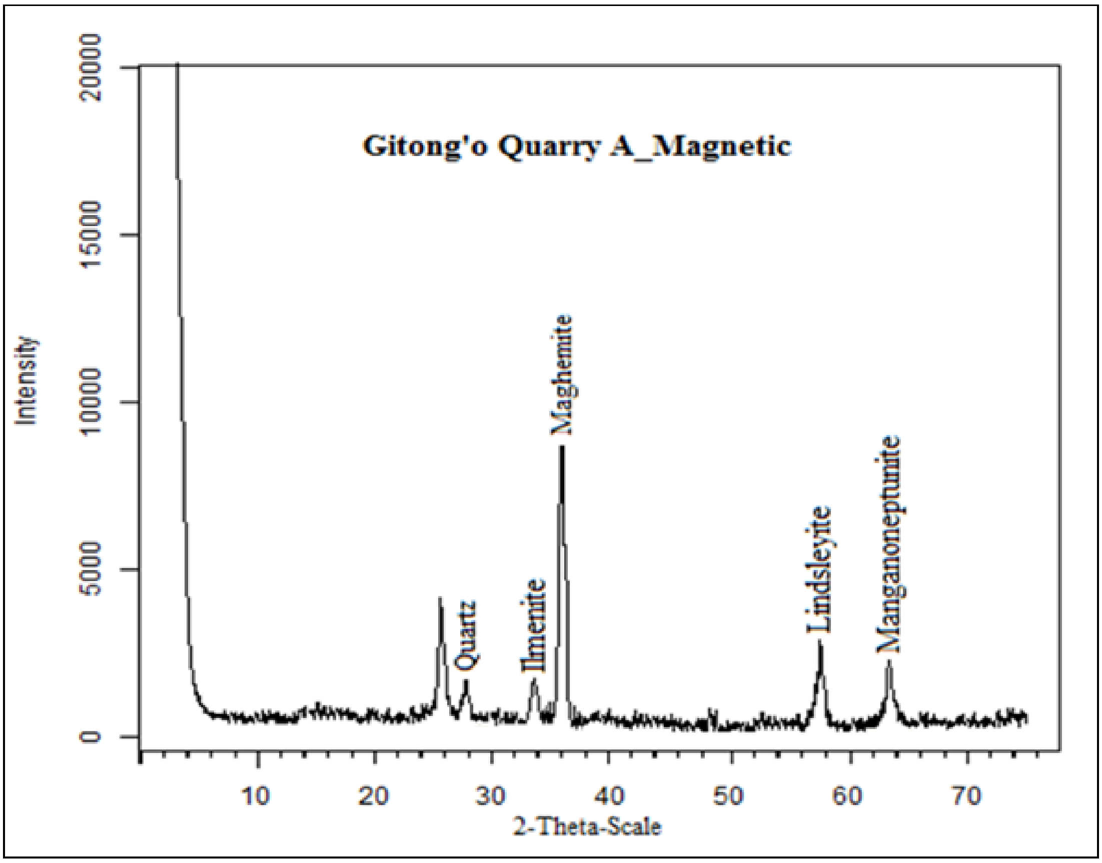

Figure 2.2: Spectra of the same sample after heat treatment with biomass
Source: Warui *et al.,* 2005.

According to Warui (2015), the gasification of biomass produced “syngas” consisting of primarily H_2, CO, CH_4, CO_2, and N_2. The specific composition of the produced syngas depends upon the type of biomass used, the origin of fuel, and the processing technique (Couto *et al.,* 2013). Ilmenite mineral is paramagnetic with relatively low magnetic susceptibility (Raieevio *et al.,* 1990; Warui *et al.*, 2015). Magnetic susceptibility of ilmenite can be increased significantly by roasting it in a reducing environment (Cui *et al.*, 2002). This makes it possible to separate ilmenite from most minerals (Steenkamp and Pistorius, 2003).

Further studies done by Mutembei *et al.* (2014), confirmed that the concentration of titanium in laterite soils was possible at the temperature range of 800 to 1200 °C. When laterite was reduced using charcoal at temperatures range of between 500 and 700 °C and separated using a strong magnet, ilmenite minerals were both found in the concentrate and the tailing. This confirmed that within the temperature range, ilmenite was not decomposed. An increase in temperatures from 800 to 1200 °C, ilmenite was reduced to rutile and metallic iron as shown in equation 2.4 and figure 2.3 (Mutembei *et al.*, 2014). The non-magnetic tailing that remained contained mainly rutile, and aluminosilicates.

$$FeTiO_{3(s)} + CO_{(g)} \xrightarrow{800-1200^\circ C} TiO_{2(s)} + Fe_{(s)} + CO_{2(g)} \qquad 2.4$$

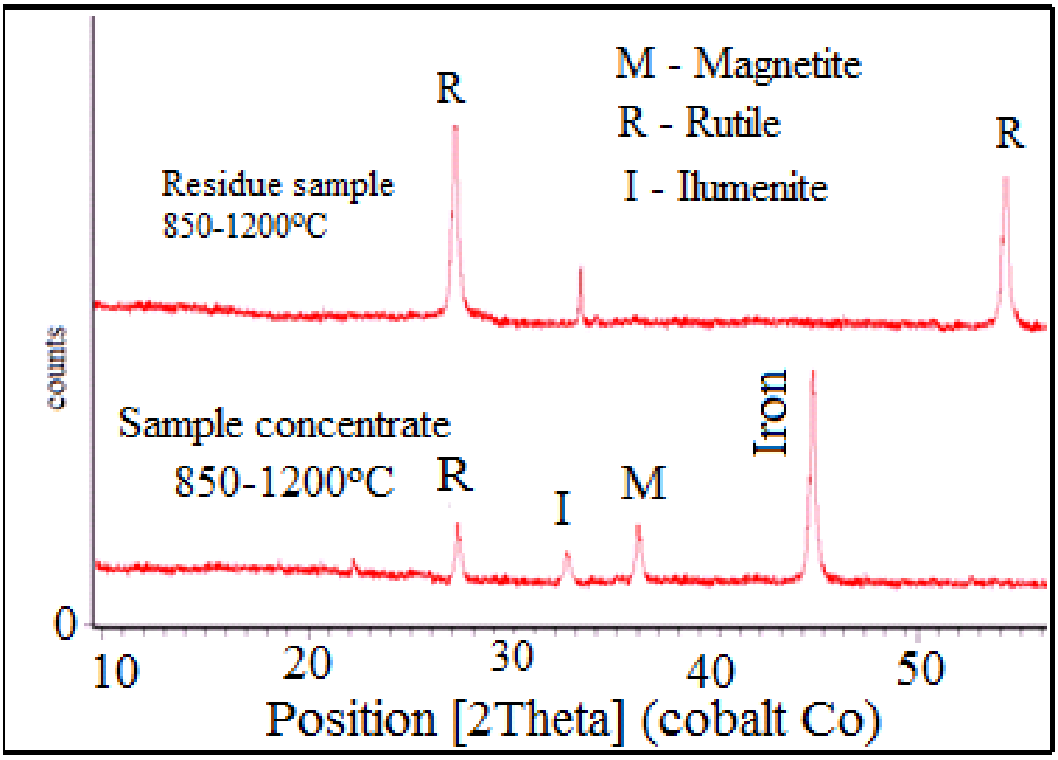

Figure 2.3: Spectra of residue sample and concentrate after heat treatment of 850 – 1200°C. **Source**: Mutembei *et al.*, 2014

At the above temperature range, rutile concentration increased from about 1-2 percent to about 2-5 percent in the tailing. According to Mutembei *et al.* (2014), hot carbon was also reported to reduce ilmenite to rutile as shown in equation 2.5.

$$FeTiO_{3(s)} + C_{(s)} \xrightarrow{850-1200^\circ C} TiO_{2(s)} + Fe_{(s)} + CO_{(g)} \qquad 2.5$$

Richards Bay Minerals (RBM), a South African company extract rutile from ilmenite by reduction process using carbon at the temperature range of between 730 and 800 °C (Williams & Steenkamp, 2006). Ilmenite is reduced to iron and a slag containing 85 percent TiO_2. Rutile is the primary product and other gases containing mainly 85 percent CO. In the current study, laterite rich in iron was added to the low iron-ilmenite containing chalcopyrite ore. The iron from laterite was used to enhance the conversion of ilmenite minerals to rutile and thereafter enabling magnetic separation. This method enabled the concentration of rutile from titanium ores with low iron content.

2.6 Other Methods Used to Concentrate and Extract Titanium Oxide

The recovery of rutile from synthetic industrial waste has proven to be a possible source of titanium (Ahmad *et al.,* 2017). In their study, Ahmad *et al.* (2017) investigated the influences of acid concentration and temperature of the caustic hydrothermal method when extracting the rutile from synthetic rutile waste from industries. The caustic hydrothermal method involved decomposition and the sulfate process. In the decomposition process, 100 g of rutile waste was decomposed with 200 g sodium hydroxide pellets at 550 °C. The decomposition lasted for 3 hours to obtain sodium titanate as shown in equation 2.6.

$$\mathrm{TiO_{2(s)} + 2NaOH_{(s)} \rightarrow Na_2TiO_{3(s)} + H_2O_{(g)}} \quad 2.6$$

The product obtained was washed with deionized water and then filtered and dried at room temperature. The dry Na_2TiO_3 obtained was mixed with three different sulphuric acid concentrations of 1, 2, and 3 M. The solutions were then heated at 70 °C, 80 °C and 90 °C for 4 hours respectively. The white residue obtained was then rinsed with deionized water and ethyl alcohol. The solid obtained was then dried at 80 °C for 4 hours to obtain TiO_2.

Studies on extraction of rutile from beach sand along the Ecuador coastline have been done by a process involving acid digestion and iron metal as a reducing agent (Perez & Sharadqah, 2018). Perez & Sharadqah (2018) first heated the samples to remove impurities. Such impurities were difficult to be removed by conventional physical or mechanical treatments. The second step involved mixing the samples with sodium hydroxide pellets and heating at 1100 °C as shown in equations 2.7 and 2.8.

$$\mathrm{FeO.TiO_{2(s)} + 2NaOH_{(s)} \xrightarrow{1100^\circ C} Na_2TiO_{3(s)} + FeO_{(s)} + H_2O_{(g)}} \quad 2.7$$

$$\mathrm{4FeO.TiO_{2(s)} + 8NaOH_{(s)} + O_{2(g)} \xrightarrow{1100^\circ C} 4Na_2TiO_{3(s)} + 2Fe_2O_{3(s)} + 4H_2O_{(g)}} \quad 2.8$$

After heating the samples, the products were hydrolysed to obtain hydrated titanium dioxide shown in equation 2.9 and 2.10.

$$Na_2TiO_{3(s)} + H_2O_{(l)} \rightarrow TiO_{2(s)} + 2NaOH_{(aq)} \qquad 2.9$$

$$TiO_{2(s)} \xrightarrow{H_2O} TiO_2.H_2O_{(aq)} \qquad 2.10$$

The last step of chemical treatment is acid digestion using iron metal as a reducing agent of the titanate. The reduction process produced high purity TiO_2 of about 92 percent. The recovery of ilmenite from red sand also known as Teri sand in Tamil Nadu in India has been investigated using the spiral method (Babu *et al., 2*009). The ore consisted of 5.5 percent of total heavy minerals out of which 3.7 percent was ilmenite. They used the spiral method followed by dry high-intensity magnetic separator and high tension separator. After processing the feed, the ilmenite concentrate obtained was 99.1 percent ilmenite with 3.5 percent recovery.

2.7 Methods of Copper Extraction

A variety of methods are used in various countries to concentrate and extract copper depending on the ore mineralogy (Wills & Napier, 2006). Since some of these ores are of low grade, the common method used for extraction is pyrometallurgy and hydrometallurgy process (Baba *et al.,* 2012). The pyrometallurgical process first involves the concentration of sulfide ore. The second step involves smelting the concentrate using furnaces to remove sulfur and other impurities. Then the copper is obtained by electrolysis of the melt as a pure copper cathode product.

Baba *et al.* (2012) investigated the hydrometallurgical process for the production of copper from copper ore. The method involves grinding the ore to fine particles and placing it into a heap. An acidic leach solution is poured over the heap so that the leach solution flows through the heap dissolving copper. At the bottom of the leached heap, a copper leachate solution is obtained. The leachate is then mixed with an immiscible organic solvent in a mixer. The organic solvent in the aqueous state extracts copper from the leach solution forming a loaded organic stream. The mixture of leach solution and organic extractant is then mixed in a large agitated tank. Later the mixture is transferred to a settler tank. The mixture separates into two phases, the upper copper loaded organic layer and the lower copper depleted acidic phase. The lower phase is then recycled as leachate for heap leaching. The organic phase is then transferred to an electro winning cell to refine copper.

Iron scrapping or cementation is another process which involves the displacement of copper from an aqueous solution of copper sulfate by iron metal (Habashi, 2009). The process occurs because iron is more reactive than copper. During the displacement process, copper deposit occurs (or cements) on the surface of iron metal. The deposit is then scraped off easily. This method was first used in China in the tenth century and later spread in Europe in the thirteenth century. The cementation method is however no longer in use because iron metal was very expensive at the time. Besides, the products obtained contained impurities (Annamalai & Murr, 1979; Habashi, 2009).

The cementation process is done in a large quantity of dilute copper-bearing solutions of about 0.5 to 3.0 grams of copper per liter concentration (Agrawal & Kapoor, 1982). Such solutions are produced *in-situ* from the dump, low percolation leaching of low grades ores. Solutions from waste obtained from mine and electro refining operations are also used. According to Agrawal & Kapoor (1982), the direct electro winning method of such dilute copper solution is usually not economical. Cementation from such a solution has been done by precipitation of an electropositive metal from solution by an electronegative metal. This is one of the ancient hydrometallurgical processes used to recover copper metal from dilute solutions. From their study, Agrawal & Kapoor (1982) observed that the cementation of copper with iron was a first-order reaction. This was concerning the copper ions concentration in the solution. The overall rate of the cementation process was controlled by mass transport in the aqueous phase. The rate of cementation increased with stirring speed, the surface area of the precipitant metal, increasing temperature and pH. Further studies on the cementation process showed that copper ion removal by cementation onto the iron rod was increasing with increasing velocity of the solution (Eltaweel *et al.*, 2014). The rate of copper ion removal was decreasing with decreasing initial concentration of copper ions and the whole process of cementation was diffusion controlled.

2.8 Copper Extract Using Aluminium

Investigation of copper cementation on some reactive metals like aluminium, iron, and zinc have been investigated (Karavasteva, 2005). The three reducing agents, tested at conditions of 60 °C and pH 1, were found to cement copper differently. From the study, aluminium displaced copper ions from solution less than either iron or zinc. Aluminium metal and its oxide are known to displace copper at low pH. Relatively neutral solutions, slow displacement is observed due to the passivity of the aluminium oxide layer (Arellanes *et al.,* 2014). In the presence of aggressive ions like chlorides and fluorides the oxide layer is attacked thus exposing the metal to further corrosion (Natishan & O'Grady, 2014; Arellanes *et al.,* 2014). Aluminium has not been used in the extraction of copper probably due to its corrosion effects. Its use in copper extraction means the huge cost for obtaining aluminium for a significance mining venture.

2.9 Copper Extraction Using Hydrazine Compounds

The preparation of hydrazine compounds from ammonia and urea has been studied (Adams & Brown, 1922; Schirmann & Bourdauducq, 2002). According to Schirmann & Bourdauducq (2002), when ammonia and urea were bubbled in a solution of sodium hypochlorite in a basic media, hydrazine was obtained as shown in equations 2.11 and 2.12.

$$2NH_{3(g)} \xrightarrow{NaOCl} H_2NNH_{2(aq)} + NaCl_{(aq)} + H_2O_{(l)} \qquad 2.11$$

$$(H_2N)_2CO_{(s)} + NaOCl_{(aq)} \xrightarrow{2NaOH} N_2H_{4(aq)} + H_2O_{(l)} + NaCl_{(aq)} + Na_2CO_{3(aq)} \qquad 2.12$$

Hydrazine compounds react with alkanones to form hydrazine which are also strong reducing agents as shown by equation 2.13 (Day and Whiting, 1988).

$$(CH_3)_2CO_{(aq)} + N_2H_{4(aq)} \rightarrow 2H_2O_{(l)} + [(CH_3)_2CN]_{2(aq)} \qquad 2.13$$

Amine and urea compounds are found from animal wastes (also known as biomass), a by-product of protein decomposition (Eller *et al.,* 2000; Kugeria *et al.,* 2018). From equations 2.8 and 2.9 above, animal waste can be used to prepare hydrazine compounds if they are treated with chlorine in alkaline media. Hydrazine is known as chelates makers with metal ions **(**Adams & Brown, 1922; Schirmann & Bourdauducq, 2002; Mostafa, 2011). Hydrazine can effectively be employed in the reduction of various metal cations to the elemental state (Chen & Lim, 2002). The reduction potential of hydrazine in a basic environment occurs as shown in equation 2.14.

$$N_2H_{4(aq)} + 4OH^-_{(aq)} \longrightarrow N_{2(g)} + 4H_2O_{(l)} + 4e^- \quad E^0 = +1.15V \qquad 2.14$$

This shows that hydrazine can effectively be employed in the reduction of various metal cations to the elemental state. This was reported by Chen and Lim (2002) while investigating the recovery of copper in synthesized wastewater in batch reactors. In their study, they used hydrazine as the reducing agent as shown in equations 2.15 and 2.16.

$$2Cu^{2+}_{(aq)} + N_2H_{4(aq)} \longrightarrow 2Cu_{(s)} + N_{2(g)} + 4H^+_{(aq)} \qquad 2.15$$

$$Cu^{2+}_{(aq)} + 2N_2H_{4(aq)} + 2OH^-_{(aq)} \longrightarrow Cu_{(s)} + N_{2(g)} + 2NH_{3(g)} + 2H_2O_{(l)} \qquad 2.16$$

Fresh chicken manure, in particular, is used as an organic fertilizer and usually contains about 0.9 to 1.5 percent nitrogen (Foreman and Long, 2013). Chicken manure has pH ranging from 5.6 to 9.4. It has inorganic forms of N (NH_4-N and NO_3-N), accounting for approximately 14 percent of the total N. The remaining portion of the total N (73 percent) occurs in the organic form (Sharpley & Mayor, 2000). Nitrogen is found in organic matter in the form of amines compounds which are derivatives of ammonia (McMurry, 1992; Kugeria *et al.,* 2018). Important amines include amino acids, biogenic amines, trimethylamine and aniline (Eller *et al.,* 2000). Chicken dung is rich in urea, nitrogenous compounds, and proteins which can be used to prepare hydrazine compounds (Burford & Williams, 2001; Kugeria *et al.,* 2018).

Currently, hydrazine is used as a foaming agent in the process of preparing polymer foams Schirmann & Bourdauducq, 2002. It is also used as a precursor to polymerization catalysts, pharmaceuticals process, and agrochemical processes (Toki *et al.,* 1994). Hydrazine has been used as rocket fuels (Clark, 1972; Mitchell *et al.,* 2007). It is also used in both nuclear and electrical power plants (Tsubakizaki *et al.,* 2009). Hydrazine is also used as a precursor in hydrazones preparation by reacting with ketones and other hydrazones (Day and Whiting, 1988).

2.10 Methods of Analysis

There are several instrumental analytical methods that can be employed to determine the concentration level of various elements in various samples. The most predominant methods for elemental analysis are: inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS), atomic emission/ fluorescence spectrometry (AES/AFS), neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS), anodic stripping voltammetry (ASV), and X-ray fluorescence (XRF) (Helaluddin *et al.,* 2016). In this study, AAS and AES/AFS were used because background interferences can easily be corrected such as interference that occurs due to light scattering by particles in the flame. Besides, it is a technique that is suitable for analysis of about 70 elements (The Perkin-Elmer Corporation, 1996; Helaluddin *et al.,* 2016).

X-ray fluorescence spectroscopy (XRFS) is an elemental analytical technique for elements from sodium to uranium in the periodic table (Beckhoff *et al.,* 2007). This modern method was chosen because it requires minimal sample preparation which includes solid samples. The X-ray powder diffraction method is a mineralogical analytical technique used over 40 years (Brindley, (1980). That is why the method was used in this study. Fourier transform infrared (FTIR) spectrometry is another technique which was used in this study. It was used because it overcomes most limitations that are encountered with dispersive instruments. Besides, it was chosen because it is able to measure all the infrared frequencies simultaneously, rather than measuring single frequency (Griffiths and Holmes, 2002). The other technique used was the mass spectrometry (MS). The method was used because, in today’s technological world, computer simulation of ionization, and fragmentation processes are easily done (Tureček and McLafferty, 1993). The use of these processes in mass spectrometer has made the technique to be a primary tool for assigning structures to a molecule. The principles of these methods are discussed in the following subsections.

2.10.1 Atomic Absorption Spectroscopy

The modern atomic absorption instruments are designed to measure both atomic absorption and atomic emission (The Perkin-Elmer Corporation, 1996; Jeffery *et al.,* 1989). According to The Perkin-Elmer Corporation (1996), the working concepts of both atomic absorption and atomic emission are quite different. In atomic emission spectroscopy, the Air-acetylene flame or plasma is preferred for the determination of most elements. The temperature given by this flame is about 2,300 °C. The flame produces heat energy that converts the sample aerosol into an atomic vapour. The atoms are then elevated from the ground state to an excited state. The excited state is usually unstable and therefore, the atoms spontaneously return to the "ground state". As they return to the ground state they emitting light is detected by the detector in the instrument. The intensity of the light emitted is proportional to the concentration of the analyte of interest in the solution sample.

In atomic absorption spectroscopy, the technique makes use of absorption to obtain the concentration of the analyte in a sample (The Perkin-Elmer Corporation, 1996). In this technique, the only function of the flame is to aspirate the sample aerosol into atomic vapour. The atoms in the vapour then absorb light from the primary light source or hollow cathode lamp and enter the excited state. The amount of light absorbed by the analyte in a given sample is proportional to the number of atoms in the atomic vapour. This enables the quantitative determination of all analyte present in a sample (García & Báez, 2012). The use of a specific hollow cathode lamp of a given wavelength allows the specific determination of individual elements.

The AAS technique requires standards with known analytic content to establish the relation between the measured absorbance and the analytic concentration and relies therefore on the Beer-Lambert law given in equation 2.17.

$$A = -\log T = -\log \frac{I}{I_o} \qquad 2.17$$

Where T is transmittance**,** α is the absorption coefficient, L is path length, I_o- incident radiation at a given wavelength, I - transmitted intensity or attenuated radiations.

The AAS method is usually free from any spectral or radiation interferences. This occurs because every metal has its unique characteristic absorption wavelength. Depending on varying environmental matrices, information like dissolved metals, total recoverable metals, total metals, and suspended metals can easily be obtained (Mendham *et al.,* 1989). According to Mendham *et al.* (1989), the most common interferences that occur in atomic absorption are chemical interferences. This occurs when the sample being analyzed contains a thermally stable compound together with the analyte. When the stable compound, is not decomposed by the energy of the flame, then chemical interference occurs. This leads to a reduced number of atoms in the flame that are capable of absorbing light energy.

Chemical interferences are controlled by the use of a higher temperature flame or by the addition of a releasing agent solution (The Perkin-Elmer Corporation, 1996). A releasing agent is usually a competing cation that when added to the sample solution will preferentially react with the interference and remove it from the analyte. At higher temperatures, flame produces additional energy. This energy breaks down a compound that is stable in a lower temperature flame thus removing the interference. Another interference that is encountered in atomic absorption is Ionization interferences (The Perkin-Elmer Corporation, 1996). This occurs when the flame temperature produces enough energy that causes complete removal of an electron from an atom, creating an ion. This ionic state depletes the number of ground-state atoms thus reducing atomic absorption. Ionization interferences can be removed by the addition of an excess of an easily ionized element to the standards, samples, and blank. The easily ionized elements are alkali metals (K, Na, Rb, Cs) because of their very low ionization potential (The Perkin-Elmer Corporation, 1996).

The amount of energy used during transitions is in the form of photons (García & Báez, 2012). This light is measured by a detector which compares them to the standard wavelengths of the sample originally passed through the sample. This technique is preferred more due to its lower detection limits and for trace analysis in a wide range of samples. According to García & Báez (2012), the study of trace metals in wet and dry precipitation has increased in recent decades. This is because trace metals have adverse environmental and human health effects. Anthropogenic activities have substantially increased trace metal concentrations in the atmosphere. In recent decades, heavy metal concentrations have increased not only in the atmosphere but also in pluvial precipitation.

2.10.2 The X- Ray Diffraction

The X-ray diffraction spectrometry (XRD) is a non-destructive method used for characterizing crystalline substances (Myers, 2002; Bunaciu *et al.*, 2015). According to Bunaciu *et al.* (2015), the XRD technique provides precise information on structures, orientations, crystal strain, crystallinity, and crystal defects. The X-ray diffraction peaks are produced by constructive interference of the monochromatic beam of X-rays. These rays are scattered at specific angles from each set of crystalline lattice planes in a sample as given in figure 2.4.

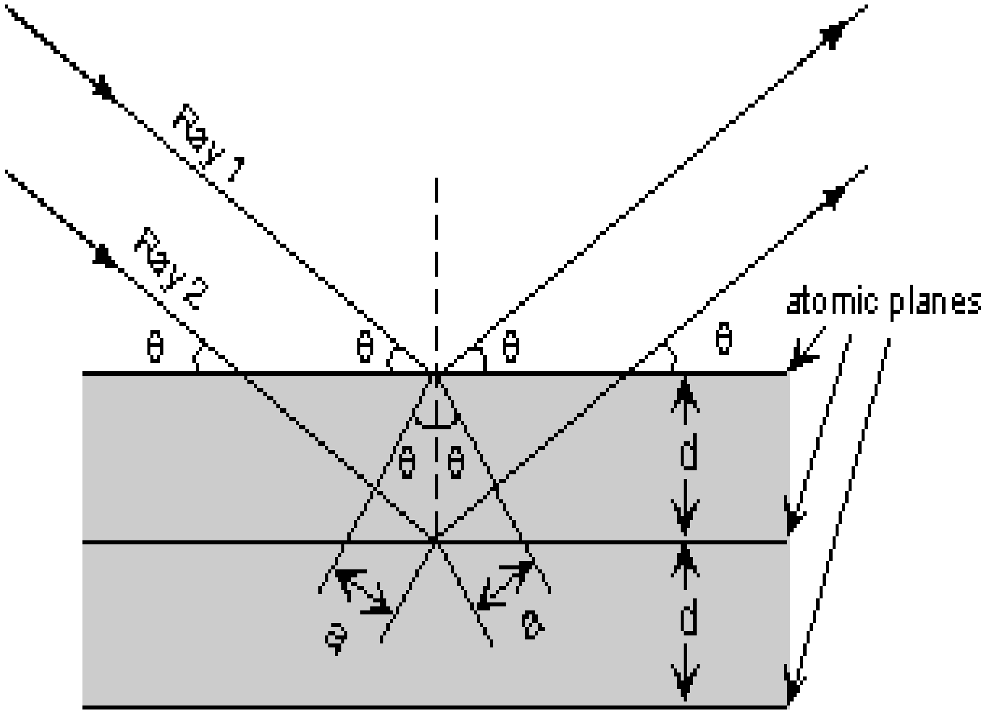

Figure 2.4: Bragg's Law Reflection (Myers, 2002)

The peak intensities are determined by the distribution of atoms within the crystal lattice. The X-ray diffraction pattern usually obtained is a finger print of periodic atomic arrangements in a given material (Jones and Childers, 1993). X-ray powder diffraction analysis utilizes X - rays of a known wavelength that is passed through a sample for identification of the crystal structure. The wave nature of the X - rays diffracted by the lattice of the crystal, gives a unique pattern of the peaks at different angle 2θ. This condition is given by the Bragg equation shown in equation 2.18 (Myers, 2002).

$$2d\sin\theta = n\lambda \qquad 2.18$$

Where *d* is the spacing between diffracting planes, *λ* is the wavelength of the beam, θ is the incident angle, *n* is an integer which is a multiple of the wavelengths for the phases of the nth number of beams that strikes the layers of atoms in a mineral.

Since every mineral has a set of unique d - spacing, the X-ray detector moves around the sample and measures the intensity and the position of these peaks (diffraction angle 2θ). The measurement of the d - spacing is compared with the standard referencing pattern (Moore and Reynolds, 1997). The X-ray diffraction is a popular analytical technique, which has been used for the analysis of the following: molecular and crystal structures; qualitative identification of various compounds; quantitative resolution of chemical species; measuring the degree of crystallinity; isomorphous substitutions; stacking faults; polymorphisms; phase transitions and particle sizes (Das *et al.*, 2014). Thus XRD technique can analyze structural features with other ambiguities of a wide range of materials. Such materials are inorganic catalysts, superconductors, bimolecular, glasses, and polymers and so on. According to Das *et al.* (2014), geologists use this technique as a reliable and fast characterizing tool to compile major and trace elements. They also use it to calculate the degree of clay mineralization and phase analysis. Besides, XRD spectroscopy is used to measure specimen purity and find out mismatch lattice. It also deduces stress and strains, calculates unit cell dimensions, and perform quantification.

2.10.3 The X - Ray Fluorescence Spectroscopy

The X-ray fluorescence (XRF) is the technique that involves the emission of characteristic fluorescent X-rays from an atom. This occurs when an atom has been excited by bombarding with high-energy gamma radiation or X-rays (Kalnicky & Singhvi, 2001). According to Kalnicky & Singhvi (2001), the technique is widely used for elemental analysis of materials like metals, soils, glass, mineral rocks and ceramics. The method is also widely used in geochemistry research, forensic science, archaeology, art objects, etc. XRF is also a non-destructive and multi-element analytical method for both quantitative and qualitative analysis. Each element is known to have an electronic orbital of a unique characteristic energy. The technique involves the ejection of an electron to the higher electronic state by using a high energy photon from a primary radiation source. After this, another electron from an outer shell drops into its place. Each of the transitions from one energy level to the other yields a fluorescent photon which contains characteristic energy. This energy is equal to the difference in energy of the initial and final orbital. The energy characteristics are then calculated using Plank’s law, given in equation 2.19.

$$\lambda = \frac{hC}{E} \qquad 2.19$$

Where; λ is the wavelength, *h*is plank's constant, *E* is the energy of the electron**,** C is the velocity of light.

There are two types of dispersive analysis in XRFS spectroscopy, energy dispersive and wavelength dispersive analysis (Kalnicky & Singhvi, 2001). In energy dispersive analysis, the fluorescent X-rays emitted by the sample are directed into a detector which produces a continuous signal. The signal produced is processed by a multichannel analyzer (MCA) which produces an accumulating digital spectrum that is transformed into analytical data. In wavelength dispersive analysis, the fluorescent X-rays emitted by the sample are passed through the diffraction grating monochromator. Usually, the diffraction grating monochromator is made of a single crystal. A single X-ray wavelength is selected by varying the angle of incidence of rays and take-off on the crystal. After sorting, the intensity of each characteristic radiation produced is directly proportional to the amount of each element in the material.

2.10.4 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is a method which obtains an infrared spectrum of absorption or emission from a liquid, solid, or gas sample (Griffiths and Holmes, 2002; Griffiths and Hasseth, 2007). The FTIR spectrometer usually collects high-spectral-resolution data over a wide spectral range. The spectrometer begins by generating a broadband light usually from a black-body radiator containing the full spectrum of wavelengths to be measured. The light is collimated and directed to a beam splitter into a Michelson interferometer. This is a unique configuration of mirrors which are moved by a motor. The 50 percent of the light is refracted towards the fixed mirror while another 50 percent is transmitted towards the moving mirror. Light from the two mirrors is reflected in the beam splitter and some fraction of the original light passes into the sample compartment. In the compartment, the light is focused on the sample. On leaving the sample compartment the light is refocused on to the detector. The difference in optical path length between the two arms to the interferometer is known as the retardation or optical path difference (OPD). The raw data (also known as interferogram) is obtained by varying the retardation and recording the signal from the detector for various values of the retardation. Afterwards, a computer takes all the generated data and works backward to infer on the absorption for each wavelength. A systematic diagram of how Michelson interferometer works is given in figure 2.5 (Griffiths and Holmes, 2002).

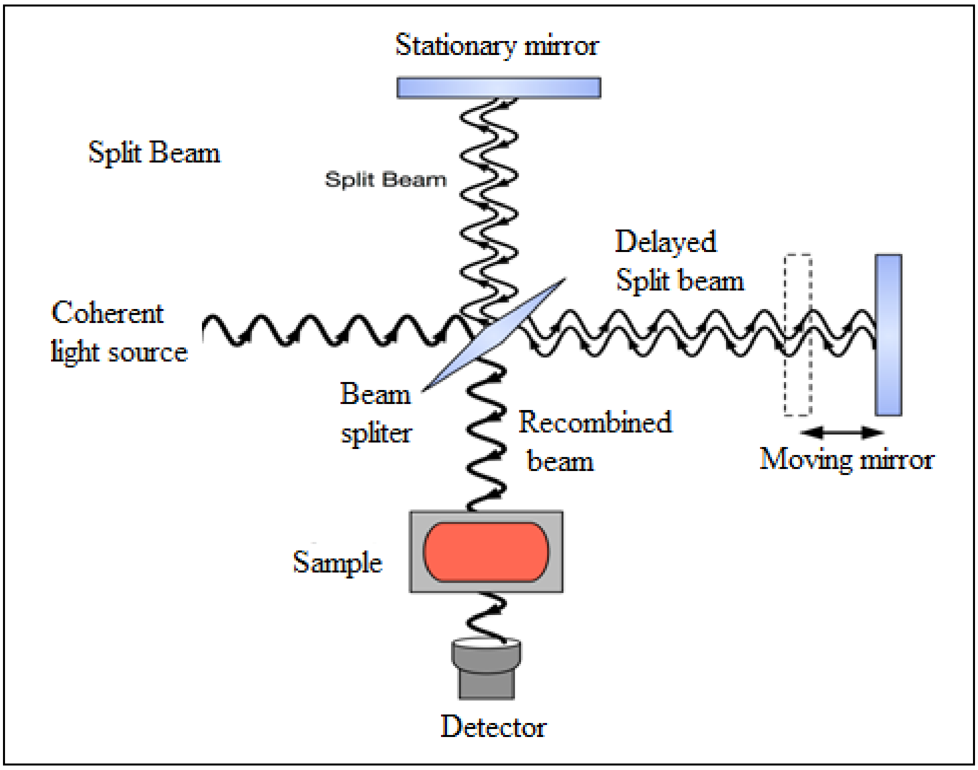

Figure 2.5: Schematic Diagram of a Michelson Interferometer, Configured for FTIR

In the absence of a sample in the sample compartment, the form of the interferogram depends on factors such as the variation of source intensity and splitter efficiency with wavelength. The results are a maximum at zero retardation. However, constructive interference may occur at all wavelengths, followed by a series of "wiggles". At this position, zero retardation is determined accurately by finding the point of maximum intensity in the interferogram. When a sample is present the background interferogram is modulated by the presence of absorption bands in the sample (Griffiths and Holmes, 2002).

2.10.5 Mass Spectrometry (MS)

This is an analytical technique that ionizes chemical species and later sorts the ions into a spectrum based on their mass-to-charge ratio (Sparkman, 2000). According to Sparkman (2000), the technique is widely used in many different fields and is applied to both pure samples as well as complex mixtures. In the MS procedure, a sample that is either solid or liquid is first vaporized. The sample in the gaseous state is then passed into the ionization chamber. The chamber contains an electrically heated metal coil that gives off a stream of electrons. The atoms or molecules in the sample are bombarded by this stream of electrons thus knocking off electrons from the gaseous molecules or atoms. This causes some of the sample molecules to break into a positively charged ion. Most of the ions formed have a +1 charge and it is difficult to remove a second electron from an already positive ion. The positively charged ions are then repelled from the ionization chamber (which is positively charged). The charged ions are then directed through negatively charged slits that focus and accelerate them into a beam. The beam is then passed through a magnetic or electric field where it is deflected depending on both masses of the ion and charge of the ion. Here, the lighter ions will be deflected more than heavier ones and ions with a greater charge than +1 are deflected more. The deflected beam is focused on the ion detector in order of increasing mass/charge ratio. When an ion hits the detector, the charge is neutralized, and this generates an electrical current. The electric current produced is usually proportional to the abundance of the ions. The electric current is then sent to a computer for analysis. The results are displayed as spectra of the relative abundance of detected ions as a function of the mass-to-charge ratio.

The atoms or molecules in the sample are identified by correlating known masses of atoms, molecules or masses of a characteristic fragmentation pattern (Tureček and McLafferty, 1993). According to Tureček and McLafferty (1993), the precise structure of the molecule is deciphered through the set of fragment masses, the interpretation of the mass spectra will require the combined use of several techniques. The first method for the identification of unknown compounds is to compare its experimental mass spectrum against that of the library of mass spectra. If no matches’ result from the search, then a manual interpretation is done. Another method is by use of software-assisted interpretation of mass spectra. Today, computer simulation of ionization and fragmentation processes occurring in mass spectrometer is the primary tool for assigning structure to a molecule.

CHAPTER THREE

MATERIALS AND METHODS

3.1 The Overview of the Study Area, Sample Collection and Preparation

The study area lies within the semi-arid region of Tharaka North Sub County in Tharaka Nithi County. Several mineral deposits were found in Maragwa and Kamwathu sub-locations (Kugeria *et al.*, 2018; Kugeria *et al.*, 2019). Several deposits were assessable having been exposed due to agents of erosion. However, there were several deposits found in both sub-locations which required to be explored to determine their viability.

3.1.1 The Study Area

Samples for analysis were obtained from selected areas in Maragwa location, Tharaka North Sub - County in Tharaka Nithi County. In the location, two sub-locations were selected namely Kamwathu and Maragwa. The geographical locations of the deposits lies within the UTM 37M 0393699, 9973201, 37M 0395154, 9972356, 37M 0400793, 9979152, and 37M 0399821, 9979449. The map of the study area is given in Figure 3.1.

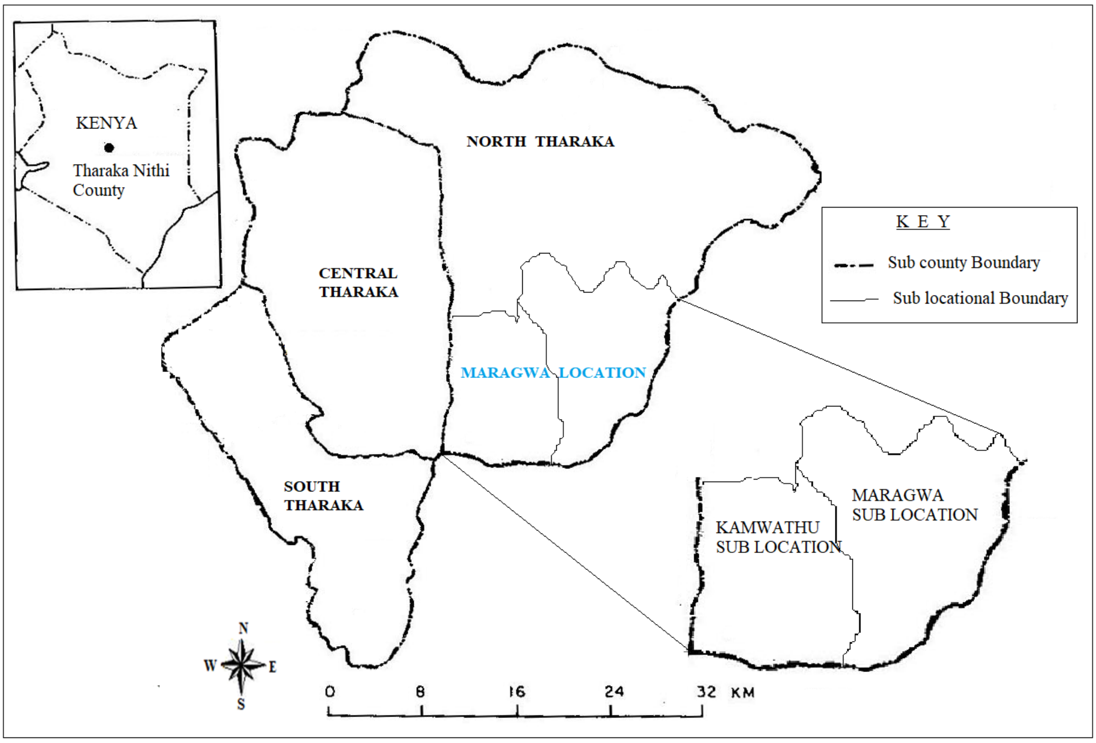

Figure 3.1: A Map of Tharaka indicating the Study Area in Maragwa Location
Source: Mutembei *et al.*, 2014

In the region of the study, copper mineral occurs in reefs that are almost parallel to each other traversing from North East to the southwest direction. The reefs are spaced at about 1.0 to 1.5 kilometres apart.

3.1.2 Sample Collection and Preparation

Five quarries from each of the two sub-locations were randomly selected for sampling. The quarries selected were spaced about one to two kilometres apart. The quarries selected from Kamwathu were coded as 3227, 3230, 3231 3232 and 3233. Those of Maragwa were coded as 3234, 3238, 3240, 3242 and 3244. From each of the quarries, three sampling sites were identified within a distance of about 10.0 m apart. A pick mattock was used to dig and break the rocks. A shovel was used to scoop out the mineral samples. About a kilogram of the mineral samples was obtained from each of the selected sites at a depth of 30.0 cm (named as level A). The mineral samples were crushed using a hummer into small particles ranging between 4.0 and 8.0 meshes. The crushed mineral particles were then mixed carefully. About two kilograms of the mixture were obtained and packed in labelled plastic bags. The samples were labelled as follows; 3227A, 3230A, 3231A 3232A, 3233A, 3234A, 3238A, 3240A, 3242A and 3244A. Another sample was obtained the same way at one-meter depth (named level B) from each quarry. The samples were then labelled as follows; 3227B, 3230B, 3231B 3232B, 3233B, 3234B, 3238B, 3240B, 3242B and 3244B.

Laterite samples for reduction of the ores were obtained from Gitong'o quarry in Tunyai location, in Tharaka Nithi County. At the quarry, three sampling sites were selected within a distance of about 10.0 m apart. A pick mattock was used to dig and break the rocks. A shovel was then used to scoop out the laterite samples. The samples were crushed into small particles ranging between 4.0 and 8.0 meshes. The laterite samples were mixed carefully and 5 kg of it packed in plastic bags and labelled. The laterite samples and the mineral samples were then transported to the laboratory for further preparation. At the laboratory, all the samples were transferred into the oven for drying at 105 ^{o}C for 9 hours and later ground to 60.0 meshes (250 microns) using a ball mill.

3.2 Mineralogical and Chemical Composition

3.2.1 Sample Analysis Using XRD

The X-ray diffraction was carried out using an X'Pert³ MRD XL diffractometer model. The diffractometer was configured using the PreFIX (pre-aligned, fast interchangeable X-ray) concept for the soil samples. A 3.0 g portion of the sample was put into the sample holder and loaded into the goniometer, and the measurement is taken.

3.2.2 Sample Analysis Using XRFS

The elemental composition of the samples was done using the X-ray fluorescence spectrophotometer model S1Titan 300, from Bruker Company. The analyzer was configured with calibrations that were optimized for the soil samples. Each sample was placed in the XRF cup and loaded into the analyzer. The samples were then irradiated with a high energy-dispersive X-ray beam and the measurement taken.

3.2.3 Sample Analysis Using AAS

A mass of 0.1 g of the sample was put in a 100 -mL plastic measuring cylinder. A 1.0 mL of concentrated aqua-regia (1:3 nitric acid to hydrochloric solution) was added followed by 3.0 mL of 1.0 M hydrofluoric acid. The sample was then left to digest for 8 hours. 50.0 ml of 0.92 M boric acid was added then allowed to react for one hour. The solution was then topped up to mark using distilled water. The Syenite (SY-3) and Mount Royal Gabbro (MRG) rock standards were used to calibrate the AAS. The standards were weighed and digested following the same procedure used to digest the samples. Samples were then analyzed alongside the standards (Mutembei *et al.*, 2013).

3.2.4 Loss of Ignition

A mass of 1.0 g of the samples was weighed into crucible boats and then transferred into the furnace. The samples were then heated to 1,000 °C for four hours to ensure all organic materials were burnt. The samples were removed from the furnace and then cooled in a desiccator. The cooled samples were re-weighed and the percentage difference calculated and recorded (Mutembei *et al.*, 2013; Waithaka *et al.*, 2014).

3.3 Concentration of Titanium in the Ores Using Biomass, Biomass – Laterite Mix Vis a Vis Froth Floatation

3.3.1 Concentration of Titanium in the Ores Using Biomass

3.3.1.1 Biomass Collection and Preparation

Biomass was collected from the municipal waste and sundried for five days to a constant mass. After drying they were ground using a pestle and a mortar to sizes of 30 - 35 meshes. Part of the biomass was used in part 3.3.2.

3.3.1.2 Concentration Chamber for Titanium

The concentration chamber was assembled in accordance with Waithaka *et al.* (2014). It was made up of a hollow ceramic tube with a length of 60.0 cm and a diameter of 15.0 cm. Both ends of the tube were reduced to 3 cm using steel tubes which served as gas inlet and outlet. The gas inlet was sealed with clay to prevent gas leakage from the chamber. A thermocouple was fitted into the chamber through the outlet opening. The chamber used a charcoal heated heat exchanger as a source of energy to fire its content. The chamber was then covered with a ceramic cover to minimize energy loss. A current of air from an air cylinder was allowed through the gas inlet. The flow rate of air to the chamber ranged between 0.5 - 0.7 cm^3 per second. The gas flow meter model 270134.003 from TA Instruments was used to regulate the airflow. The temperature inside the chamber was regulated by the opening and closing of the air hole. A schematic representation of the chamber and its heat exchanger is given in figure 3.2.

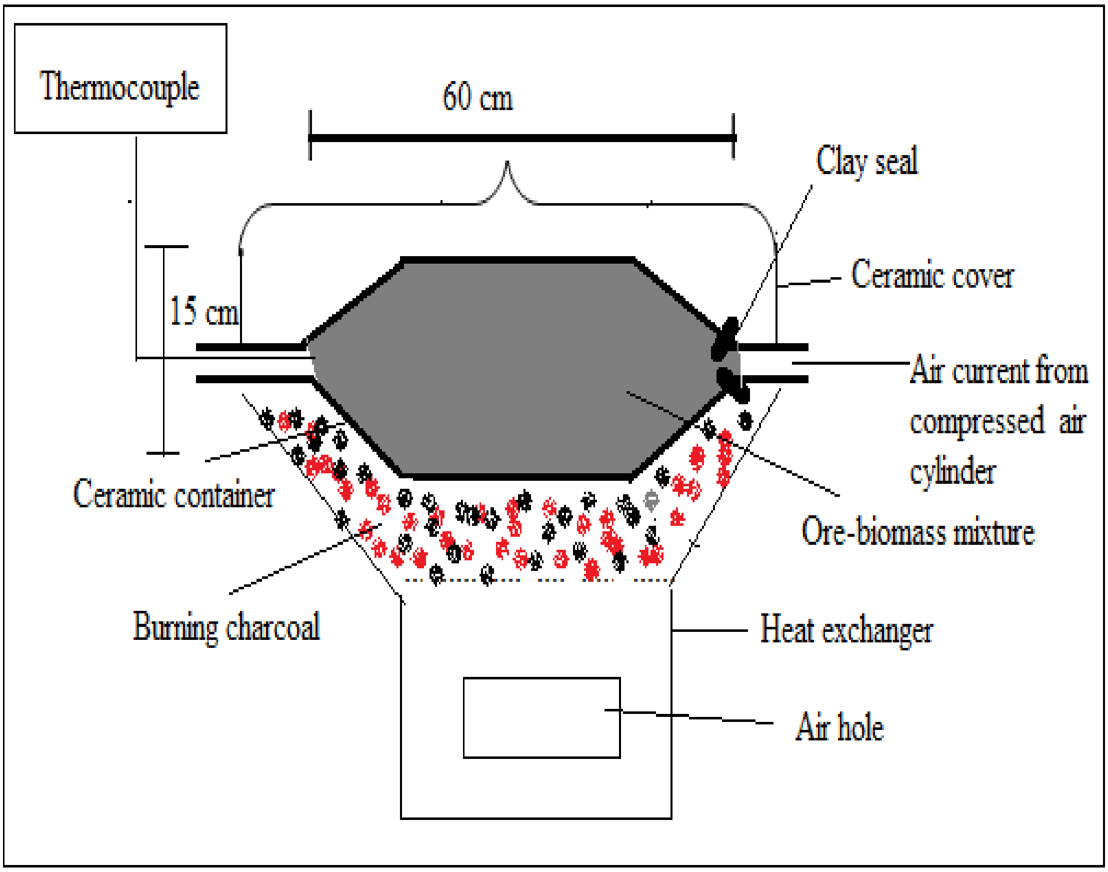

Figure 3.2: Titanium Concentration Chamber Set-Up
Source: Waithaka *et al*., 2014.

3.3.1.3 Optimization Studies

A mixture of 5.0 g of the ground mineral sample and 1.0 g of ground biomass was put into the concentration chamber. The chamber was then placed on the heat exchanger. The mixture was then heated at a temperature range of 800 – 900 °C for two hours while monitoring the temperature using a thermocouple. A current of air was allowed to pass through from an air cylinder at a flow rate of 0.5 - 0.7 cm^3 per second. After two hours, the samples were allowed to cool to room temperature. The samples were then spread on a wooden flat surface. A permanent horseshoe magnet of about 92 milliTeslas was wrapped in a polythene paper. The magnet was passed over the sample to pick the magnetic portion as per Mutembei *et al.* (2013) and Waithaka *et al.* (2014). Both the tailing and the concentrate were analyzed for chemical constituent and mineralogy using AAS and XRD. The experiment was repeated by varying the mass of the mineral sample from 5.0 g to 50.0 g at an interval of 5.0 g. The mass of the biomass was maintained at 1.0 g. The flow rate and the temperature were held constant at 0.5 - 0.7 cm^3 per second and 800 - 900 °C respectively.

3.3.2 The Concentration of Titanium from Ore - Laterite Mixture Using Biomass

A mixture of 5.0 g of the ground mineral sample, 2.0 g of laterite and 1.0 g of biomass was put into the concentration chamber. The equipment was then placed on a heat exchanger. The mixture was heated at a temperature range of 800 - 900 °C for two hours while monitoring the temperature using a thermocouple. A current of air was allowed to pass through from an air cylinder at a flow rate of 0.5 - 0.7 cm^3 per second. After two hours, the samples were cooled to room temperature. The samples were then spread on a wooden flat surface. A strong horseshoe magnet was wrapped in a polythene paper. The magnet was passed over the sample to pick the magnetic portion as per Mutembei *et al.* (2013) and Waithaka *et al*. (2014). Chemical analysis for both the tailing and the concentrate samples were done using AAS and XRD.

The above procedure was repeated by varying the mass of the mineral sample from 5.0 g to 40.0 g at an interval of 5.0 g. The mass of the biomass was maintained at 1.0 g and that of laterite at 2.0 g. The flow rate and the temperature were held constant at 0.5 - 0.7 cm^3 per second and 800 - 900 °C respectively. Chemical analysis for both the tailing and the concentrate samples were done using AAS/XRF and XRD.

3.3.3 The Concentration of Titanium Using Froth Flotation

3.3.3.1 Optimization Studies for Frother Chemicals

A mass of 50 g of the sample was put into the flotation cell, provided by Mines and Geology, Kenya, and 750.0 mL of the distilled water added. 10.0 mL of the oleic acid and 5.0 mL of the bromoformium solution was added into the flotation cell. The agitation of the mixture was done for five minutes at 1400 revolution per minute. The froth produced was filtered to obtain a residue. The residue obtained from the froth and that left into the flotation cell were both dried into the oven at 40 °C. After drying, the residues were analyzed using AAS. The procedure was repeated by varying the volume of oleic acid from 10.0 mL to 20.0, 30.0, and 40.0 mL at an interval of 10.0 mL. The volume of the bromoformium collector was maintained constant at 5.0 mL. The agitation time was maintained at 5 minutes at 1400 revolutions per minute. The residues obtained were oven-dried at 40 °C and later analyzed using AAS. The procedure was repeated using Aeroflot solution, 2- butoxyethanol and UCON frother R-22 instead of oleic acid. The volumes used were varied as 10.0, 20.0, 30.0, and 40.0 mL at an interval of 10.0 mL. Bromoformium collector was maintained constant at 5 mL, and agitation time at 5.0 minutes at 1400 revolutions per minute. The residues obtained were dried into the oven at 40 °C and later analyzed using AAS.

3.3.3.2 Optimization Studies for Collector Chemicals

50.0 g of the ore sample was put into the flotation cell and 750.0 mL of distilled water added. 20.0 mL of the oleic acid solution and 5.0 g of polyacrylamide collector was added into the flotation cell. Agitation time was maintained at 5.0 minutes at 1400 revolutions per minute. The residue obtained from the froth and flotation cell was dried and analyzed using AAS. The above procedure was repeated by varying the mass of the polyacrylamide collector to 10.0, 15.0, and 20.0 g at an interval of 5.0 g. The mass of the mineral samples and the volume of the oleic acid solution were maintained at 50.0 g and 20.0 mL respectively. The residue obtained from the froth and flotation cell was dried and analyzed using AAS.

The above procedure was repeated but this time by using a bromoformium solution, tetrabutylether solution, and tri-cresyl phosphate collectors. For each collector, the experiment was done at volumes of 5.0, 10.0, 15.0 and 20.0 mL at an interval of 5.0 mL. The volume of the oleic acid and the mass of the ore were maintained at 20.0 mL and 50.0 g respectively. The agitation time was maintained at 5 minutes at 1400 revolutions per minute. The residue obtained from both the froth and floatation cells was dried in the oven at 40 °C and later analyzed using AAS.

3.4 Copper Extraction Using Iron in Acidic Media

3.4.1 Leaching of Copper from Ores

A mass of 200.0 g of the mineral sample was weighed into a one-litre beaker and 400.0 mL of 2.0 M HCl was added. The mixture was stirred using a glass rod and left to react for one hour. The content was filtered and the residue was washed two times using distilled water. The filtrate was transferred into a 500.0 mL volumetric flask and the content made to the mark using distilled water. The filtrate was reserved for the procedures in part 3.5 and 3.6. Prepared samples of various ores and sample leachate solutions are given by plate 3.1 and 3.2.

Plate 3.1: Prepared Samples of Different Ores Awaiting Analysis

Plate 3.2: Digested Sample Solution from Samples 3238 (green) and 3242 (blue)

3.4.2 Temperature Optimization

A volume of 100.0 mL of the prepared copper ore leach solution was put into a 250-beaker. The temperature of the copper leachate was taken. A clean iron electrode was dipped in the solution. The electrode was used to stir the solution slowly while monitoring the time taken for the complete displacement of copper. The determination of complete copper displacement was done by monitoring copper content in a solution using AAS. The displaced copper was analyzed for copper purity using XRFS. The experiment was repeated by varying the temperature from 30 to 70 °C at an interval of 5.0 °C. All the resulting solutions were monitored using AAS for any presence of remaining copper ions.

3.5 Copper Extraction Using Chlorinated Chicken Dung Leach Solution

3.5.1 Preparation of Chicken Dung Leachate

A 1.0 kg portion of chicken dung was weighed and placed in a desiccator. 2,000.0 mL of water was added and stirred for 5.0 minutes to ensure a heterogeneous mixture was achieved. The content was covered and left to equilibrate for 15 days. The content was then filtered using 50-micron sieve (66.7 meshes) to obtain impure brown chicken dung leachate as shown in plate 3.3.

Plate 3.3: Prepared Chicken Dung Solution Before and After Filtration

The leachate was characterized using the FTIR spectrophotometer model Alpha 1005 4238 from Bruker. The FTIR instrument was initialized and calibrated by conducting a background scan. Hydrazine hydrate solution was injected into a liquid cell for measurement as a standard. A sample of chicken dung leachate was injected into FTIR and scanned. The leachate and hydrazine hydrate was also analyzed using MS model Waters micro mass ZQ ESCI multi-mode ionization enabled. The method of analysis was the electron impact ionization.

To 100.0 ml of chicken dung leachate, the temperature was adjusted 70 °C and pH of 11 as optimized by Kugeria *et al.* (2018). Chlorine gas was then bubbled into it at a flow rate of 0.5 - 0.7 cm^3 per second for three minutes while stirring. A sample of the chlorinated chicken dung leachate was then characterized using FTIR and MS.

3.5.2 The pH Optimisation Studies

A solution of 100.0 mL of chicken dung leachate was put into a 200-mL beaker. The pH and temperature were recorded. To this solution, 30.0 mL of the copper leachate solution was added. Chlorine gas was then bubbled in it for six minutes while stirring. After six minutes, chicken dung leachate was slowly added while stirring. This process continued until no further precipitate was observed to occur. The chlorine gas flow rate was 0.5 - 0.7 cm^3 per second. The gas flow rate was measured using a gas flow meter model 270134.003 from TA Instruments. The residue formed was filtered and rinsed two times using distilled water. The residue was dried in an oven at 40 °C and then analyzed using XRF. The procedure was repeated by varying the pH from 7.0 to 12.7 using 1.0 M NaOH at an interval of 1.0 pH (Kugeria *et al.,* 2018).

3.5.3 Chlorine Bubbling Time Optimisation

After obtaining the optimal pH, the chlorination period was varied from one to six-minute before the addition of the copper leachate and later four minutes after the addition of copper leachate. All experiments were done at optimal pH while maintaining all other parameters constant. The content of copper present was later determined using XRFS (Kugeria *et al.,* 2018).

3.5.4 Temperature Optimisation

After establishing the optimal pH and the suitable chlorine bubbling time, the procedure was again repeated while holding pH constant at 11.0, the optimal pH. Chlorine bubbling time was kept at three minutes. The temperature of the chicken dung leachate was varied from 28 to 90 °C at intervals of 5 °C. In each case, the precipitate formed was filtered and rinsed two times using distilled water. The residue was dried in an oven at 40 °C and then analyzed using XRF. After optimization, 100.0 mL of copper leachate from all deposits for level A was reduced using the optimized parameters and the precipitate obtained analyzed using XRF (Kugeria *et al.,* 2018).

3.5.5 *In-Situ* Reduction of Copper from Ores Using Chicken Dung Leachate

A 100.0 mL solution of chicken dung leachate was put in a 250-mL beaker. A 1.0 g portion of the ore was added and the content stirred for 20 minutes using a magnetic stirrer. The content was filtered using a 300-micron sieve. The filtrate was allowed to stand for 5 minutes for any fine particles to settle and decant. More of chicken dung leachate was added to make a volume of 200.0 mL. The pH of the solution was adjusted to 11.0. The mixture was heated to 70 °C and then chlorine gas was bubbled for three minutes. The content was cooled and the precipitate filtered using Whatman filter paper number 4. The residue was rinsed two times and dried in an oven at 40 °C and then analyzed using XRF. The procedure was repeated using different masses of the mineral samples from 2.0 g to 10.0 g at intervals of 2.0 g. The optimized temperature was maintained at 70.0 °C. The optimized pH was maintained at 11.0. The residue obtained was rinsed two times and dried in an oven at 40 °C and then analyzed using XRF.

The procedure was repeated holding temperature at 70 °C. The mass of the mineral sample was maintained at 6.0 g and chlorine bubbling time at three minutes. The stirring time was varied using the magnetic stirrer from one to sixteen minutes at intervals of two minutes. The content was cooled and filtered using Whatman filter paper number 4. The residue formed was filtered and rinsed two times using distilled water. The residue was dried in an oven at 40 °C and then analyzed using XRFS (Kugeria *et al.,* 2018).

3.6 Monitoring of Copper Extraction Process Using Aluminium Electrode

The 100.0 mL of copper leachate solution was put into a 500-mL beaker (cell 1) containing 100.0 mL of chlorinated chicken dung leachate. Another 100.0 mL of the chlorinated chicken dung leachate was put into the second beaker (cell 2). The initial pH and temperatures of the solutions in the two cells were taken. A clean aluminium rod of 0.4 cm thickness was weighed and dipped into cell 1. It was then connected to a graphite electrode in cell 2 using a copper wire. Two graphite electrodes were each dipped into the two cells and later connected using copper wire as shown in Figure 3.3.

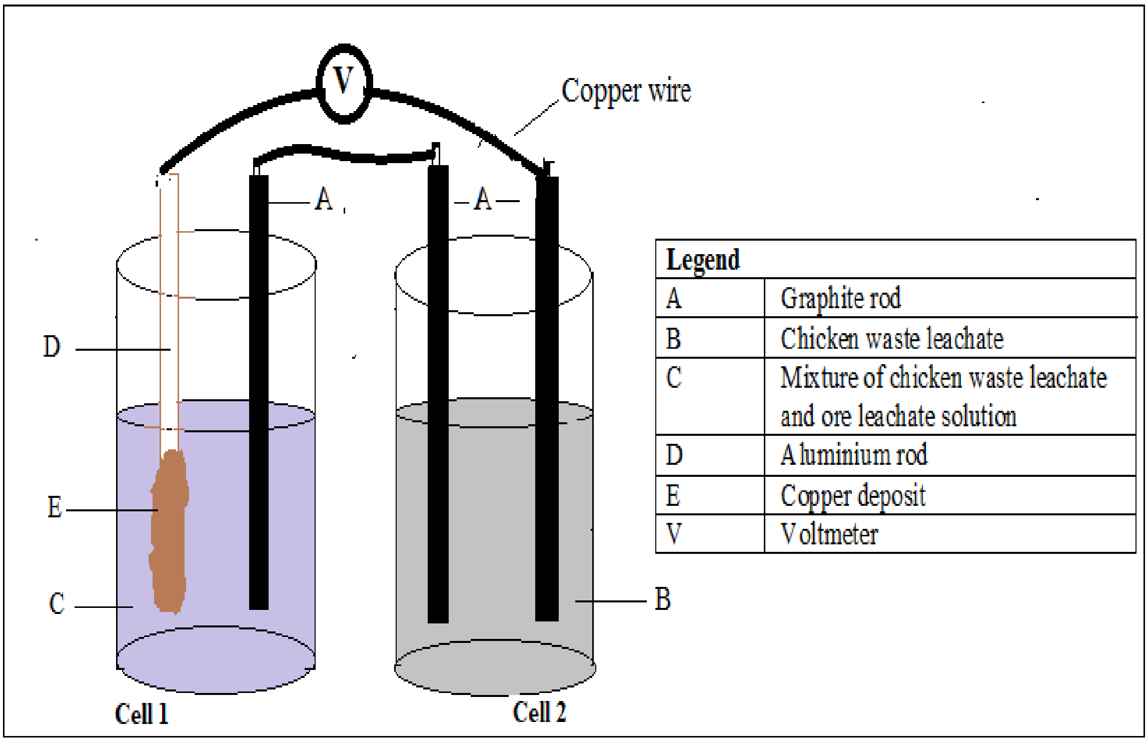

Figure 3.3: A Diagrammatical Presentation of an Electrochemical Cell
Source: Kugeria *et al.*, 2019.

The reaction was monitored until no further displacement of copper on the electrode was observed. Complete copper displacement was further confirmed using AAS analysis. The resultant solution from cell 1 was filtered and the residue rinsed twice using water. The residue was dried in the oven at 40 °C. The residue was weighed and the percentage calculated from the original mass of the mineral sample. The residue was later analyzed using XRFS for the percentage purity of copper. The aluminium rod was reweighed after the experiment and the results recorded.

3.6.1 The pH Optimization

The procedure 3.6 was repeated by adjusting the pH values in both cells from 4.0 to 14.0 using 1.0 M NaOH at an interval of 2 pH. The temperature of the solutions was maintained at 28 °C during the reaction. The copper obtained was filtered and rinsed twice using distilled water. It was then dried in the oven at 40 °C and later analyzed using XRFS.

3.6.2 Temperature Optimization

The 100.0 mL of copper leachate solution was put into a 500-mL beaker (cell 1). In the same cell 1, 100.0 mL of chlorinated chicken dung leachate was added. Another 100.0 mL of the chlorinated chicken dung leachate was put into a 500-mL beaker (cell 2). The pH of both cells was maintained at the optimized value of 11.0. The two cells were placed on a hot plate and the temperature adjusted to 30 °C. The temperature was adjusted using a thermometer while stirring using a glass rod. The two cells were removed from the hot plate and the electrodes connected immediately as in procedure 3.6. The reaction was monitored until no further displacement of copper on the electrode was observed. The copper obtained was filtered and rinsed twice using distilled water. The residue was dried in the oven at 40 °C. The obtained copper was weighed and the percentage calculated from the original mass of the ore. The copper extract was later analyzed using XRFS for the percentage purity. The aluminum electrode was reweighed after the experiment and the mass recorded.

The procedure 3.6.2 was repeated while varying the temperature from 30 to 100 °C at an interval of 10 °C. The copper precipitates produced at every varied temperature were filtered and rinsed twice using distilled water. It was dried in the oven at 40 °C and later analyzed using XRFS. The aluminum rod was reweighed at the end of every experiment and the difference obtained was recorded.

3.6.3 Relationship between Rates of Copper Ions Reduction with Electrode Potential

Procedure 3.6 was repeated by measuring the change in potential during the reduction of copper ions and oxidation aluminum electrode against time. The volume of the chicken dung leachate used was maintained as 100.0 mL. The pH was maintained at optimized values of pH of 11.0 and 30 °C. The voltage produced by the cell was recorded for 150 minutes at an interval of 25 minutes. The copper produced at every time interval was filtered and dried in the oven at 40 °C and later analyzed using XRFS.

3.7 Data Analysis

The results of the analyses obtained using AAS and XRFS in all measurements were done in triplicate and the arithmetic mean obtained by use of equation 3.1

$$\bar{x} = \sum_i x_i / n \qquad 3.1$$

Where; $\bar{x}$ - Arithmetic mean of the samples, x_i - Sample measurements and n - Population.

Comparison of experimental mean of methods of analysis, AAS and XRF were done using ANOVA. A comparison of experimental means of the methods of analysis was done using significance (t-test). The standard deviation of the means was calculated using equation 3.2 given below (Kothari, 2004).

$$s = \sqrt{\sum_i (x_i - \bar{x})^2 / (n-1)} \qquad 3.2$$

t- Calculated was given by equation 3.3 (Kothari, 2004).

$$t_{cal} = \left(\bar{x}_1 - \bar{x}_2 \right) \Big/ \sqrt{\left(s_1^2 / n_1 + s_2^2 / n_2 \right)} \qquad 3.3$$

The number of degrees of freedom was calculated from equation 3.4 (Kothari, 2004).

$$\text{Degrees of freedom} = \{ \frac{(s_1^2 / n_1 + s_2^2 / n_2)^2}{(s_1^2 / n_1)^2 / (n_1 + 1) + (s_2^2 / n_2)^2 / (n_2 + 1)} \} - 2 \qquad 3.4$$

CHAPTER FOUR

RESULTS

4.1 The Overview of the Results

The study investigated the extraction of copper and concentration of titanium in ores with low levels of iron. The results have shown that magnetic separation can be used to concentrate titanium by mixing iron-rich laterites with titanium ores with low levels of iron. The results have shown that the froth floatation method can also be used to concentrate on titanium minerals. The results have shown that copper can be extracted from leachate by displacement using iron metal. Results have also shown that chicken dung, as a source of impure hydrazones, can be used to reduce copper and thus extract copper. Further, results have shown that a cell made of chlorinated chicken dung leach and aluminium electrode can be used to monitor copper reduction by hydrazine.

4.2 Mineralogical and Chemical Composition of the Ores

4.2.1 Mineralogical Composition

Table 4.1 gives the mineralogical composition of the sampled ores from Maragwa Location, Tharaka Nithi County, Kenya. The ores were characterized by the high content of quartz, microcline and albite minerals. Other minerals were found in low proportions. The minerals of interest were copper and titanium mineral and were found in the form of chalcopyrite and ilmenite respectively.

Table 4.1: Common Minerals Found in Sampled Deposits in Maragwa Location in Tharaka Nithi County

Mineral	Chemical formula
Chalcopyrite	$CuFeS_2$
Ilmenite	$FeTiO_3$
Albite	$NaAlSi_3O_8$
Anatase also is known as brookite and rutile.	TiO_2
Quartz	SiO_2
Magnetite	Fe_3O_4
Microcline	$K(AlSi_3O_8)$
Hematite	Fe_2O_3
Calcite also known as aragonite and vaterite	$CaCO_3$
Magnesio hornblende	$Ca_2[(Mg,Fe_2+)_4Al](Si_7Al)O_{22}(OH)_2$
Sodium chromium phosphate hydrate	$NaCrPO_4•6H_2O$
Mizzonite	$NaCa_3AIsSi_7O_{24}CO_3$
Sodium praseodymium sulphite	$NaPr(SO3)_2$

Figure 4.1 gives a sample XRD diffractogram of the above ores. Other diffractograms are given in appendix 1, 2 and 3.

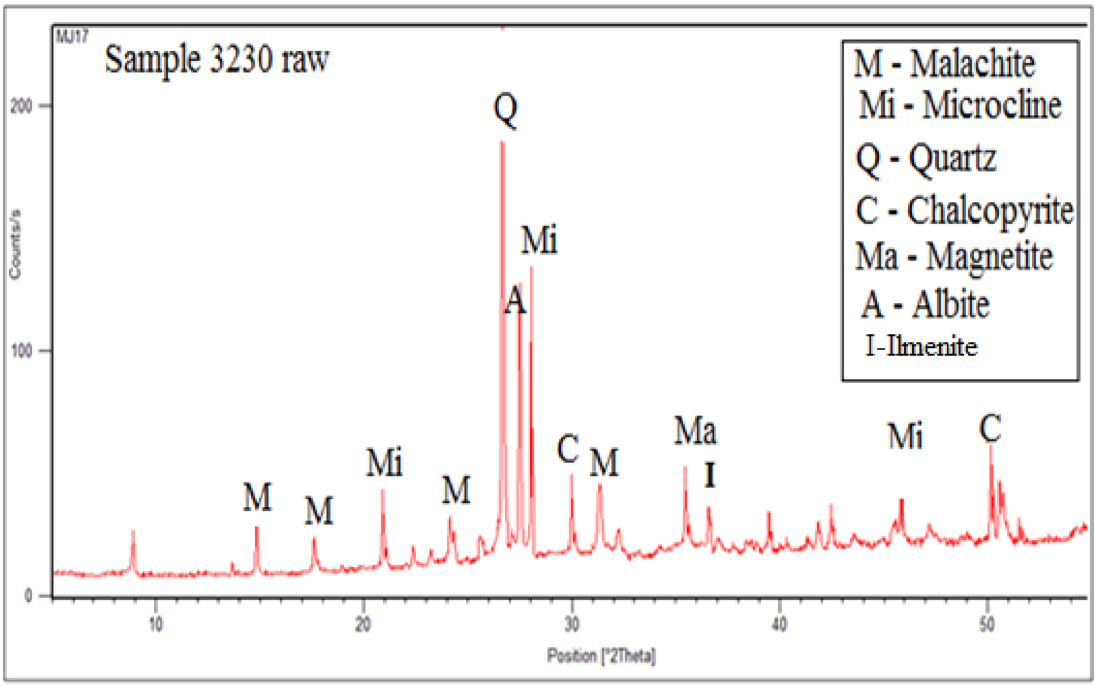

Figure 4.1: The XRD Spectrum for Raw Ore Sample 3230

Table 4.2 gives the mineral abundance of the ores sampled from Maragwa Location.

Table 4.2: Percentage Mineralogical Abundance of Some of Common Minerals Found in Maragwa Location in Tharaka Nithi County

Sample Code	Albite	Calcite	Chalcopyrite	Hematite	Magnetite	Microcline	Quartz	Titanium Oxide
3227	22.7	9.1	13.2	4.8	0.8	22.2	25.4	0.8
3230	9.5	3.7	19.5	0.2	17.3	33.5	14.8	0.6
3231	11.4	18.7	3.1	1.3	2.9	36.5	23.8	1.7
3232	14.9	12.2	3.8	0.1	9.30	27.0	31.5	0.2
3233	17.7	6.8	11.2	9.8	6.5	26.1	21.3	0.3
3234	13.4	17.9	7.4	3.1	8.2	19.4	29.8	0.6
3238	19.3	8.1	3.2	12.4	4.2	29.9	21.9	0.9
3240	8.5	5.4	4.7	1.6	22.1	31.0	25.4	0.5
3244	21.3	6.2	2.6	2.1	17.2	26.1	24.2	0.6
3242	20.6	8.0	5.2	5.4	11.7	29.2	18.6	0.9
Mean	15.83 ±1.63	9.61 ±1.62	7.35 ±1.77	4.08 ±1.31	10.02 ±2.21	28.10 ±1.61	23.57 ±1.50	0.71 ±0.13
P-Value (95.0%)	3.682	3.658	4.009	2.957	4.996	3.632	3.401	0.298

The percentage of mineral abundance was determined using XRD by calculating the percentage of mineral composition per sum of all minerals found in a sample. The chalcopyrite abundance had a mean of 7.35±1.77 with p=4.009. This shows no significant difference in the mineral distribution in all deposits in Maragwa location. All deposits had iron minerals with a mean abundance of 4.08±1.31percent hematite and 10.02±2.21percent magnetite. There was no significant difference in hematite and magnetite distribution in Maragwa location ($p>0.05$ at 95 percent confidence level). Quartz, albite and microcline minerals had mean abundances of 23.57±1.50, 15.83±1.63 and 28.10±1.61 respectively. These minerals were well distributed with no significant difference in their mineral abundance ($p>0.05$ at 95 percent confidence level). Calcite minerals were also found well distributed in Maragwa location with no significant difference in mineral abundance (p=3.658 at 95 percent confidence level). The calcite minerals mean abundance was found to be 9.61±1.62 percent. Titanium minerals in Maragwa location were found in low abundances with a mean of 0.71±0.13 percent. However, all deposits had no significant difference in rutile abundance.

4.2.2 Mineralogical Composition of Laterite Minerals

Table 4.3 gives results for the mineralogical content of ores sampled in Gitong'o in Tunyai Location, Tharaka Nithi County, Kenya. A sample diffractogram of the ores is given in figure 4.2.

Table 4.3: The Most Common Minerals in the Laterites

Name of the mineral	Chemical formula
Quartz	SiO_2
Ilmenite	$FeTiO_3$
Goethite	$FeO.OH$
Strontium dicalcium hexapropionate	$C_{18}H_{30}Ca_2O_{12}Sr$

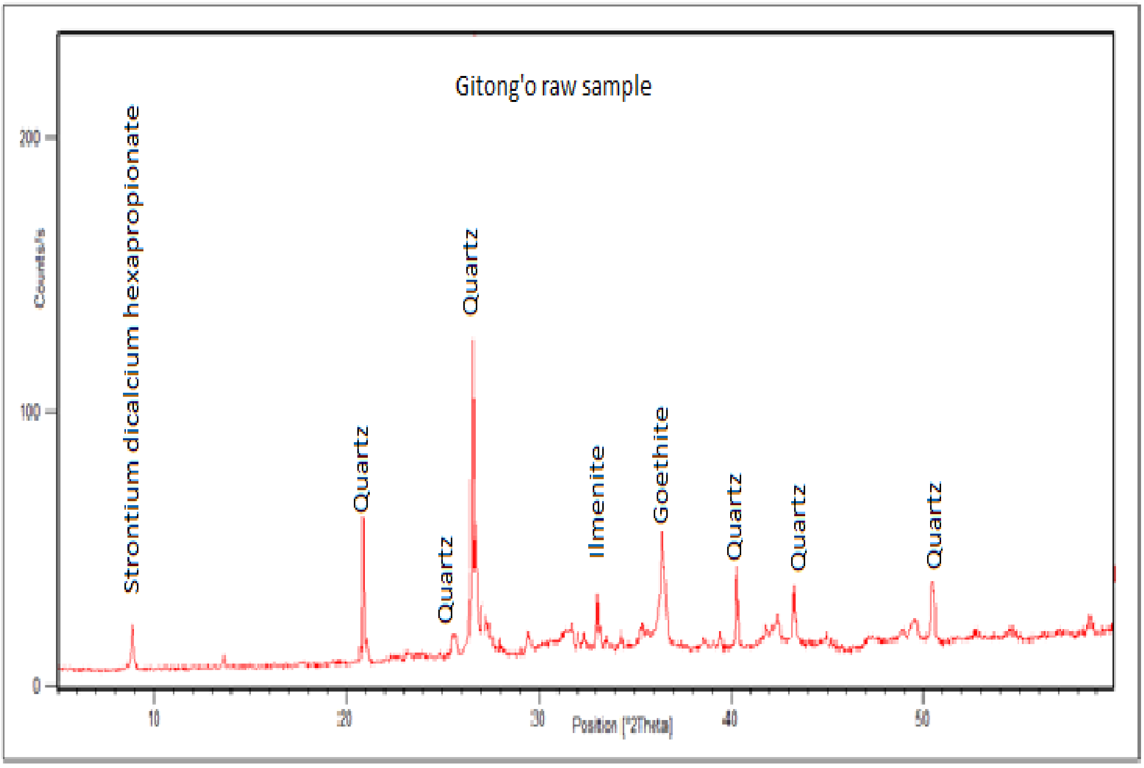

Figure 4.2: Spectrum of Raw Laterite Sample

The most common minerals in laterite were quartz and goethite. The laterite was also found to contain ilmenite mineral. The quartz mineral was abundant and this was likely to contribute to impurity during concentration of titanium. Ilmenite composition was also likely to affect the final composition after concentration.

4.2.3 Chemical Composition of the Ores from Maragwa Location, Tharaka Nithi County

Table 4.4 gives the mean chemical composition for each of the ore deposits from Maragwa Location. The statistical means for level A and B were determined and the results given in table 4.5. Other mineral distributions by level are given in appendix 4 and 5. The copper minerals from levels A and B have a mean value of 4.47±0.70 level A and 4.44±0.60 level B. Other mineral found include silica, calcium oxide, alumina, and iron oxides. It was found that across levels A and B, there was no significant difference in the mineralogical composition of all mineral oxides ($p>0.05$)

Table 4.4: Mean Percentage Composition for Ore Deposit from Maragwa Location, n = 6

Oxides Sample Code	SiO_2 Mean± SE	Al_2O_3 Mean± SE	K_2O Mean± SE	Na_2O Mean± SE	CaO Mean± SE	TiO_2 Mean± SE	MnO Mean± SE	Fe_2O_3 Mean± SE	Cu Mean± SE	CuO Mean± SE	MgO Mean± SE
3227	48.82± 0.05	9.01± 0.67	8.65± 0.98	6.84± 1.79	14.68± 0.91	0.82± 0.20	0.35± 0.11	8.89± 3.96	3.59± 0.50	4.46± 0.65	2.09± 0.06
3230	39.02± 2.70	7.21± 1.07	7.35± 0.44	13.36± 0.52	2.15± 0.15	0.99± 0.04	0.12± 0.01	4.08± 0.29	8.42± 1.35	10.51± 1.72	6.36± 0.61
3231	48.23± 3.31	6.28± 0.09	5.86± 1.09	5.98± 0.15	20.29± 1.38	0.44± 0.06	1.11± 0.31	8.28± 0.72	5.14± 0.78	6.41± 0.95	4.16± 0.45
3232	37.15± 6.14	10.34± 1.18	11.19± 0.77	2.49± 1.54	9.71± 7.78	1.98± 0.18	0.20± 0.06	19.36± 1.88	2.56± 0.17	3.21± 0.22	4.85± 0.69
3233	27.30± 1.59	10.54± 1.49	5.82± 1.08	6.25± 2.82	1.63± 0.33	1.37± 0.52	0.26± 0.07	39.76± 1.33	5.00± 0.66	6.25± 0.81	3.01± 0.16
3234	35.06± 0.88	3.22± 0.40	0.86± 0.19	10.25± 2.06	21.03± 2.88	0.53± 0.09	0.28± 0.09	14.45± 1.50	1.76± 0.19	2.1± 0.24	4.64± 0.53
3238	44.16± 1.85	13.01± 2.43	3.42± 0.78	15.41± 2.56	11.83± 1.34	1.63± 0.09	0.43± 0.23	9.75± 0.35	5.50± 1.20	6.87± 1.50	2.72± 0.97
3240	68.52± 6.32	4.34± 1.21	2.73± 0.26	10.98± 2.13	1.54± 0.50	0.53± 0.12	0.05± 0.03	2.01± 0.51	3.09± 0.17	3.88± 0.20	1.05± 0.08
3244	37.67± 10.32	11.81± 3.16	2.79± 0.32	15.64± 0.80	10.28± 2.39	1.27± 1.19	0.06± 0.01	0.05± 0.02	3.49± 0.27	4.37± 0.35	4.66± 0.40
3242	40.88± 1.29	6.47± 1.33	2.28± 0.64	4.55± 0.74	15.64± 1.90	1.11± 0.10	0.35± 0.07	23.45± 3.34	6.01± 0.72	7.50± 0.91	3.14± 0.07

Table 4.5: The Mean Statistical Analysis for Level A and B at 95.0 % Confidence Level, n = 30

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	CuO	MgO	LOI
Mean Value (level A)	44.23± 3.90^a	8.2± 1.12^a	4.7± 1.03^a	8.7± 1.45^a	9.5± 2.50^a	0.77± 0.16^a	0.25± 0.07^a	12.02± 3.84^a	4.47± 0.7^a	5.58± 0.87^a	3.49± 0.49^a	2.23± 0.32^a
P -Value	8.824	2.54	2.328	3.276	5.658	0.370	0.16	8.678	1.58	1.977	1.097	0.457
Mean Value (level B)	39.24± 3.09^a	6.8± 0.83^a	4.73± 0.81^a	9.69± 1.78^a	12.22± 2.23^a	0.86± 0.17^a	0.36± 0.12^a	11.18± 2.67^b	4.44± 0.6^a	5.55± 0.75^a	3.44± 0.51^a	1.96± 0.20^a
P - Value	6.988	1.886	1.827	4.016	5.041	0.388	0.281	6.029	1.367	1.708	1.156	0.729

Mean values followed by the same small letter in Superscript within the same column are not significantly different in chemical composition at level A and B

4.2.4 The Chemical Composition of Laterite from Gitong'o Quarry

Table 4.6 gives the results of the chemical composition of the laterite sampled from Gitong'o in Tunyai Location in Tharaka Nithi County.

Table 4.6: The Chemical Composition of Laterite from Gitong’o Quarry

Sample Source	SiO_2 Mean ±SE	Al_2O_3 Mean ±SE	K_2O Mean ±SE	Na_2O Mean ±SE	CaO Mean ±SE	TiO_2 Mean ±SE	MnO Mean ±SE	Fe_2O_3 Mean ±SE	MgO Mean ±SE	LOI Mean ±SE
Gitong’o	45.48 ± 0.12	17.15 ± 0.07	0.02 ± 0.03	0.04 ± 0.02	0.04 ± 0.03	0.27 ± 0.01	0.21 ± 0.03	29.31 ± 0.01	0.24 ± 0.02	5.12 ± 0.03

The results show the ore has a rutile composition with a mean of 0.27±0.01 percent. The composition of iron oxides was 29.31±0.01 percent.

4.3 Concentration of Titanium in Ores from Maragwa Location Using Biomass, Biomass – Laterite Mix Vis a Vis Froth Floatation

4.3.1 Concentration of Titanium in the Ores Using Biomass

Tables 4.7 gives the optimized results of the reduction of sample 3231A (from Maragwa Location) using biomass. The mineral sample used for the reduction had a mean of 0.46± 0.03 TiO_2.

Table 4.7: Percentage Rutile of Magnetic and Non-Magnetic Samples Obtained after Reduction of Maragwa Ore Using Biomass

Mass of biomass (g)	Mass of the ore (g)	% TiO_2 from non-magnetic portion after reduction using biomass	% TiO_2 from magnetic portion after reduction using biomass
1.0	5.0	0.64	0.03
1.0	10.0	0.74	0.02
1.0	15.0	0.78	0.01
1.0	20.0	0.83	0.02
1.0	25.0	0.85	0.03
1.0	30.0	0.81	0.02
1.0	35.0	0.73	0.03
1.0	40.0	0.62	0.03
1.0	45.0	0.57	0.02
1.0	50.0	0.46	0.01

The results show that 25.0 g of the mineral and 1.0 g of the biomass gave the highest concentration of titanium. The results obtained had 0.85 percent TiO_2 in non-magnetic concentrate and 0.03 percent in magnetic concentrate. Further increase of the mineral ore at the constant mass of biomass decreases TiO_2 content in the non-magnetic concentrate. The analysis of the magnetic concentrate contained low values of TiO_2 ranging between 0.01 to 0.03 percent TiO_2. There was no noted relationship between TiO_2 in magnetic concentrate, the mass of the biomass used and mass of the ore used.

Table 4.8 shows the summary of rutile in raw sample, magnetic and non-magnetic concentrate. Figures 4.3, 4.4 and 4.5 show mineralogical transformation after reduction.

Table 4.8: Common Minerals in the Raw Sample, Magnetic and Non-Magnetic Sample

Name of the Mineral	**Chemical Formula of common minerals**		
	Raw Sample	**Tailings**	**Magnetic sample**
Quartz	SiO_2	SiO_2	SiO_2
Microcline	$KAlSi_3O_8$	$KAlSi_3O_8$	$KAlSi_3O_8$
Chalcopyrite	$CuFeS_2$	-	-
Ilmenite	$FeTiO_3$	-	-
Hematite	Fe_2O_3	-	-
Rutile	-	TiO_2	-
Copper zinc sulphide	-	CuS ZnS	CuS, ZnS
Iron	-	-	Fe

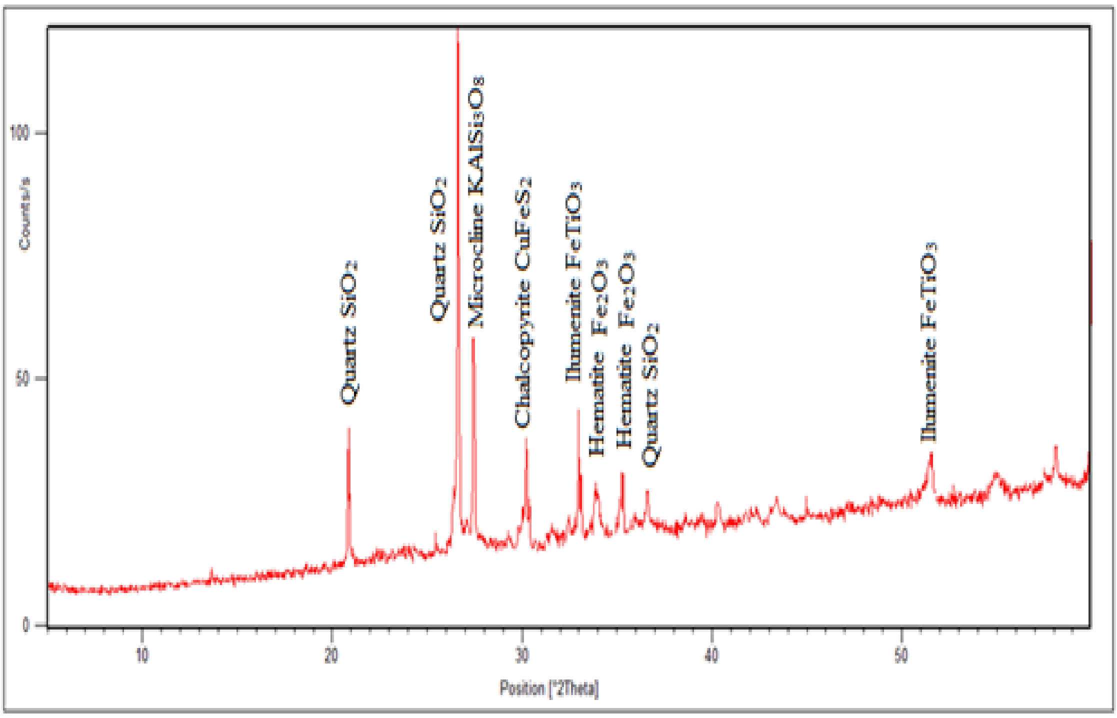

Figure 4.3: The Spectrum of Raw Sample before Heat Treatment (3231)

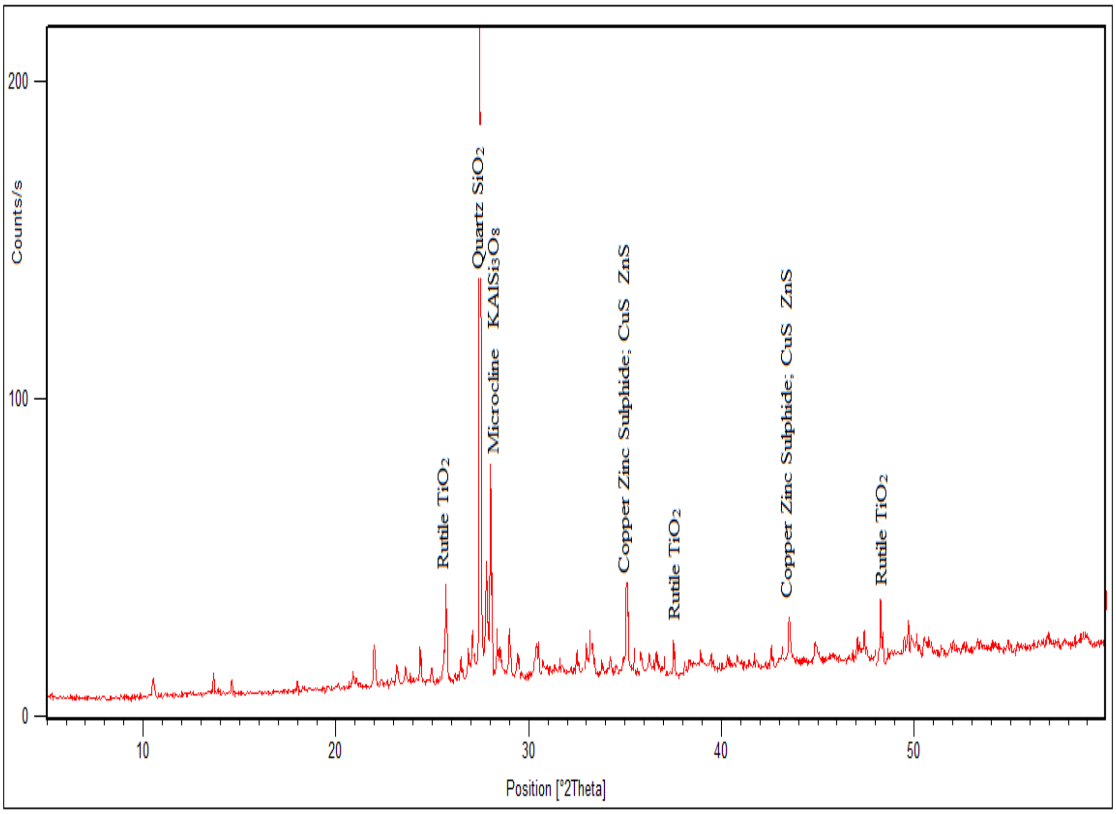

Figure 4.4: The Spectrum of the Tailing (Non - Magnetic Sample) after Heat Treatment (3231)

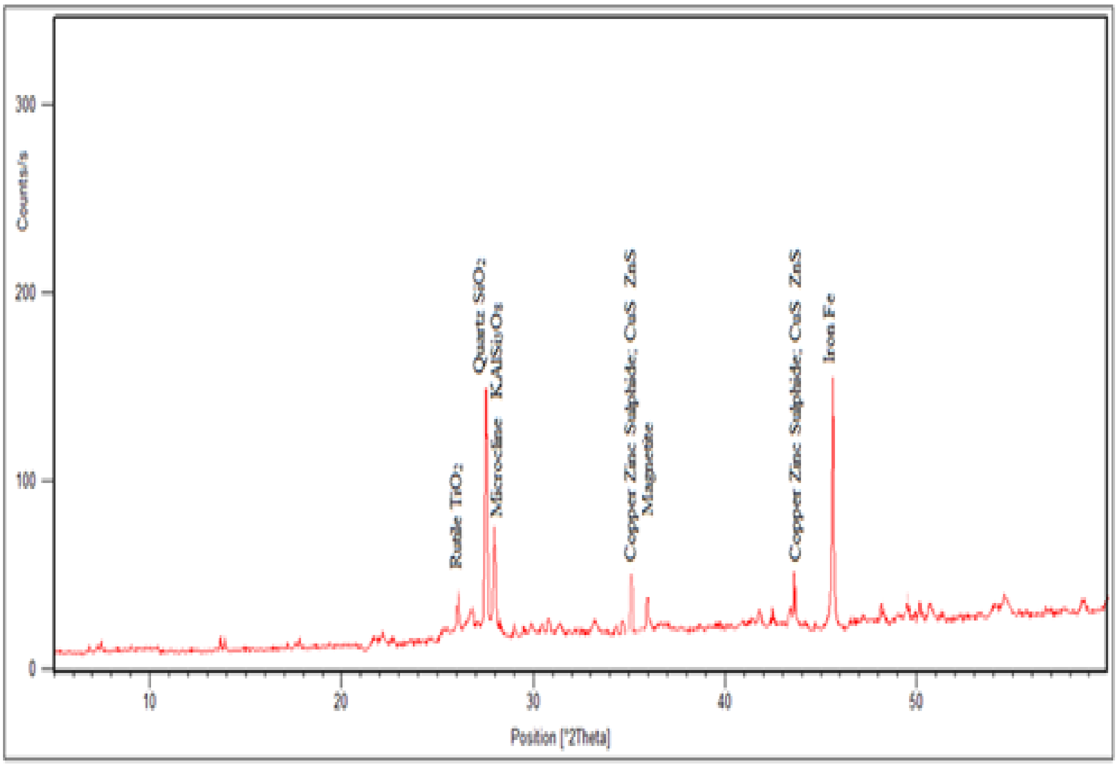

Figure 4.5: The Spectrum of the Magnetic Sample after Heat Treatment (3231)

In the magnetic sample, the rutile reduced significantly and the iron peak was observed. This occurs because rutile is not magnetic susceptible hence collected in the tailing. In the tailing, the ilmenite, and hematite peaks disappeared while the rutile peak increased.

Figure 4.6 gives results for the rutile concentration of the ten sampled ore from Maragwa Location using biomass. The results given are for titanium changes from the raw ore, magnetic and non - magnetic portions (tailing). Results for other chemical component changes are given in appendix 6, 7 and 8.

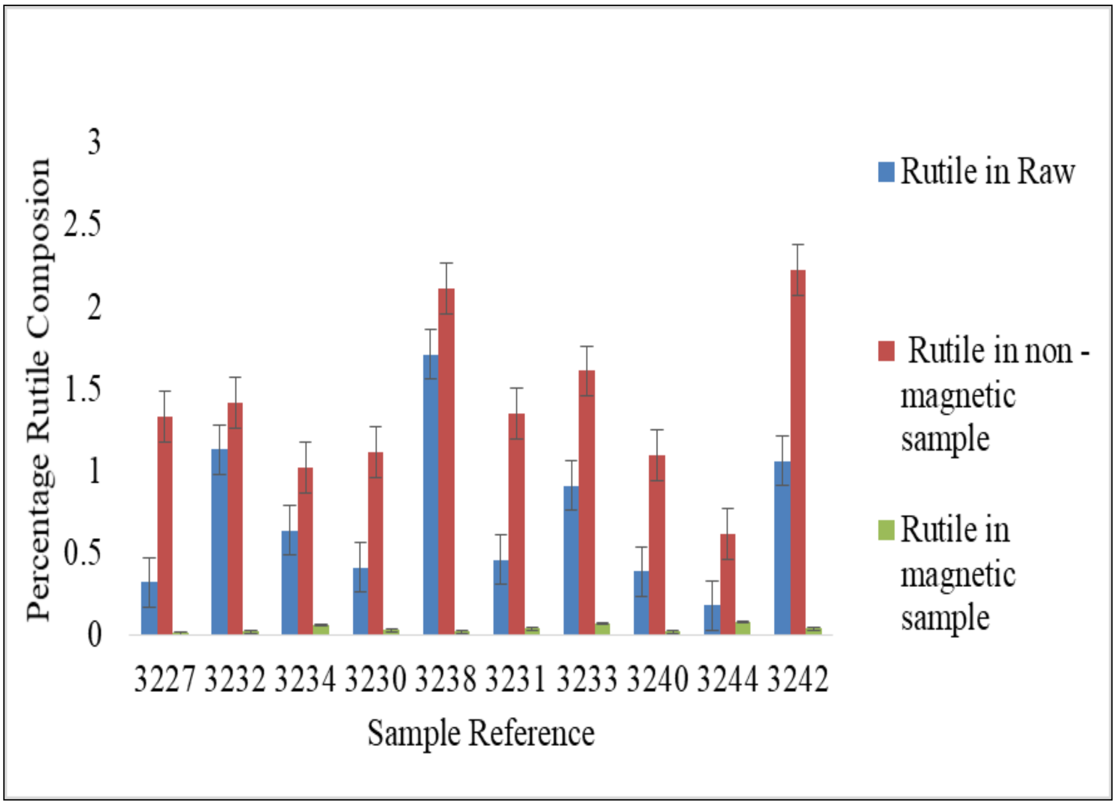

Figure 4.6: Percentage Rutile Before and After the Concentration of the Ore Using Biomass

The results show an increase in the tailing in all samples and relatively low rutile in the magnetic concentrate. Comparing the results of sample 3227, the rutile content in the raw sample was 0.32 percent. After concentration rutile content increased to 1.33 percent which represents a 315.63 percent increase.

4.3.2 The concentration of Titanium from the Mixture of Titanium Ore and Laterite Using Biomass

Table 4.9 gives the results for optimization studies for the concentration of titanium in titanium ore-laterite ore - biomass mixture. Sample 3231A from Maragwa was used as titanium ore in the studies.

Table 4.9: The Optimized Results of Magnetic and Non-Magnetic Separated Portions after Reduction of Ore - Laterite Mixture Using Biomass

Mass of biomass(g)	Mass of the ore (g)	Mass of laterite (g)	% TiO_2 from non-magnetic portion after reduction of ore - laterite mixture using biomass	% TiO_2 from magnetic portion after reduction of ore - laterite mixture using biomass
1.0	5.0	2.0	0.97	0.02
1.0	10.0	2.0	1.18	0.03
1.0	15.0	2.0	1.32	0.02
1.0	20.0	2.0	1.42	0.03
1.0	25.0	2.0	1.48	0.03
1.0	30.0	2.0	1.35	0.01
1.0	35.0	2.0	1.31	0.02
1.0	40.0	2.0	1.01	0.02
1.0	45.0	2.0	0.91	0.03
1.0	50.0	2.0	0.19	0.02

The results showed that 25.0 g of the titanium ore was the optimum amount of the titanium ore for the concentration. It gave the highest concentration of titanium in the tailing.

Table 4.10 shows the summary of the minerals in the magnetic and non - magnetic concentrate. Figure 4.7, and 4.8 shows the mineralogical transformation in the tailings and magnetic sample.

Table 4.10: Common Minerals in the Raw Sample, Magnetic and Non-Magnetic Sample

Name of the Mineral	Chemical formula of common minerals		
	Raw Sample	**Tailings**	**Magnetic sample**
Quartz	SiO_2	SiO_2	SiO_2
Microcline	$KAlSi_3O_8$	$KAlSi_3O_8$	$KAlSi_3O_8$
Chalcopyrite	$CuFeS_2$	-	-
Ilmenite	$FeTiO_3$	-	-
Goethite	FeO.OH	-	-
Rutile	-	TiO_2	TiO_2
Copper Oxide	-	CuO	CuO
Iron	-	-	Fe
Bustamite	-	$CaMnSi_2O_6$	-
Titanomagnetite	-	-	Fe_3TiO_6

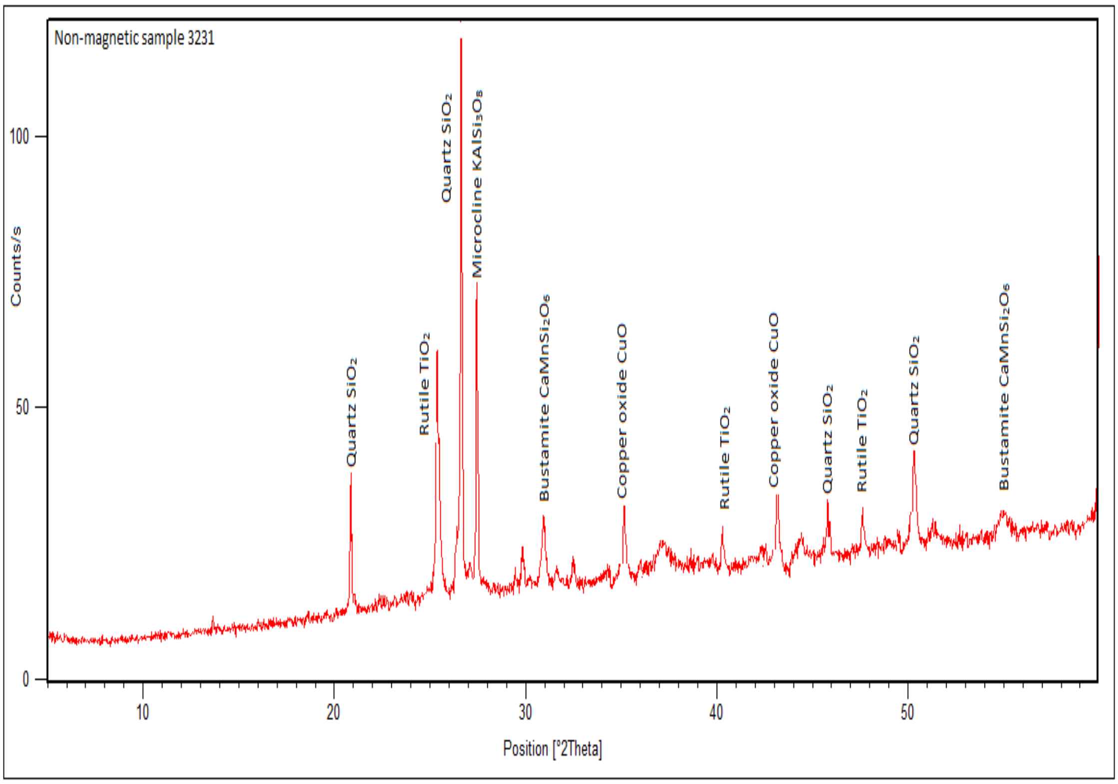

Figure 4.7: The Results of the Mineralogical Composition in the Tailing after Magnetic Separation

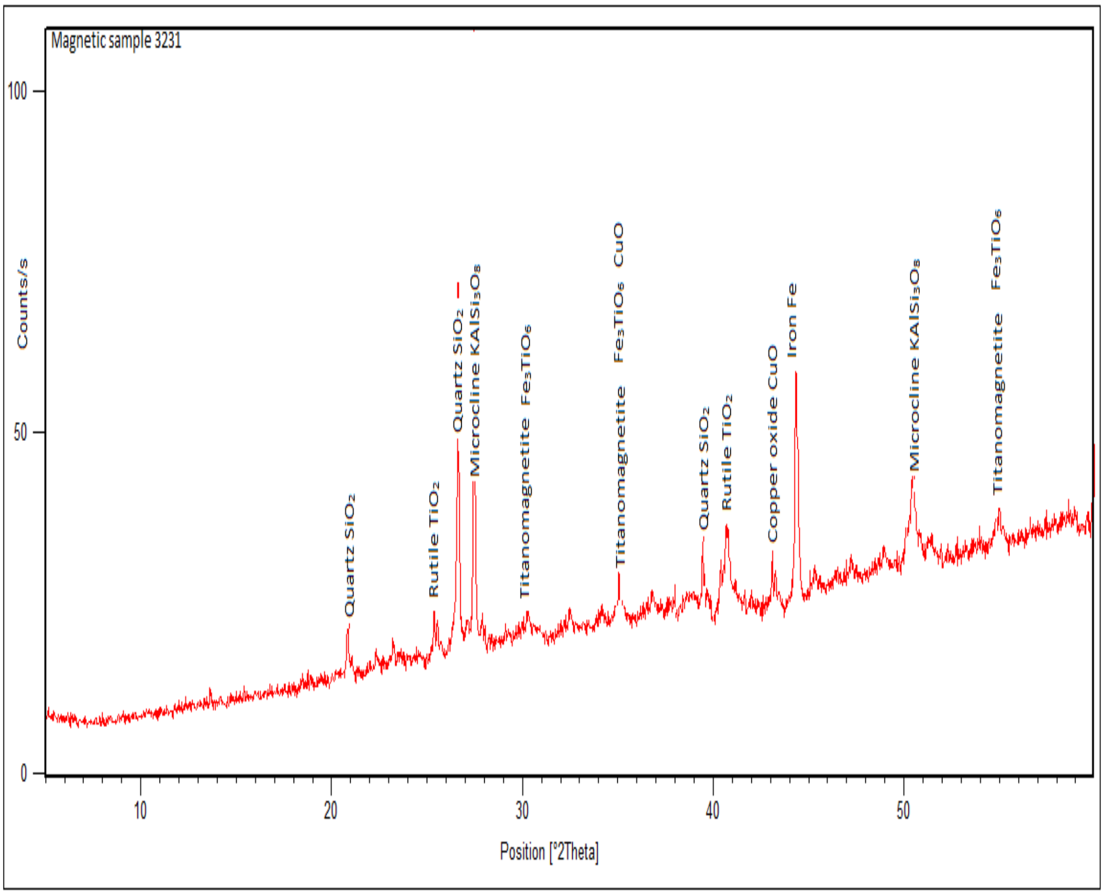

Figure 4.8: The Results of the Mineralogical Composition in the Magnetic Sample after Magnetic Separation

The results show that silica and microcline minerals increased in the tailing and their composition decreased in the magnetic sample. The ilmenite and hematite found in the raw sample were chemically transformed and were not present in the tailings and the concentrate. In the tailings rutile increased and the traces of impurities found in the magnetite sample. The titanomagnetite and iron mineral were formed and found in the magnetic concentrate.

Figure 4.9 shows the rutile concentration in the tailings and the magnetic concentrate for all deposits at level A after the concentration of ore - laterite mixture using biomass. The results for other chemical component changes are given in appendix 9, 10 and 11.

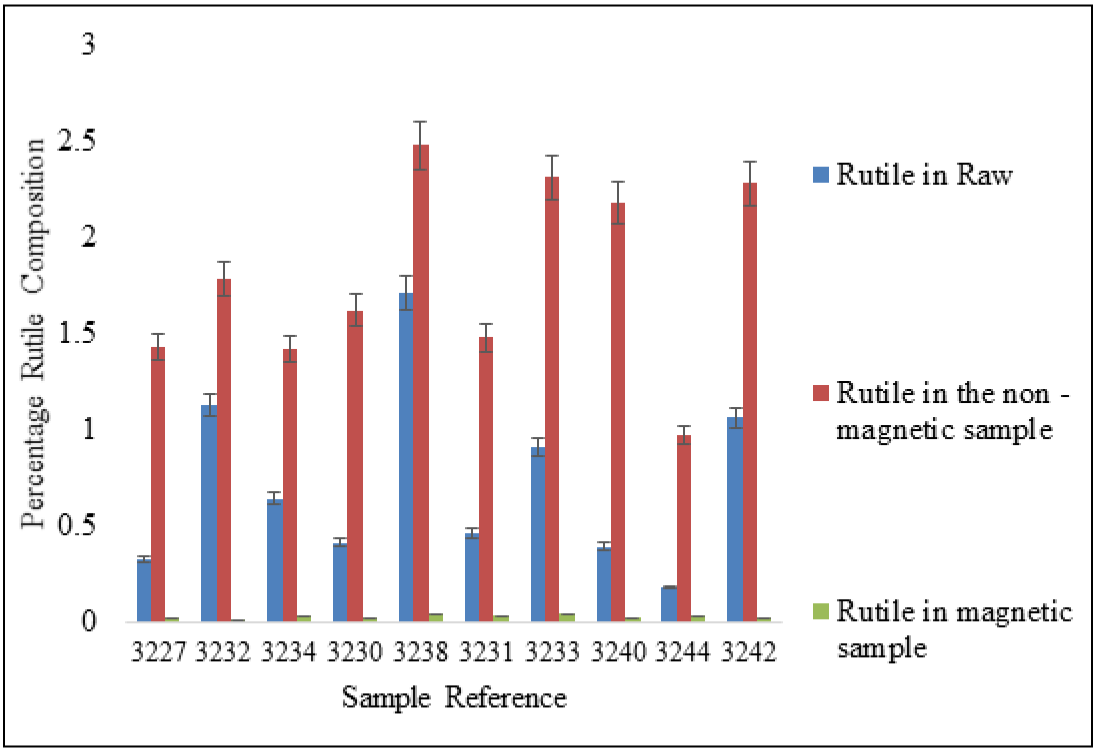

Figure 4.9: The chemical composition in raw, non-magnetic tailing and the concentrate after heat treatment of ore - laterite and biomass mixture.

The results show that rutile composition increased in the tailings in all deposits. Comparing sample 3227, the rutile content in the raw sample was 0.32 percent. After the concentration, the rutile composition increased in the tailings to 1.43 percent. This represents a 346.88 percent increase.

4.3.3 The concentration of Titanium Using Froth Flotation

Table 4.11 and 4.12 shows the optimization studies of froth floatation process using different frothers and collectors.

Table 4.11: Results of the Rutile after Optimization of Froth Flotation Process of 50 g of the Ore Using Different Volumes of Frother with Fixed Volume of 5 mL of Bromoformium Solution as Modifier

Frothers	**10 ml** **% TiO_2**		**20 ml** **% TiO_2**		**30 ml** **% TiO_2**		**40 ml** **% TiO_2**	
	Residue	**Froth**	**Residue**	**Froth**	**Residue**	**Froth**	**Residue**	**Froth**
Oleic acid	0.21	0.72	0.02	0.92	0.08	0.91	0.03	0.92
Aerofloat solution	0.52	0.59	0.49	0.51	0.37	0.48	0.58	0.42
2butoxyethanol	0.41	0.62	0.39	0.68	0.53	0.58	0.57	0.52

Table 4.12: Results of the Optimization of Froth Flotation Process of 50 g of Ore Using Different Volumes of Cationic and Anionic Collectors with Fixed Volume of 20 mL of Oleic Acid Solution

Collectors	**5 ml** **% TiO_2**		**10 ml** **% TiO_2**		**15 ml** **% TiO_2**		**20 ml** **% TiO_2**	
	Residue	**Froth**	**Residue**	**Froth**	**Residue**	**Froth**	**Residue**	**Froth**
Polyacrylamide (cationic)	0.21	0.69	0.53	0.61	0.59	0.63	0.58	0.53
Bromoformium solution (modifier)	0.15	0.87	0.01	1.03	0.02	1.02	0.03	1.03
Tetrabutylether	0.12	0.92	0.19	0.99	0.18	0.97	0.22	0.91
Tricresylphosphate (anionic)	0.47	0.76	0.23	0.81	0.58	0.73	0.42	0.74

The results obtained in table 4.11, done using 10 mL of bromoformium as a modifier and 20 ml of oleic acid gave higher values of rutile with 1.03 percent. The value was highest in the froth than other frothers investigated. The frother that gave the highest rutile value was used to optimize the modifiers. Oleic acid then was used to optimize the values of the collectors and modifier. The values from table 4.12 show that 20 mL oleic acid and 10 mL of bromoformium solution was appropriate for the concentration of rutile in 50 g of the ore. Oleic acid was used as a frother as well as the anionic collector for ilmenite minerals.

Figure 4.10 shows rutile composition in raw and concentrate for all samples after froth floatation. Other results of the chemical transformation are given in appendix 12 and 13.

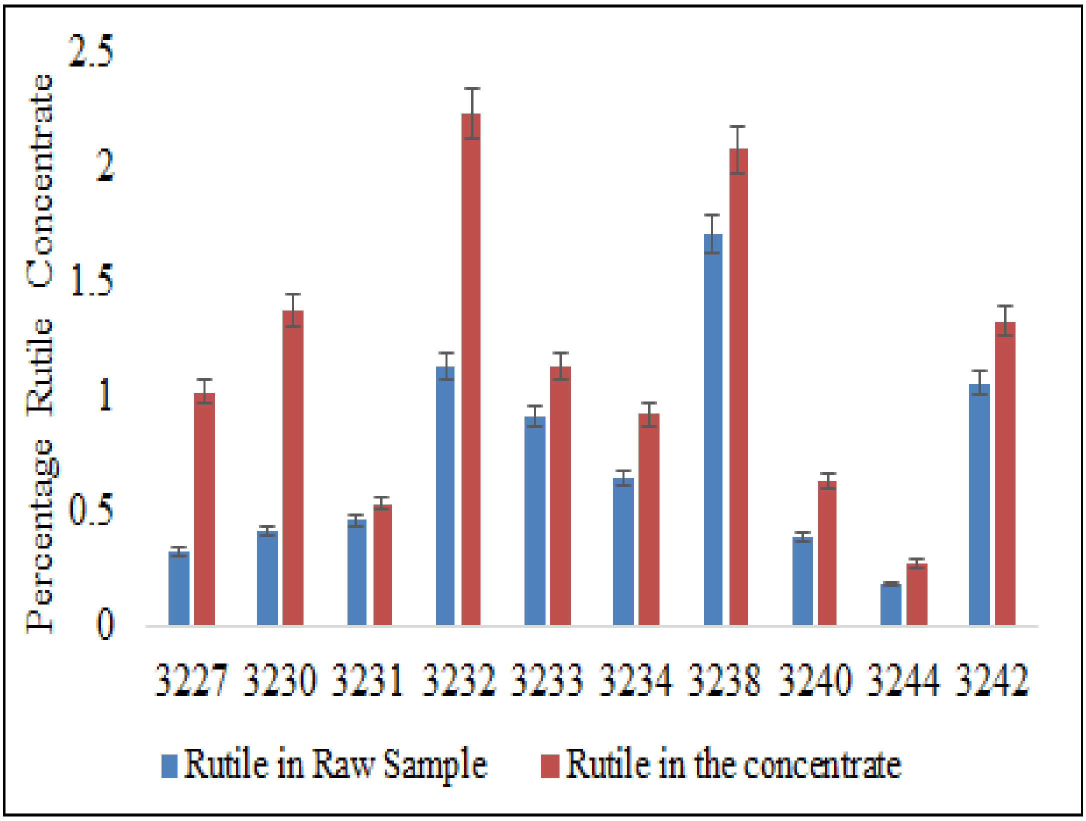

Figure 4.10: Chemical Composition of Raw and in Concentrate after Concentration Using Froth Flotation Method

The results show a gradual increase in rutile composition in all the deposits. Taking an example of sample 3227, the rutile increased from 0.32 percent in raw to 1.02 percent which represents a 218.75 percent increase. However, in samples 3227, 3230, and 3232 there was a significant increase in rutile composition compared to other samples.

4.4 Copper Extraction Using Iron

Figure 4.11 shows the relationship between times taken for copper displacement against temperature using an iron electrode in acidic media.

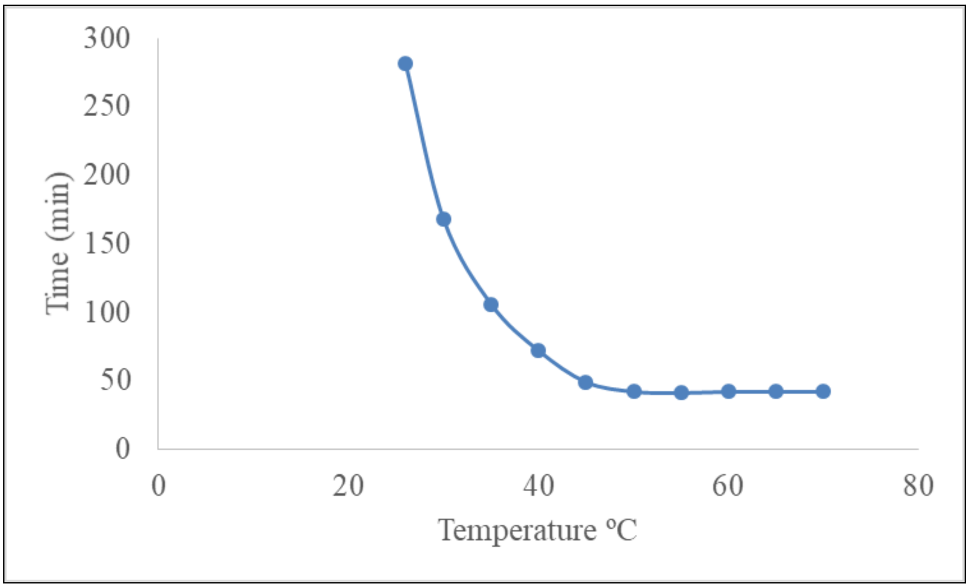

Figure 4.11: Time Taken for Copper Reduction with Increase in Temperature

Time taken for copper displacement using an iron electrode in electronic media decreased with an increase in temperature (figure 4.11). The optimized reduction temperature was 45 °C.

Figure 4.12 shows the rate of copper ions reduction with an increase in temperature.

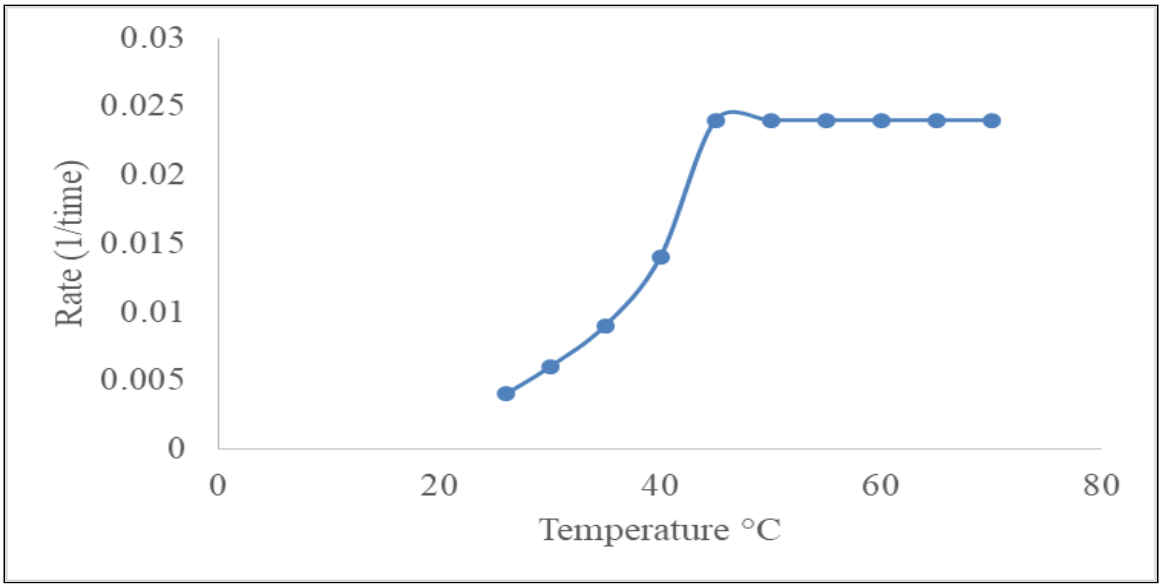

Figure 4.12: Rate of Copper Reduction with Increase in Temperature

The results show that the rate of copper reduction increases with temperature up to 45 °C. Table 4.13 shows the amount of copper obtained after reduction using the optimized temperature.

Table 4.13: Copper Extract Using Iron Electrode in Acidic Media

Sample Code	% Cu In Raw Sample	Cu (g) Available /200 g Ore	Impure Copper Extract (g) /200g Ore	%Copper Purity	Cu Extract (g) / 200g of Ore Extract	% Cu extract
3227	4.04	8.08	5.2	86.8	4.51	55.9
3230	9.6	19.2	11.92	87.3	10.41	54.2
3231	4.42	8.84	7.14	85.4	6.10	69.0
3232	2.76	5.52	3.36	84	2.82	51.1
3233	4.43	8.86	3.2	82.5	2.64	29.8
3234	1.96	3.92	2.4	81.4	1.95	49.8
3238	4.44	8.88	8.16	85.3	6.96	78.4
3240	3.19	6.38	4.5	83.8	3.77	59.1
3244	3.19	6.38	5.44	84.8	4.61	72.3
3242	6.69	13.38	6.24	84.6	5.28	39.5

The copper extracts obtained after reduction ranged from 1.95 g to 10.41 g from different ores. The extracts had a purity ranging from 81.4 to 87.3 percent. The percentage efficiency of the method ranged from 39.5 to 78.4 percent.

Figure 4.13 shows the copper extract from the sample 3227 using the iron electrode.

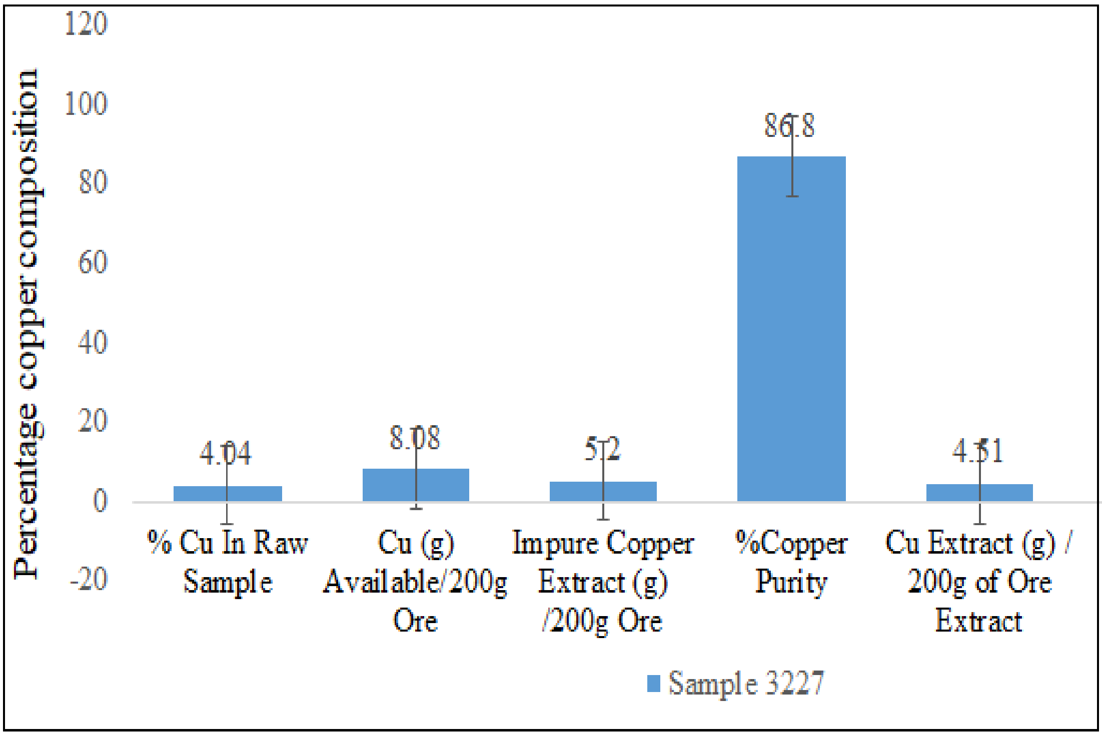

Figure 4.13: Comparison of the Copper Composition in Raw Ore to that of the Extract Using Iron Electrode

Copper available from the raw sample was 8.08 per 200 g of the ore. After the reduction, the copper recovered by the method was 4.51 g. This represents 55.82 percent efficiency of the method.

4.5 Copper Extraction Using Chlorinated Chicken Dung Leached Solution

4.5.1 Characterization of Chicken Dung Leachate

Figure 4.14 shows the overlay of IR- spectra of the chemical transformation in the chicken dung leachate before and after chlorination. The hydrazine hydrate was used as a reference.

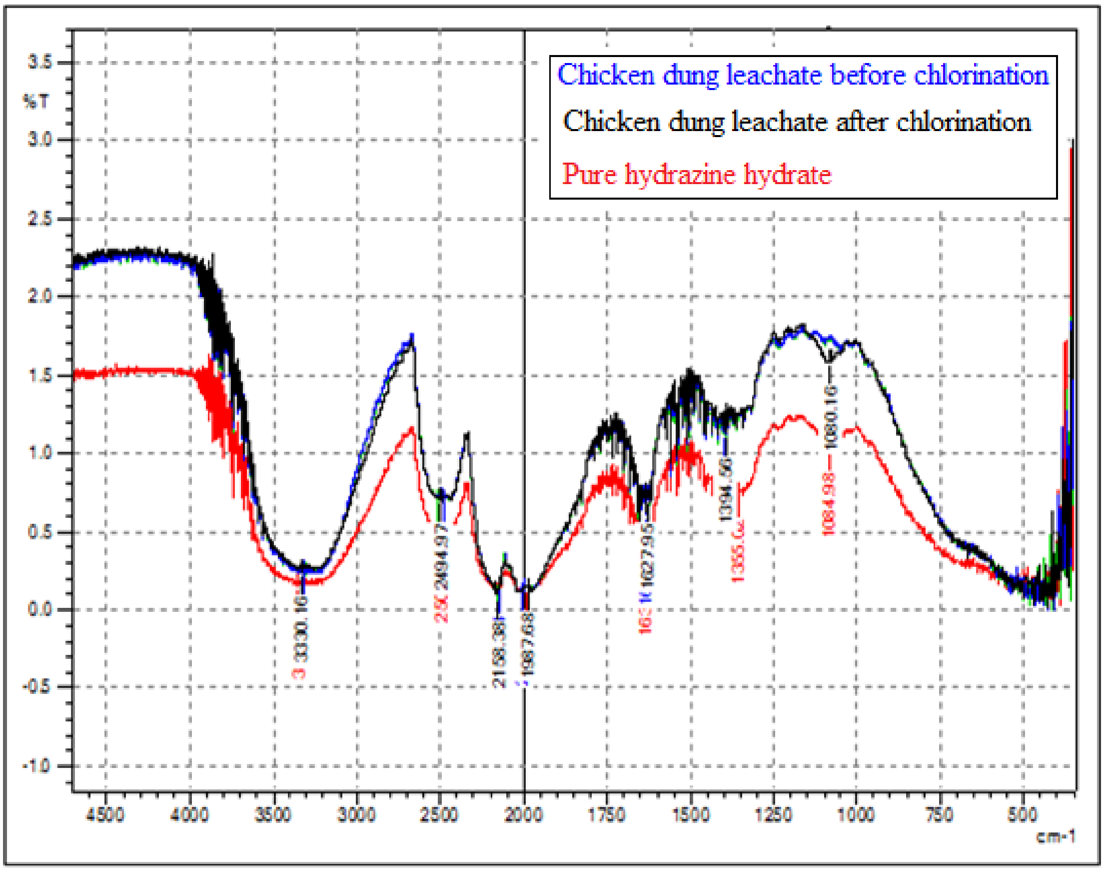

Figure 4.14: The IR spectrum of Chicken Dung Leachate Before and After Chlorination

The overlay shows that chicken dung leachate before and after chlorination contains the same peaks except for a peak at around 1084 cm^{-1}. After chlorination, a peak at around 1084 occurred like the one in hydrazine hydrate.

Table 4.14 shows the functional groups found in the chicken dung leachate before chlorination.

Table 4.14: The Functional Groups in Chicken Dung Leachate before Chlorination

	Wave number (cm^{-1})	**Functional groups**
1	3000 – 3500	OH, 1°&2°NH (amines), and C-H stretch
2	2400 – 2600	SH
3	2100	CN triple bond stretch
4	1500 – 1750	C=O, & C=N, N-H bend
5	1350 – 1450	C-H bend

Table 4.15 shows the function groups found in the chicken dung leachate after chlorination.

Table 4.15: The Functional Groups in Chicken Dung Leachate after Chlorination

	Wave number (cm^{-1})	Functional groups
1	3000 – 3500	OH, 1°&2°NH (amines), and C-H stretch
2	2400 – 2600	SH
3	2100	CN triple bond stretch
4	1500 – 1750	C=O, & C=N, N-H bend
5	1350 – 1450	C-H bend
6	**1050 – 1150**	**N-N**

The results from tables 4.14 and 4.15 show that chicken dung contains amines as given by a peak of around 300 – 3500 cm^{-1}. The NH and the C-H peaks at this range are associated with primary and secondary amines. A peak at 1500 – 1750 cm^{-1} occurs as a result of the carbonyl group and N-H bend. These are associated with the presence of amide compounds. After chlorination, a band appeared at 1050 – 1150 cm^{-1} wavelength (Table 4.15). This shows that a compound containing the N-N bond was produced.

Figures 4.15, 4.16, and 4.17 shows the spectra of mass charge values of compounds in chicken dung leachate before and after chlorination and that of hydrazine respectively.

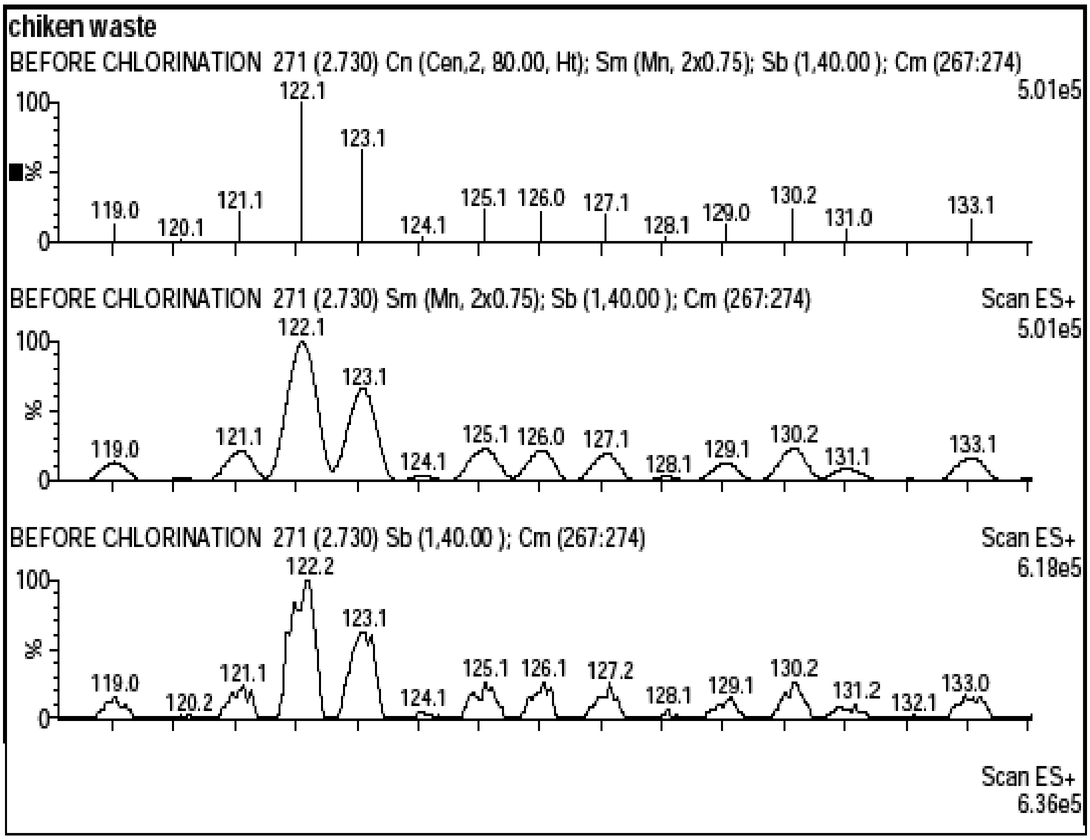

Figure 4.15: Spectra of Chicken Dung Leachate before Chlorination

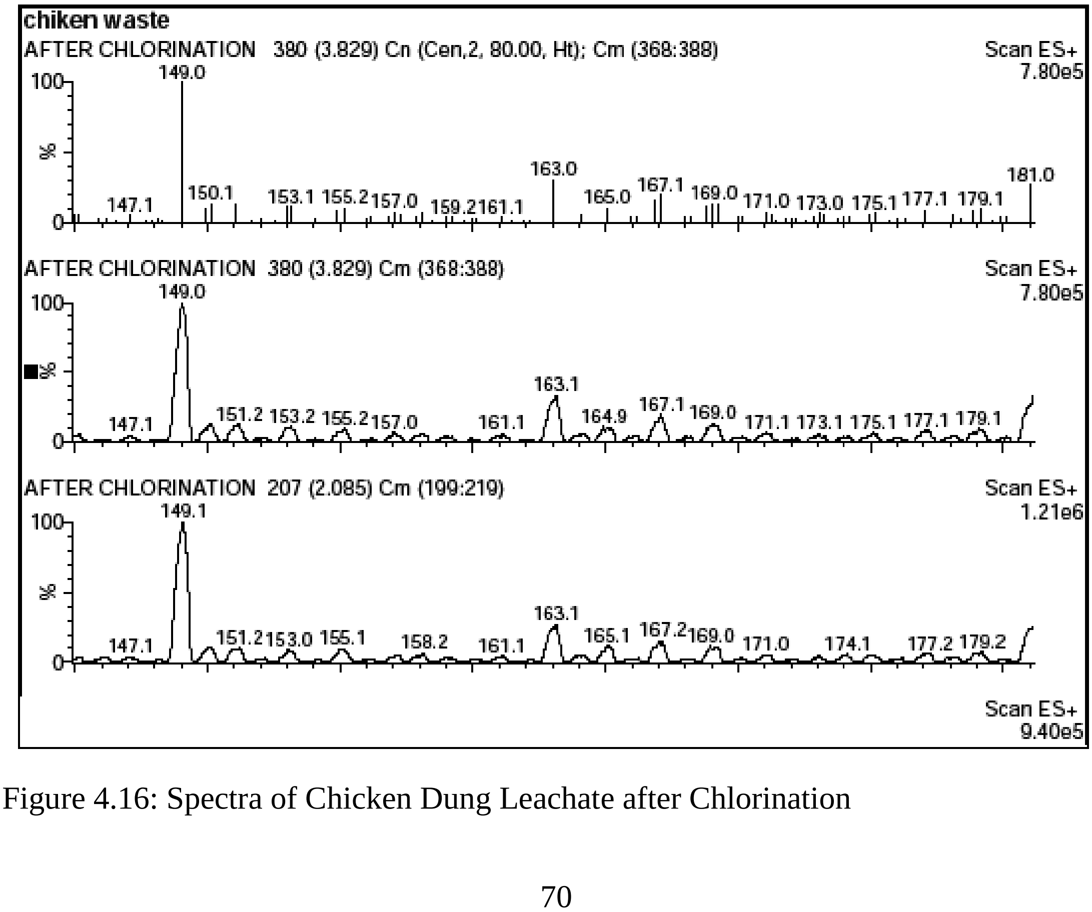

Figure 4.16: Spectra of Chicken Dung Leachate after Chlorination

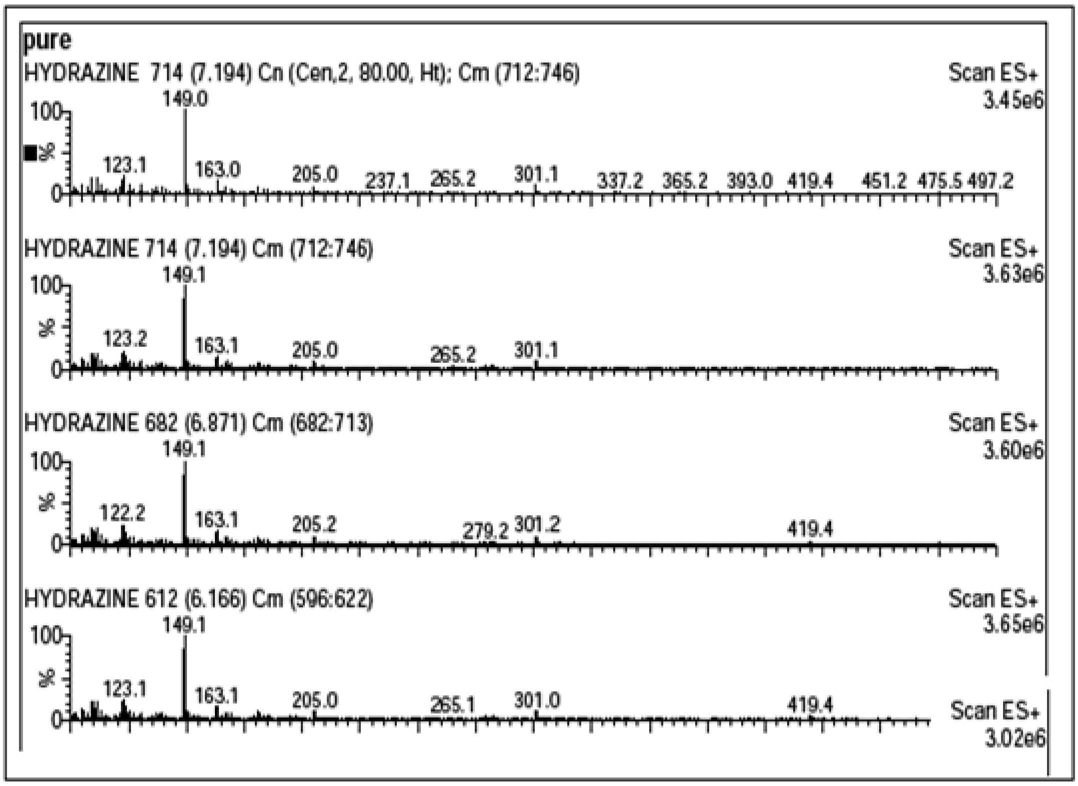

Figure 4.17: Spectra of Pure Hydrazine Hydrate

The results from figure 4.15 show that chicken dung contains many fragmented compounds. After chlorination, all m/z peaks disappeared and three new peaks appeared (figure 4.16). This shows that chemical conversion took place. The MS data of pure hydrazine gave only a peak at m/z = 149.0 (figure 4.17) which was also found in chlorinated chicken dung leachate. This confirms that some compounds in the chicken dung can be converted to hydrazones after chlorination.

4.5.2 Optimisation Studies for Chicken Dung Leachate pH

Figure 4.18 shows the optimisation studies of the pH for reduction of copper by chlorinated chicken dung leachate.

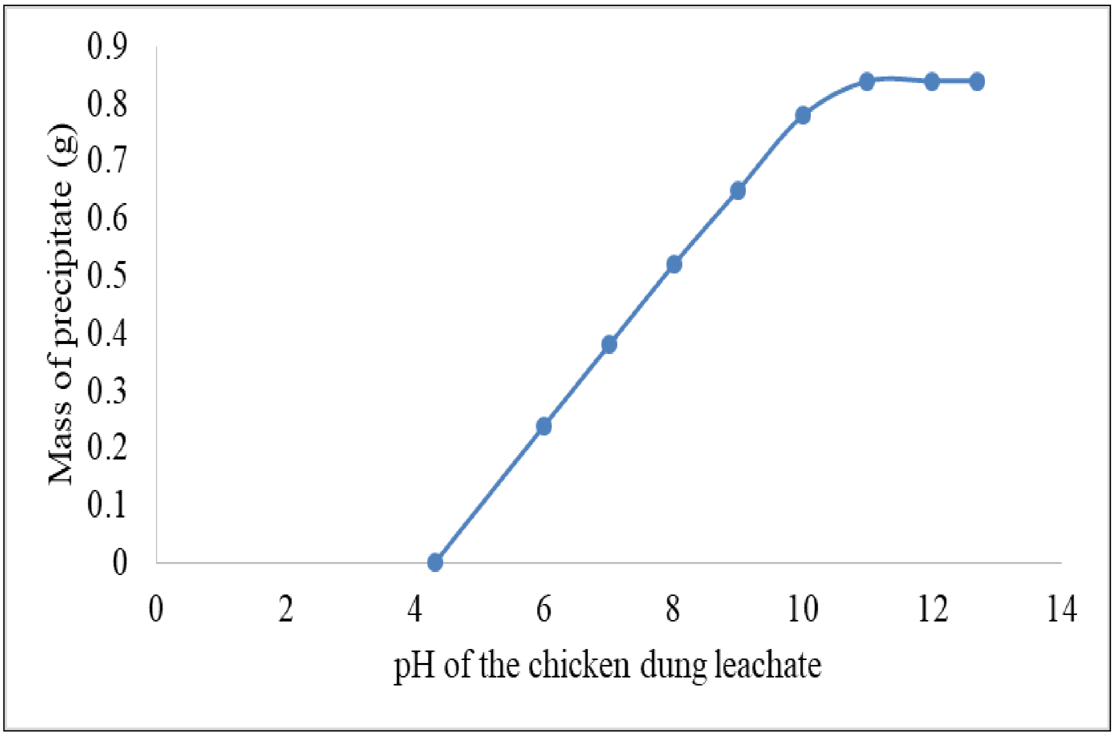

Figure 4.18: The Relationship between Increase in pH of Chicken Dung Leach and Mass of Precipitate Produced

The emergence of precipitate started after pH of 4.3 and increased with an increase in pH up to the plateau at pH 11.0.

4.5.3 Optimization Studies for Time for Chlorination of Chicken Dung leachate

Figure 4.19 shows optimization studies of the time required for complete chlorination of chicken dung leachate.

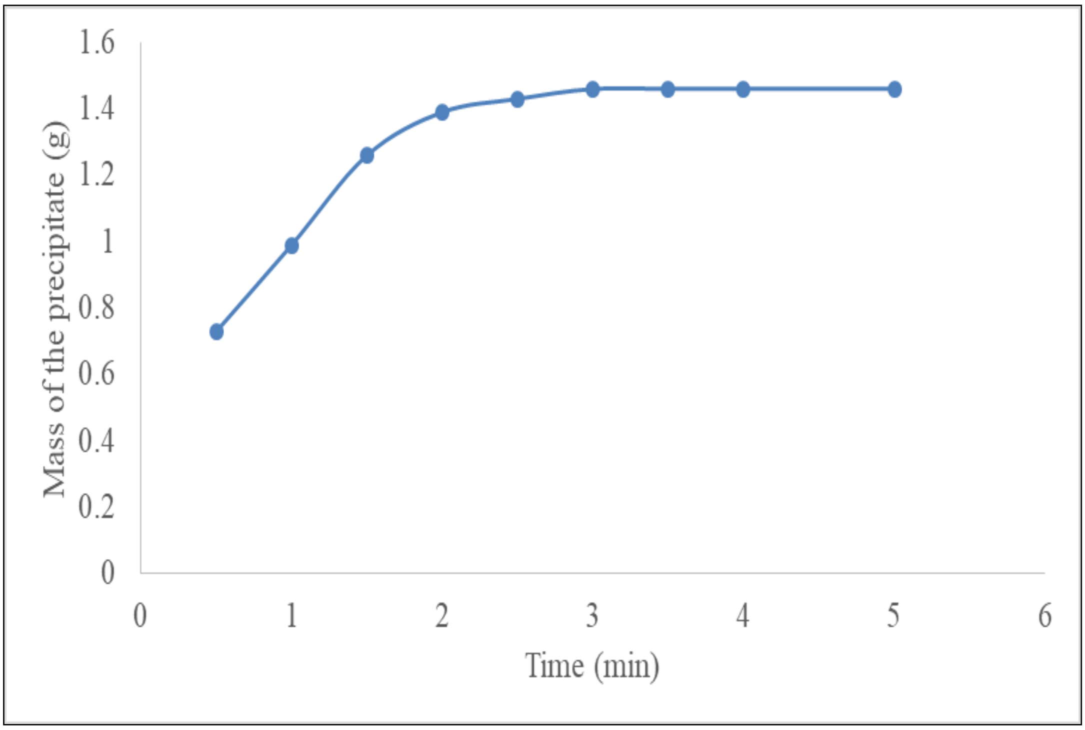

Figure 4.19: Chlorination Time versus Mass of the Precipitate Produced

The results show that bubbling chlorine gas into the chicken waste for three minutes was sufficient for the formation of the required amount of reducing agent.

4.5.4 Optimized Temperature for the Formation of Hydrazones from Chicken Dung Leachate

Figure 4.20 shows the optimization studies for the temperature required for the complete reduction of copper from chicken dung leachate.

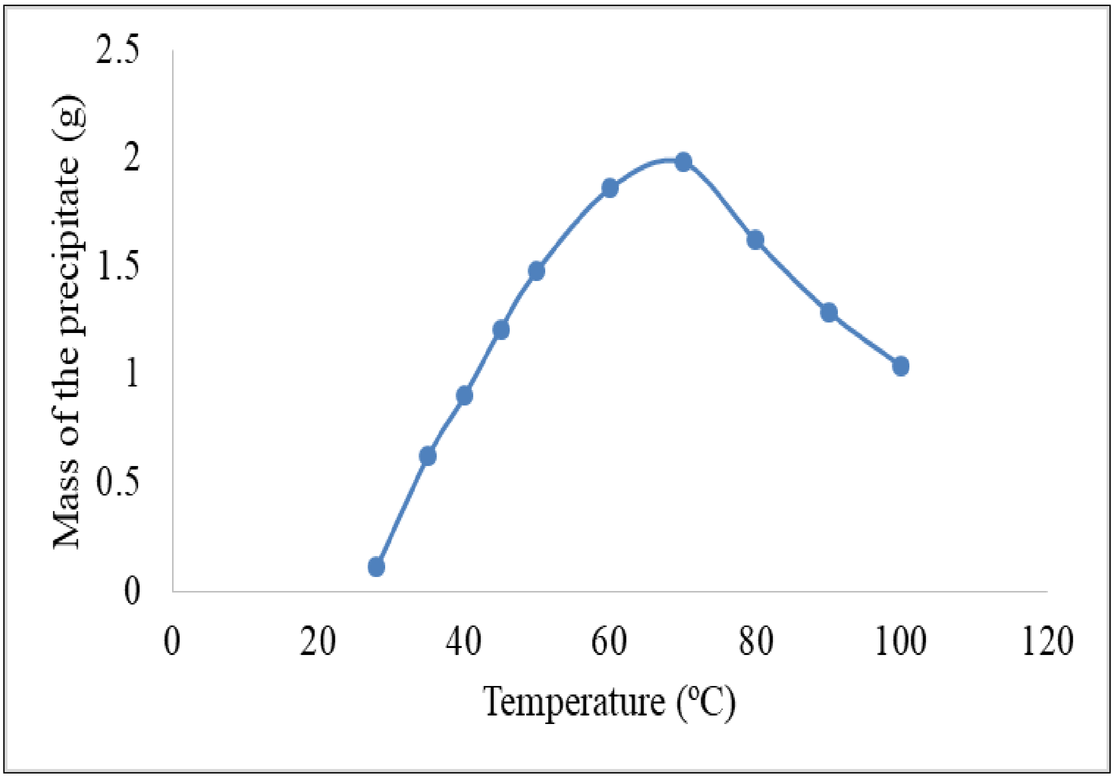

Figure 4.20: Appropriate Temperature for Hydrazones Formation

The results show that the mass of the precipitate increases with temperatures up to 70 °C. At temperatures above 70 °C, the amount of precipitate formed decreased.

4.5.5 Optimization studies for Masses of the ore required for *In-Situ* extraction of Copper Using Chicken Dung Leachate

Figure 4.21 shows the optimization studies for the direct extraction of copper from the ore using chicken dung leachate. This was done to investigate the ability of chicken dung leachate to extract copper directly from mineral ores without using the copper leachate.

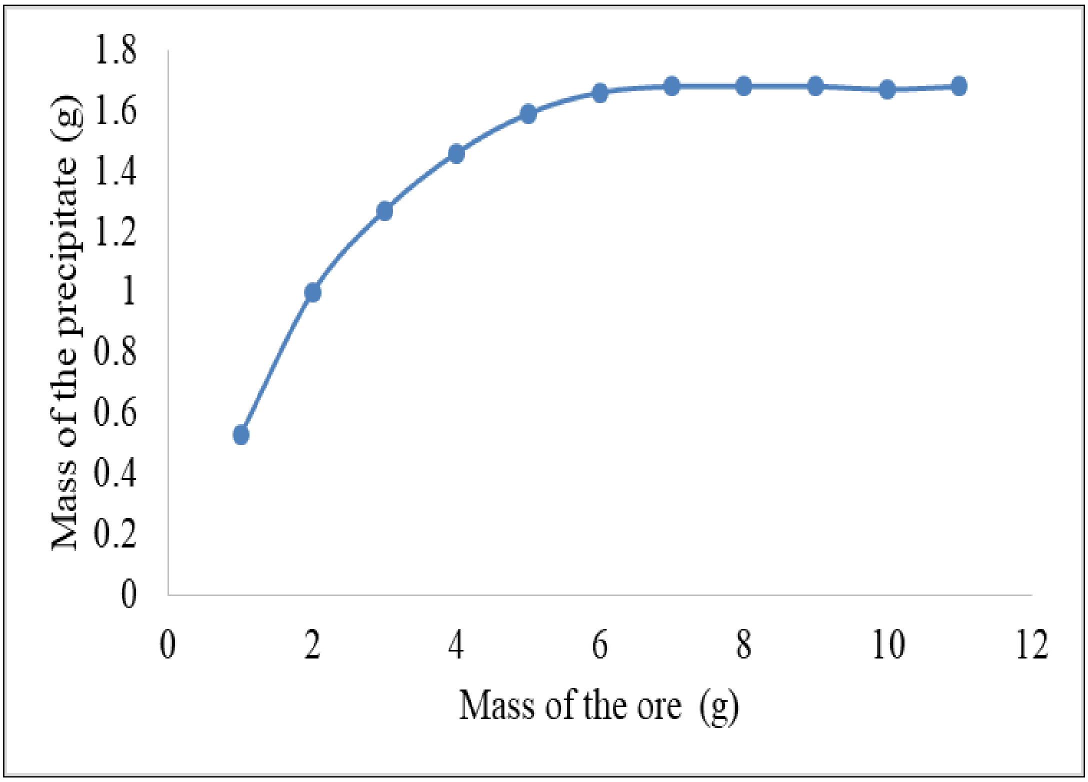

Figure 4.21: The Relationship between Masses of Ore Used in Extraction against Mass of the Precipitate Produced

The copper extracted increased with ore mass in 100.0 mL chicken dung leachate. The optimal mass of the ore required for copper extraction using 100.0 mL of chicken dung leach was found to be 6.0 g.

4.5.6 Optimization of copper extraction time from ores using chicken dung leachate

Figure 4.22 Time taken for copper extraction from ore using chicken dung leachate solution.

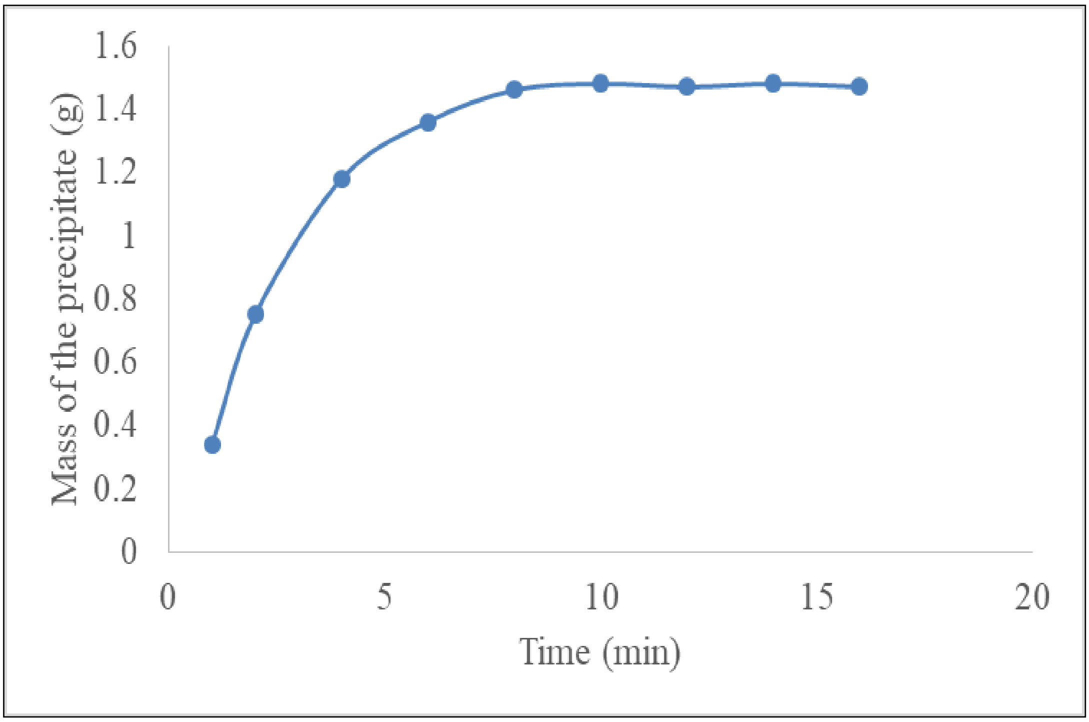

Figure 4.22: The Time Required for Copper Extraction Against Mass of Precipitate Produced.

The results show that eight minutes was enough for 100.0 mL of chicken dung leachate to extract copper from 6 grams of the ore sample. After eight minutes no more precipitation was available.

Table 4.16 shows the results of copper extraction from different acid leached ores using chlorinated chicken dung.

Table 4.16: The Results of Copper Extraction from Copper Leachate Using Chlorinated Chicken Dung Leachate

Sample Code	% Cu in Raw Sample	Cu (g) /200g ore	Impure copper extract (g) / 200g ore	% Cu purity	Copper extract (g) /200g ore	% Cu Extract
3227	4.04	8.08	7.8	64.4	5.67	70.17
3230	9.6	19.2	18.1	62.47	11.24	58.54
3231	4.42	8.84	7.3	57.16	7.89	89.25
3232	2.76	5.52	5.45	74.88	4.08	73.91
3233	4.43	8.86	7.4	73.47	7.2	81.26
3234	1.96	3.92	3.51	85.22	2.99	76.28
3238	4.44	8.88	7.35	71	6.64	74.77
3240	3.19	6.38	6.16	65.46	4.97	77.9
3244	3.19	6.38	6.05	79.07	5.57	87.3
3242	6.69	13.38	11.2	67.08	10.2	76.23

The copper extracted per 200 g ore ranged from 2.99 to 11.24 g. The percentage of copper extracted ranged from 58.54 to 89.25 percent. The percentage of copper purity obtained ranged from 57.16 to 85.22 percent. This was higher than those obtained from the extraction of copper from ores using the chicken dung leach table 4.17. Comparing the results of sample 3227, copper composition in raw 8.08 g. After copper extraction, the copper extracted was 5.67 percent. This represents 70.17 percent efficiency of the method.

Table 4.17 shows the result of the copper extraction after the reaction of ore with the chicken dung leach solution and later reduction using chlorinated chicken dung leachate.

Table 4.17: The Results of In-Situ Extraction of Copper from the Ore and Reduction of Copper Using Chlorinated Chicken Dung Leachate

Sample Code	% Cu in Raw	Cu g /200g ore	mass of impure extract/ 200g ore	% Cu purity	Cu (g) extract /200g ore	% Cu extract
3227	4.04	8.08	8	10.61	0.85	10.51
3230	9.6	19.2	9.1	12.25	1.11	5.78
3231	4.42	8.84	7.4	10.82	0.8	9.04
3232	2.76	5.52	10.1	4.15	0.42	7.60
3233	4.43	8.86	7.45	12.08	0.9	10.15
3234	1.96	3.92	10.45	5.78	0.59	15.05
3238	4.44	8.88	14.35	9.08	1.3	14.63
3240	3.19	6.38	8.95	5.78	0.52	8.15
3244	3.19	6.38	8.4	9.1	0.76	11.91
3242	6.69	13.38	10.9	12.93	1.41	10.53

The results of the percentage of copper extracted using *in-situ* extraction and reduction method was low. The copper purity ranged from 4.15 to 12.93 percent with the percentage of copper extract ranging from 5.78 to 15.05 percent. However, copper extracted from this method was found to have a high percentage of impurity compared to the acid leached method table 4.16.

4.6 Monitoring the Extent of Copper Extraction from Copper Leachate in Chlorinated Chicken Dung Leach Using Aluminium Electrode

4.6.1 The pH Optimization

Figure 4.23 shows the results of the change in pH of the chlorinated chicken dung leach against the mass of reduced copper and sacrificed aluminium electrode (Kugeria *et al.*, 2019).

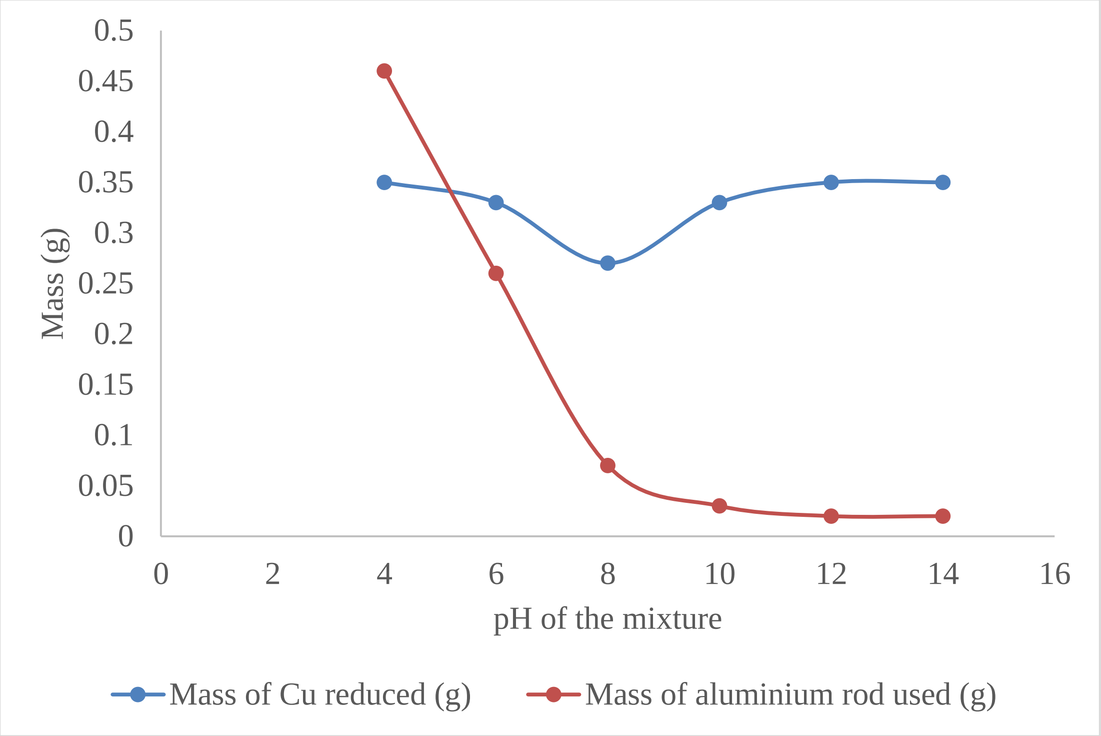

Figure 4.23: Effect of pH on the Reduction of Copper and Oxidation of Aluminium

The results show that at pH values 6.5 - 9.0, there was a decrease in the mass of copper obtained. The mass of aluminium sacrificed is high in a strongly acidic environment and reduces with an increase in pH. At pH values below 6.5 even when all copper ions have been reduced, aluminium continues to undergo oxidation due to the presence of hydrogen ions in the solution. At the pH above 11, there was little or no corrosion of aluminum, yet copper reduction takes place.

4.6.2 Temperature Optimization

Figure 4.24 shows the optimization studies of temperature against the mass of copper produced and the mass of the electrode used during copper reduction.

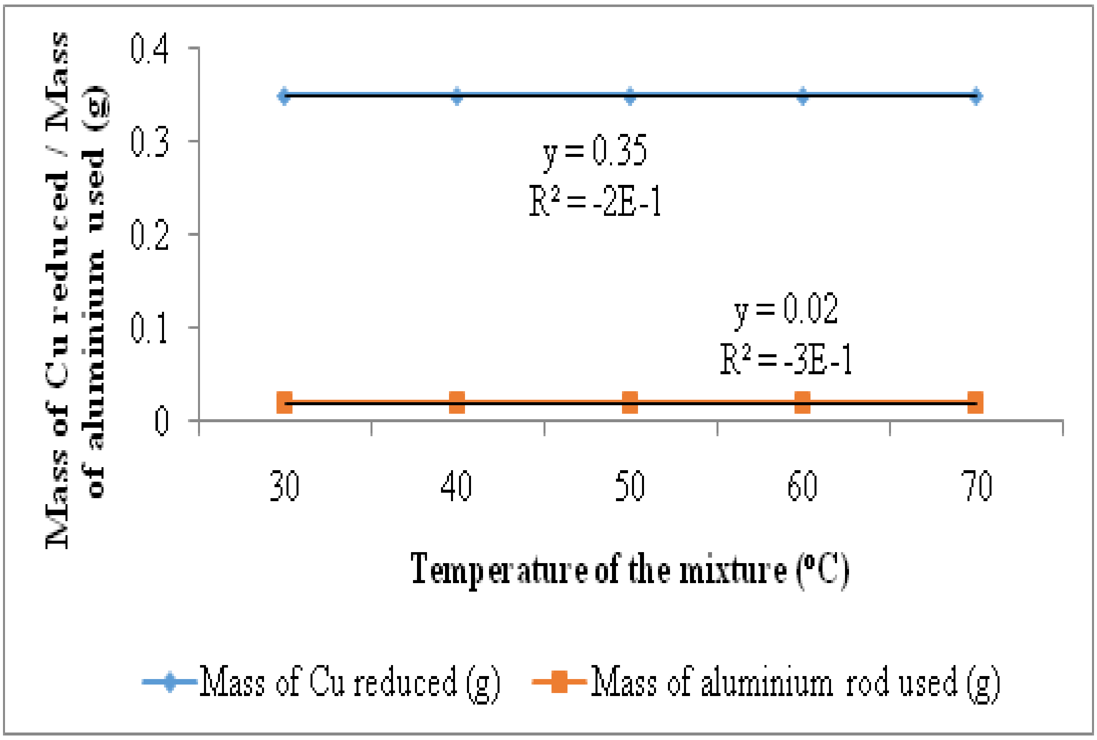

Figure 4.24: The Relationship between Temperatures, Copper Reduced and Mass of Used Aluminium

The results of the regression analysis from the two curves show that r^2 is less than 0. The reaction follows zero-order reaction were change in temperature of the chlorinated chicken waste solution has no effect on the reduction of copper ions and oxidation of aluminium at pH greater than 11(Kugeria *et al.*, 2019).

4.6.3 Relationship between Rates of Copper Ions Reduction with Potential

Figure 4.25 shows the relationship between the rates of copper ion reduction and the oxidation of the aluminium electrode against the potential produced by the reaction (Kugeria *et al.*, 2019).

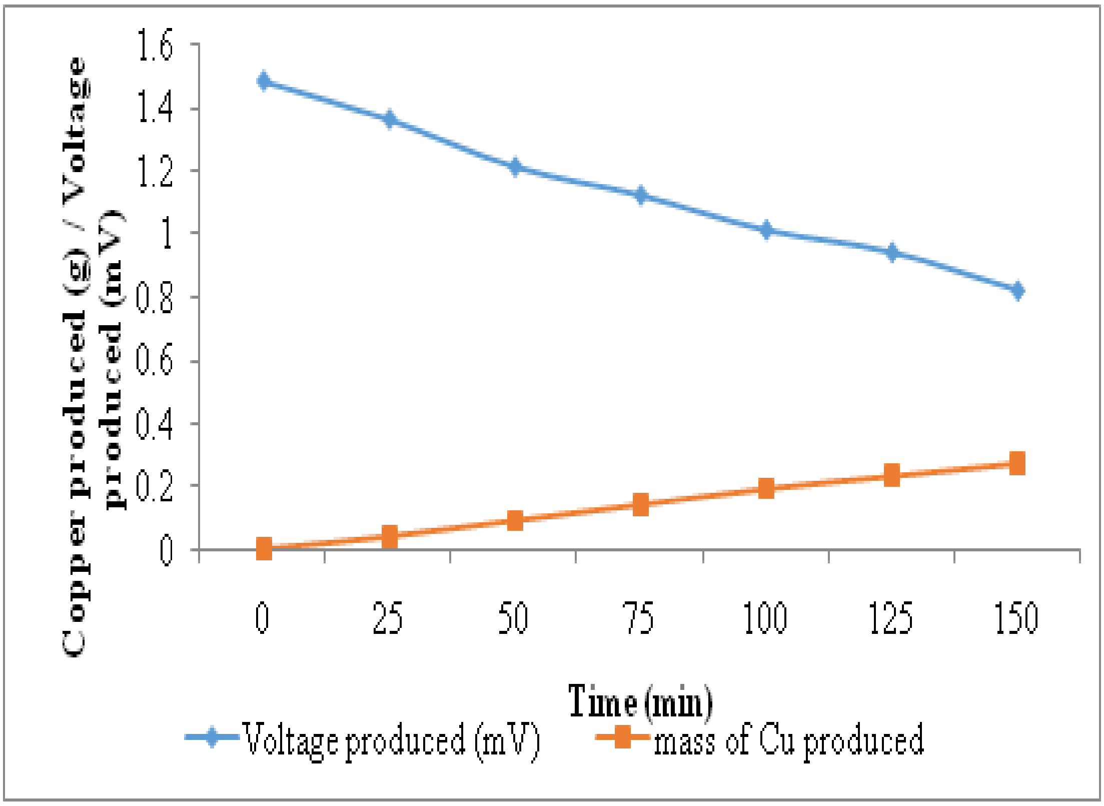

Figure 4.25: The Effects of Potential on Time Taken for Copper Reduction

From the results, the time taken for the complete reduction of Cu ions from the leachate mixture is inversely proportional to the potential produced by the reaction. That means the potential difference produced decreased with a decrease in the number of copper ions present in the electrolyte.

Figure 4.26 shows the results of the reduction of copper from samples 3234, 3238 and 3230 using aluminium electrode in chlorinated chicken dung leachate.

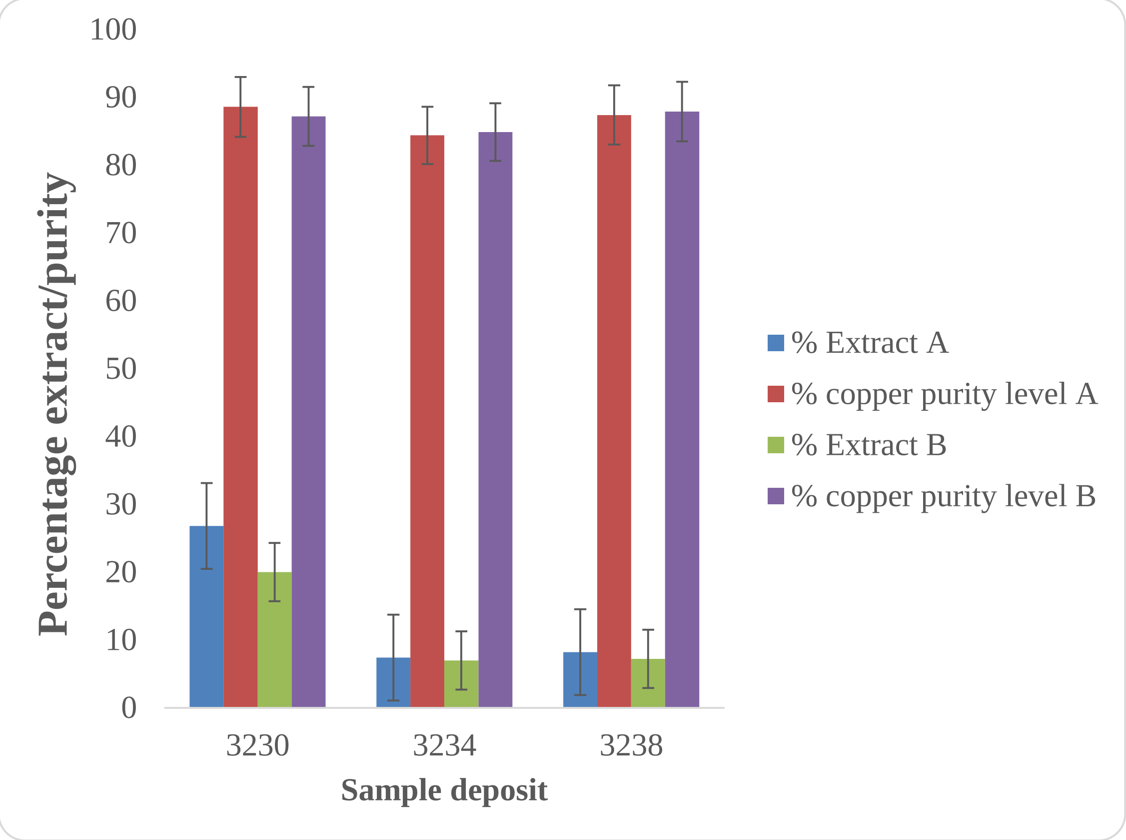

Figure 4.26: The Percentage Extract and Purity of the Reduced Copper

From the results, the copper extract was of high purity. The purity of the extract from the three ores was ranging between 82 and 89 percent. The results show that aluminium can be used to monitor the extraction process until when all copper ions were removed from the leachate (Kugeria *et al.*, 2019).

CHAPTER FIVE

DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Introduction

This chapter gives a discussion of the results given in chapter four. The chapter also details conclusions and recommendations made from the results of the study.

5.2 Mineralogical and Chemical Composition of the Ores

5.2.1 Mineralogical Composition of the Ores

The samples in this study show that the mineralogical composition is mainly albite, quartz mizzonite, and microcline minerals. These are the major impurities in the extraction of copper and titanium (Adalbert, 2005). Chalcopyrite was found to be the main copper mineral in the study area. Several methods have been used to extract copper from chalcopyrite minerals by the leaching process. The leaching is meant to dissolve copper from rocks as well as remove the impurities that don't react with acids. The minerals chalcopyrite, magnetite, and hematite are reactive with acids because of the elemental iron in them (Salmimies *et al.,* 2011). Hydrochloric acid is suitable for leaching copper ores since it does not form precipitates with other soil components as would sulphuric acid (Descostes *et al.,* 2004). According to Descostes *et al.* (2004), leaching removes metal ions such as Fe, Na, K, Ca, Mn, Mg, Ti, and Al from their oxides because they are soluble in acid. The dissolution of pyrite minerals in hydrochloric acid occurs as shown by equation 5.1. This shows that chalcopyrite mineral in Maragwa can be digested using the same process (Descostes *et al.,* 2004).

$$2CuFeS_{2(s)} + 3O_{2(g)} + 4H^{+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2Cu^{2+}_{(aq)} + 2S_{(s)} + 2SO_{2(g)} + 2H_2O_{(l)} \qquad 5.1$$

Mineral ores in Maragwa have been found to contain ilmenite minerals. Several methods of concentration of rutile from ilmenite have been done. For instance, the concentration of the titanium together with iron from lateritic materials has been done (Warui *et al.,* 2015). After concentration, the concentrate was rich in magnetic mineral-titanomagnetite. The same process was done by Mutembei *et al.* (2013), during the concentration of iron from lateritic soils. The concentration of rutile from beach sand using coke has been done (Williams & Steenkamp, 2006). In their study titanomagnetite minerals were able to be reduced using carbon dioxide to rutile at temperatures range of 800 to 1200 °C.

Some ores in Maragwa could not be concentrated using a magnetic separation method due to low iron composition. This study, therefore, explored the use of blending the ore with iron-rich - laterite and later reducing using biomass to investigate that titanium can be concentrated.

5.2.2 Chemical Composition of the Ores

The results from the ten copper deposits sampled showed a mean chemical composition of 4.46 percent Cu. These values are greater than the cut - off grade of 0.4 - 1.0 percent Cu required for commercial extraction (MaCammon, 2003). Therefore, all deposits found in the area of study could be viable for copper extraction. For instance, copper ores in Uganda, ranging from 0.48 to 2 percent Cu (Tuhumwire, 2002) and 0.5 to 2.3 percent in Zambia (Haglund, 2013). South Africa is the leading copper producer with a country mean of 0.49 to 0.71 percent. In Sudan, copper ores have a mean of 1.12 percent Cu (Taib, 2014) and 0.3 to 0.14 percent in Tanzania (Yager, 2016).

The copper distribution from level A to level B was not significantly different. This shows that copper minerals were well distributed within the depth of the study. With this copper distribution, some level of economic extraction can be done. However, further mineral exploration is required to determine mineral distribution in-depth for large scale extraction.

Silica containing mineral was dominant in all deposits with a composition greater than 40.0 percent. Other minerals found were calcium and iron minerals with both a composition greater than 10.0 percent. These minerals are impurities that pose a challenge to the extraction of copper.

The mean rutile composition in the ores in Maragwa was found to be very low for economic extraction compared with those of the countries that mine rutile. For instance, Indian titanium deposits have a chemical composition of 50 - 53 percent rutile (Gambogi, 2007). In Canada, titanium extraction takes place in ores with the average chemical composition of 12 percent TiO_2 (Heinz *et al.*, 2005). South Africa is the largest titanium producer from ores with the chemical composition of 11.6 percent TiO_2 (USGS, 2014). Titanium minerals mined in Western Australia grades at 2.4 percent TiO_2. In Kwale County in Kenya, titanium minerals mined contain a composition ranging between 5 - 6 percent rutile (USGS, 2014). This shows that for significance extraction to be achieved, the ore in this study has to be concentrated to remove most impurities and raise the concentration of rutile to above 5.0 percent.

5.3 Concentration of Titanium in the Ores Using Biomass, Biomass - Laterite Mix Vis a Vis Froth Floatation

5.3.1 The Concentration of Titanium in the Ores Using Biomass

The results showed that the optimum amount of ore sufficiently reduced by 1.0 g of biomass to be 25.0 g of the ore. Combustion of biomass under oxygen controlled condition produces syngas that reduces the ore components. When low amounts of ore are used, it is expected that the excess syngas would give excess energy and thus other reaction products than the desired would be formed. On the other hand, when excess ore is used, the syngas energy would not be sufficient for the desired reaction products.

The gasification process of biomass decomposes lignocelluloses components to char and volatiles (Warui *et al.*, 2015). Gasification of biomass produced syngas which reduced the titanium ore to non-magnetic rutile. The reactions formed are given in equations 5.2 to 5.5 (Warui *et al.*, 2015).

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \qquad 5.2$$

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \qquad 5.3$$

$$CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)} \qquad 5.4$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \qquad 5.5$$

The hot carbon is a reducing agent for ilmenite in the mixture at a temperature range of 800 - 900 °C as shown in equations 5.6.

$$FeTiO_{3(s)} + C_{(s)} \xrightarrow{800\text{–}900°C} TiO_{2(s)} + Fe_{(s)} + CO_{(g)} \qquad 5.6$$

The ilmenite minerals in the ore were reduced to rutile and metallic iron as observed from the XRD results. Rutile and aluminosilicates minerals have low magnetic susceptibility and therefore were not picked by the magnet. This increased the rutile composition in the non-magnetic sample by 315 percent in sample 3227. The use of this method would thus enable the achievement of the required grade for further extraction of titanium.

5.3.2 The Concentration of Titanium from the Mixture of Titanium Ore and Laterite

From the results, it was evident that magnetic separation can be used to concentrate titanium by blending of low iron grade titanium ore with iron-rich laterite. The iron introduced in the mix in the form of goethite and hematite. Minerals goethite and hematite are reduced at a temperature of 500 to 800 °C, to magnetite using CO gas (Purwanto, *et al.,* 2003; Mutembei *et al.,* 2014; Waithaka *et al.,* 2014; Warui *et al.,* 2015). The equations involved are given in equations 5.7 and 5.8.

$$Fe_2O_3 \cdot H_2O_{(s)} \xrightarrow{500\text{–}800°C} Fe_2O_{3(s)} + H_2O_{(g)} \qquad 5.7$$

$$3Fe_2O_{3(s)} + CO_{(g)} \xrightarrow{500\text{–}800°C} 2Fe_3O_{4(s)} + CO_{2(g)} \qquad 5.8$$

During this temperature range, goethite and magnetite further react with ilmenite to form other magnetic susceptible titanomagnetites. The reaction leads to magnetic susceptible titanomagnetite minerals as given by equation 5.9 to 5.10 (Mutembei *et al.,* 2014; Warui *et al.,* 2015).

$$FeO \cdot OH_{(s)} + FeTiO_{3(s)} \xrightarrow{500\ \text{-}800°C} Fe_2TiO_{5(s)} \qquad 5.9$$

$$FeTiO_{3(s)} + Fe_2O_{3(s)} \xrightarrow{500\ \text{-}\ 800°C} Fe_3TiO_{6(s)} \qquad 5.10$$

Further studies have shown that at temperatures above 800 °C ilmenite minerals are reduced to rutile (Steenkamp & Pistorius, 2003; Mutembei *et al.,* 2014; Williams & Steenkamp, 2006). In this study, the mixture of titanium ore with laterite was reduced using biomass at a temperature range of 800 - 900 °C. Gasification of biomass at these temperature ranges produced CO, H_2, and methane gases which are reducing agents.

All ilmenite, hematite and goethite minerals in the mixture were reduced to rutile and iron. The possible reactions that took place are given in equations 5.11 to 5.13 (Cheng *et al.,* 1997; Lobo *et al.,* 2013).

$$Fe_2Ti_3O_{9(s)} \xrightarrow{800\text{–}900°C} Fe_2TiO_{5(g)} + 2TiO_{2(s)} \qquad 5.11$$

$$Fe_2TiO_{5(s)} + CO_{(g)} \xrightarrow{800\text{–}900°C} 2Fe_{(s)} + TiO_{2(s)} + 4CO_{2(g)} \qquad 5.12$$

$$Fe_3TiO_{6(s)} + 4CO_{(g)} \xrightarrow{800\text{–}900°C} 3Fe_{(s)} + TiO_{2(s)} + 4CO_{2(g)} \qquad 5.13$$

The rutile mineral is less magnetic susceptible and therefore was collected in the tailings. The magnetic iron was collected as the magnetic concentrate. The remaining titanomagnetite minerals are collected by the magnet together with iron thus increasing the rutile levels. In one of the sample 3227, the rutile increased by 346.88. Though laterite materials had some rutile content, the very low rutile concentration in the magnetic sample makes the technique successful. This percentage increase shows that the method is viable and better than the one investigated by Mutembei (2013), Mutembei *et al.* (2014), Warui, *et al.* (2015), and Waithaka *et al.* (2014). In their methods rutile improves with a range of 1- 6 percent.

5.3.3 The Concentration of Titanium Using Froth Floatation

Froth flotation method is usually used to separate sulfides, carbonates and oxides of copper minerals before further refinement (Bulatovic, 2007; Grobler *et al.,* 2009). The method was investigated on the concentration of rutile and further comparison done with other methods investigated. During the flotation process, oleic acid was used as both frother and anionic collector for ilmenite minerals. The bromoformium solutions were used as a modifier solution. Oleic acid formed a stable froth layer compared to other frother tested. The acid was able to hold bubbles for some time before they eventually burst. Oleic acid adsorption takes place on cationic sites of ilmenite minerals. As an anionic collector, it preferentially adsorbs onto the surface with the strongest positive charge and renders them hydrophobic (Kawatra, 1995). This probably explains why there was an increase in metal oxides in the froth. According to Kawatra (1995), silica minerals have a strongly-negative surface charge at approximately neutral pH, and therefore have little affinity for anionic collectors such as oleic acid. In the floatation process, a bromoformium solution was possibly used as a depressant (or modifier) for silica minerals and to some extent copper minerals and other iron minerals. That is why rutile was collected in the froth while silicate mineral was left in the sinter. The increase of 218.75 percent rutile using froth flotation method shows that the method can be used in the concentration of titanium ore.

5.3.4 Comparison of the Rutile Obtained Using Biomass, Froth Flotation and Ore - Laterite Mixture Using Biomass

Figure 5.1 shows the comparison of rutile obtained from sample 3227 using the three methods; froth floatation, thermal reduction of titanium ore-biomass mix and thermal reduction of titanium ore - laterite ore - biomass mix.

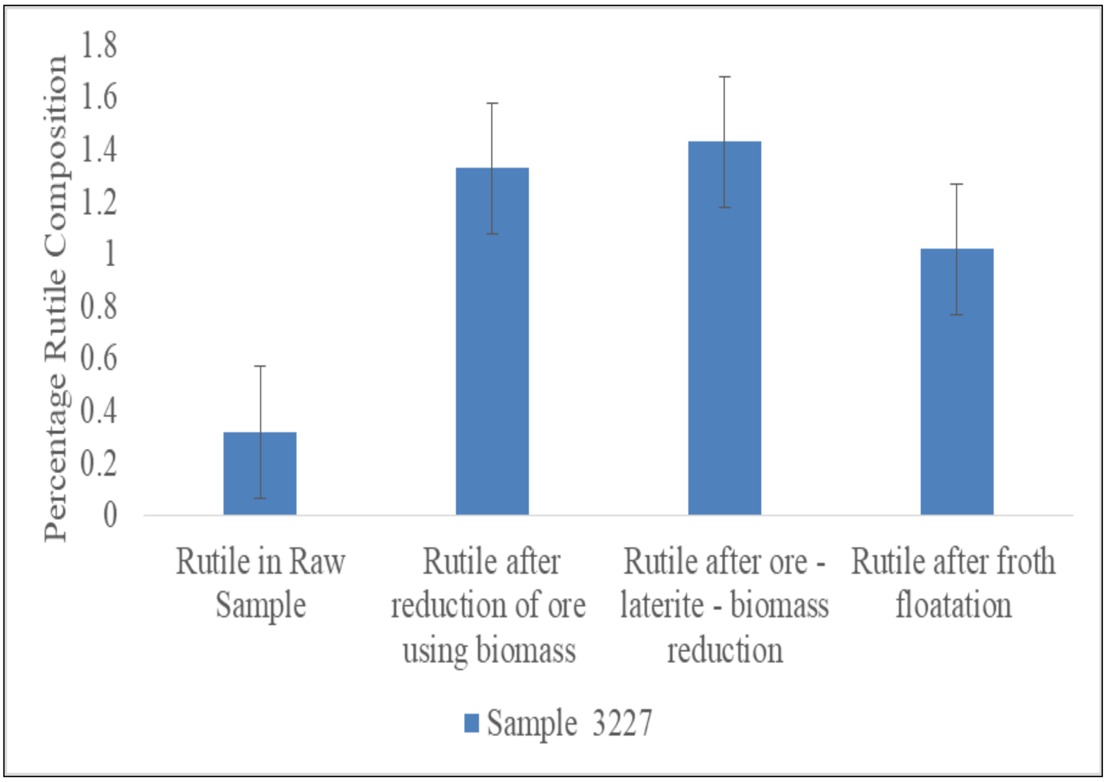

Figure 5.1: Comparison of the Rutile Obtained Using Biomass, Froth Flotation and Ore - Laterite Mixture using Biomass

The results show that the concentration of the titanium from ores by reduction of ore - laterite mixture using biomass was the best method of concentration. The statistical comparison of the means of the three methods, done in all deposits is given in table 5.1.

Table 5.1: Statistical Comparisons of the Means of Rutile Using Biomass, Froth Flotation and Ore - Laterite Mixture using Biomass

	Rutile in raw samples	Rutile after ore-biomass reduction	Rutile after ore-laterite - biomass reduction	Rutile after froth flotation
Mean	0.72±0.15	1.39±0.16	1.80±0.16	1.15±0.20
Confidence Level (95.0%)	0.339	0.352	0.353	0.454

The mean of the rutile obtained after ore - laterite - biomass reduction method was higher compared to that of ore - biomass and froth flotation methods. However there were no much significance difference in the results of the rutile obtained before and after concentration of the ores.

The results of the comparison of other deposits are given in appendix 14. The method improved rutile from 0.32 to 1.43 percent. However, sample 3232 gave significant high values of rutile using froth flotation. This probably was due to different mineral characteristics in the ore that influenced oleic acid adsorption on cationic sites of the minerals. Besides, a bromoformium solution could have acted as the best depressant for most minerals thus allowing for the collection of most rutile in the froth. The method is less expensive compared to that of froth floatation. Reason being that it does not require buying chemicals, but the use of biomass from organic waste. The method is also suitable for titanium ores with low iron minerals. Laterite rich in iron minerals are widely available and some contain a significant amount of titanium. The method is also environmental friendly since it promotes the recycling of organic wastes that would otherwise result in pollution.

5.4 Copper Extraction using Iron in Acidic Media

From the results, the copper extract was found to be of high quality between 81.4 to 87.3 percent than that of the extraction using chlorinated chicken dung leach with the ore leach. For pure copper, the remaining impurities can easily be removed using electrolysis (Baba *et al.,* 2012). However, this method of copper is an old process that was abandoned due to impurities and besides, iron metal was expensive by then (Annamalai & Murr, 1979; Habashi, 2009). Currently, iron metal is widely available though it remains relatively unaffordable. The results from this study show that the method gives few impurities which is a success. The use of an iron electrode does not require the use of electricity. This makes the method to be affordable for copper extraction. The optimal temperatures can be affordable by the use of solar radiation especially if the ores are located in tropical areas.

5.5 Copper Extraction using Chicken Dung Leachate

5.5.1 Characterization of Chicken Dung Leachate

The results showed that when the chicken dung leachate is prepared and kept to equilibrate for fourteen days, amine and amide content increases (Kugeria *et al.,* 2018). This is because chicken dung contains about 0.9 to 1.5 percent nitrogen content which is readily available for reaction (Foreman & Long, 2013). The amines in chicken dung are aerobically oxidized to amides as shown by equation 5.14.

$$\mathrm{RCH_2NH_2 + O_2 \rightarrow RCONH_2 + H_2O} \qquad 5.14$$

Where R is an alkyl group

This oxidation process increases the amide content in the leachate which may be available for conversion to hydrazones. The amines and amides compounds are potential sources for making hydrazine when suitable oxidizing agents are used. Hydrazine compound is prepared after chlorine gas reacts with sodium hydroxide as given in equation 5.15.

$$\mathrm{Cl_{2(g)} + 2NaOH_{(aq)} \xrightarrow{70°C} NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(l)}} \qquad 5.15$$

When the produced sodium hypochlorite is introduced into chicken dung leachate, it oxidizes amines and amides present to hydrazones as given in equations 5.16.

$$\mathrm{2NH_{3(g)} \xrightarrow{NaOCl} H_2NNH_{2(aq)} + NaCl_{(aq)} + H_2O_{(l)}}. \qquad 5.16$$

The chemical transformation was confirmed by the FT-IR and MS methods. Hydrazine is a strong reducing agent. It is also toxic and unstable compound and therefore found in solution form (Tsubakizaki *et al.*, 2009). In this experiment, the formation of hydrazones in chicken dung leachate makes it a potential electrolyte for the reduction of some metals like copper (Kugeria *et al.,* 2018).

5.5.2 Kinetics of Extraction and *In-Situ* Reduction of Copper using Chicken Dung Leachate

The results showed that for the in-situ prepared hydrazine in chlorinated chicken dung leachate, copper ions reduction started at a pH of 6.0. In a strongly acidic environment, no copper was produced. At the acidic environment, and reduced metal was immediately dissolved by the acid. In the region between a pH of 6.0-11.0, stable hypochlorite was formed when chlorine was bubbled. The sodium hypochlorite produced oxidized amines forming hydrazones **(**Adams and Brown, 1922; Schirmann & Bourdauducq, 2002; Mostafa, 2011; Kugeria *et al.*, 2018). The resulting hydrazones were responsible for the reduction process. Thus the reduction was found to be best in strongly basic media.

The results showed that the optimal period required for chlorination of the electrolyte was three minutes. This interaction time was enough to produce the required concentration of the hydrazones. The right temperature for hydrazones production was determined as 70 °C. As temperatures increases, the kinetic energy of the particles increases which increases the collision of particles and so is the reaction. This increases the formation of hydrazones. At temperatures above 70 °C, the amino compounds present in chicken dung leachate are possibly denatured thus affecting the formation of hydrazine.

Adsorption and in-situ reduction of copper from copper ore using chlorinated chicken dung were successful. The amines and uric acids in chicken waste were found to complex copper ions from ores instead of leaching the ore with acid. Therefore, the copper ions obtained from the ore were later reduced by *in-situ* prepared hydrazones species.

The possible reactions during the reduction of copper are given in equations 5.17 and 5.18.

$$2Cu^{2+}_{(aq)} + N_2H_{4(aq)} \rightarrow 2Cu_{(s)} + N_{2(g)} + 4H^{+}_{(aq)} \qquad 5.17$$

$$Cu^{2+}_{(aq)} + 2N_2H_{4(aq)} + 2OH^{-}_{(aq)} \rightarrow Cu_{(s)} + N_{2(g)} + 2NH_{3(g)} + 2H_2O_{(l)} \qquad 5.18$$

The reduction of copper from copper leachate using chlorinated chicken dung leachate gave a high percentage of copper purity. The leachate had less contamination of alumina, phosphorous, calcium and silica. That is why all copper produced was of purity above 60 percent. The *in-situ* extraction of copper from mineral ore using chlorinated chicken dung leachate produces copper which is of very low purity. This occurred because some of the amines and amide acted as ligands to extract the copper from ore into the solution to make it available for reduction (Moonsung *et al.,* 2005). However, copper extracted from this method was found to have a high percentage of impurity compared to the acid leaching. This may be because oxides of aluminium and silicon did not dissolve during the *in-situ* reduction method. Ammonia has also been reported to react with silica hence forming siloxane groups (NH_3-OSi_2) (Zamani *et al.,* 2009). Further studies by Blomfield and Little (1971) have shown that siloxane groups $SiNH_2$ occurs after silica reacts with ammonia as shown in equation 5.19.

$$OSi_{2(s)} + NH_{3(aq)} \rightarrow SiNH_{2(aq)} + SiOH_{(aq)} \qquad 5.19$$

This interaction could have reduced the available amine for copper extraction as well as those available for the formation of hydrazine.

The low percentage purity of copper may be attributed to the formation of amine mesoporous silica nanoparticle (amine-MSN) with a formula ($Si_rO_xC_yNHz$) (Batista *et al.,* 2016). This interaction between silica and amines introduces impurities to copper extracted. Copper extraction from ore leachate by reduction using chlorinated chicken dung leach gave higher percentage copper extract than that of the iron electrode in acidic media. However, the method had a relatively lower percentage of copper purity of extract than the iron electrode method. Although the percentage of copper purity was low, the method was viable. The chicken dung is readily available and the extraction can be done anywhere where there is a lot of water.

5.6 Monitoring the Extent of Copper Extraction from the mixture of Copper Leachate and Chlorinated Chicken Dung Leachate using aluminium electrode as an indicator

The *in-situ* reduction of copper ions using hydrazones in chlorinated chicken dung leachate was successful at 70 °C and pH of 11.0 (Kugeria *et al.,* 2018). In that environment, it was difficult to determine the stoichiometric ratios of the reacting species and therefore could not calculate their respective quantities. To enable their evaluation, an aluminium electrode was used as an indicator as it is known to reduce copper in solution (Bard *et al.,* 1985). The equation 5.20 shows that reduction process.

$$3\mathrm{Cu}^{2+}_{(aq)} + 2\mathrm{Al}_{(s)} \Leftrightarrow \mathrm{Cu}_{(s)} + 2\mathrm{Al}^{3+}_{(aq)} \qquad 5.20$$

The equilibrium constant for the equation can be expressed as shown by equation 5.21.

$$\mathrm{K_c} = \frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Cu}^{2+}]^3} \qquad 5.21$$

The K_c value determines the direction of the reaction. Thus, if less than one the reaction will move to the left and if greater than one the reaction will move to the right. The magnitude of K_c will be dependent on the concentration of the reacting species. When copper (II) ions have been depleted in the solution, K_c will be infinitely high.

For a large scale copper extraction, it is important to monitor the change in the concentration of copper and the other species involved in the redox process. In this study, the variation of the analyte species was monitored as a function of potential difference across an electrochemical cell. An aluminum electrode is most appropriate because aluminium is more reactive than copper and the redox reaction between them occurs as shown by equations 5.22 and 5.23.

$$\mathrm{Al}_{(s)} \rightarrow \mathrm{Al}^{3+}_{(aq)} + 3e^{-} \qquad 5.22$$

$$\mathrm{Cu}^{2+}_{(aq)} + 2e^{-} \rightarrow \mathrm{Cu}_{(s)} \qquad 5.23$$

Aluminium and its oxides corrode at very low pH, and its oxides also corrode at high pH (Arrellanes *et al.,* 2014; Natishan & O’Grady, 2014). At a pH of 6.5 - 9.0, aluminium forms stable oxides on its surface (Arrellanes *et al.,* 2014; Natishan & O’Grady, 2014). The oxide layer formed is expected to decrease the rate of aluminium deterioration and copper displacement. However, the aluminium electrode being amphoteric undergone a reduction at a high pH of 11.0 due to the flow of electrons from the chlorinated chicken dung leachate to zero valences as shown in the equation 5.24.

$$3N_2H_{4(aq)} + 12OH^-_{(aq)} + 4Al^{3+}_{(aq)} \rightarrow 3N_{2(g)} + 12H_2O_{(l)} + 4Al_{(s)} \qquad 5.24$$

This saves the already consumed aluminum oxide coated on the surface of the electrode hence mitigated the effects of the sacrificed metal.

In the experiment, a graphite bridge was created to ensure a balanced flow of ions in the electrolyte, as well as that of electrons in the cells. This explains why the constant mass of copper was observed with minimum corrosion of aluminium rod at pH above 11. This behaviour of aluminium was used to monitor the rate of copper ions reduction. It was done at room temperatures and pH of 11 of chlorinated chicken dung leachate. The investigation on the amount of copper reduced at varying temperatures was found to have no relationship. Therefore, the extraction could be monitored at any temperature without affecting the rate of copper reduction and aluminium corrosion.

The rate of displacement of copper ion and the potential difference obtained during the reaction was found to be a first-order reaction. This occurred because there was a decrease in the concentration of copper ions in the chicken waste with an increase in time as shown in equation 5.25.

$$\text{Rate} = {}^{-d[A]}\!/_{dt} = k[A] \qquad 5.25$$

Where the "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time).

The potential difference obtained also decreases with a decrease in the concentration of copper ions with time. Consequently, the rate of the oxidation of aluminium decreases with a decreasing number of complexed copper ions by amine and uric acids in chicken waste solution. Additionally, the higher the concentration of copper ions in solution the higher the potential difference produced during the redox process. The high positive potential difference creates a spontaneous redox reaction. The chlorinated amine and uric acid in chicken dung produced a current that was used to recharge the number of electrons used from aluminium during the oxidation process hence recovering that metal as shown in equation 5.24. The quantity of electricity produced can give a measure of the quantity of contributing species in solution as expressed in the Nernst equation given in equation 5.28. The change of potential with the concentration of copper ions can be explained by equations 5.26 to 5.28.

$$E - E^0 = \frac{RT}{nF} \text{In} Q \Rightarrow \Delta E = \frac{RT}{nF} \text{In} Q \qquad 5.26$$

The equation can be written as

$$\Delta E = \frac{RT}{nF} \text{In} \frac{\text{Reduced}}{\text{Oxidised}} \qquad 5.27$$

$$\text{For this case } \Delta E = \frac{RT}{nF} \text{In} \frac{\left[Cu^{2+}_{(aq)}\right]}{\left[Cu^{0}_{(aq)}\right]} \Rightarrow \Delta E = \frac{RT}{nF} \text{In} \left[Cu^{2+}_{(aq)}\right] \qquad 5.28$$

This implies that as the electrochemical process continues, the value of ΔE proportionally decreases with a decrease in Cu^{2+} ions in Cell 1. Eventually, when $\Delta E=0$, no more copper ions are available for the reduction.

5.7 CONCLUSIONS

(i) The copper mineral found at Maragwa location is mainly chalcopyrite with a mean of 4.46 percent. The titanium mineral found in Maragwa is ilmenite with the chemical composition of rutile as 0.77 percent level A and 0.86 percent level B.

(ii) The concentration of rutile by reduction of the ore – laterite mixture using syngas produced by biomass increased the rutile level from 0.32 to 1.43 percent. This method produced the highest results compared with that of ore - biomass reduction method (1.33 percent) and froth floatation method (1.02 percent)

(iii) The reduction of copper using an iron electrode in acidic media can occur at optimum temperatures between 45 °C, with the percentage of copper extract ranging from 51.1 to 78.4 percent

(iv) The reduction of copper using impure hydrazine from chlorinated chicken dung leachate was successful. The method gave the percentage of copper extract ranging from 58.5 to 89.25 percent.

(v) The process of reduction of copper using impure hydrazones prepared from chicken dung can be monitored using a devised aluminum electrode.

5.8 RECOMMENDATIONS

5.8.1 Recommendations for Further Research from this Work

(i) Further research work to be done on abundance investigation to determine the extraction potential of copper using the chicken dung reduced *in - situ*

(ii) That further investigation is carried out on the possibility of concentrating titanium in ore with minimal iron concentration using alternative sources of iron at temperatures below 800 °C, the temperature at which magnetic titanium compounds are formed.

5.8.2 Recommendations for Further Work

(i) The method of concentrating titanium by heating the mixture of ores - laterite and biomass, was done on a laboratory scale and therefore a pilot study should be done for large scale concentration of titanium.

(ii) The method of copper extraction by displacement of copper ions using an iron electrode was done at optimum temperatures of 40 to 45 °C on the laboratory scale. Therefore, a pilot study should be done on a large scale.

(iii) Hydrazones are chemicals with many biological functions. Studies should be done to isolate them from chlorinated chicken dung.

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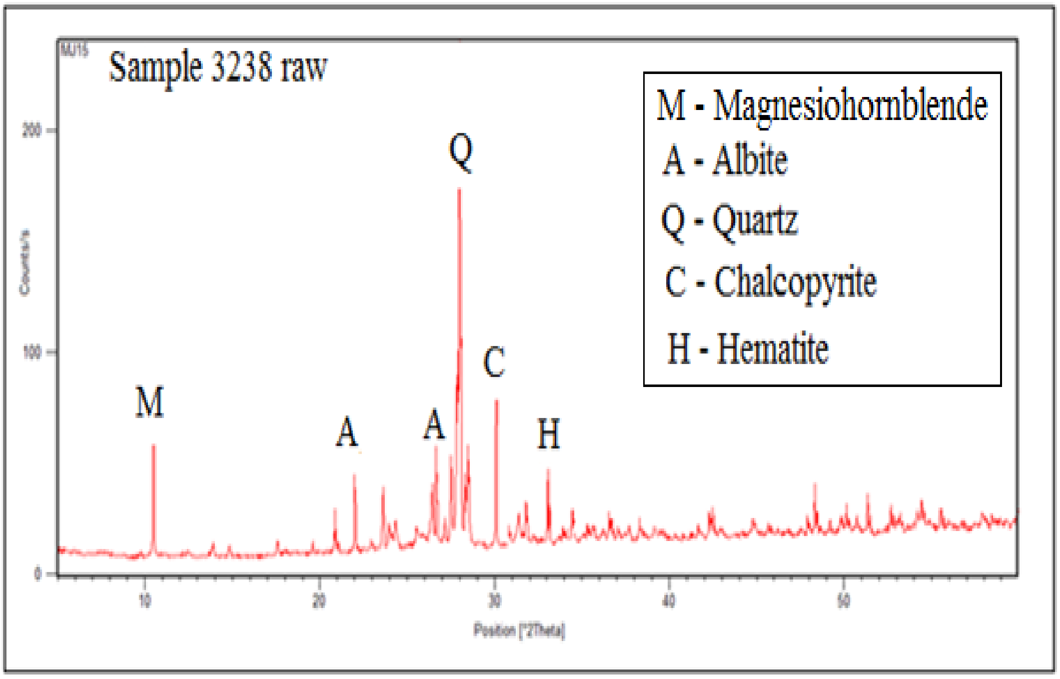
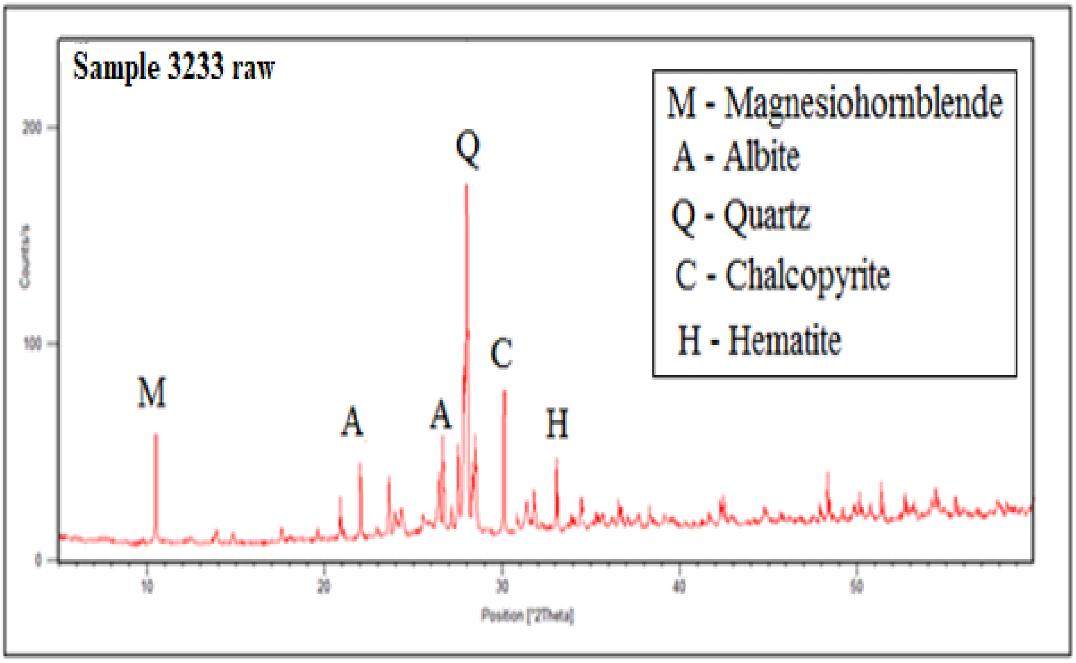
APPENDICES

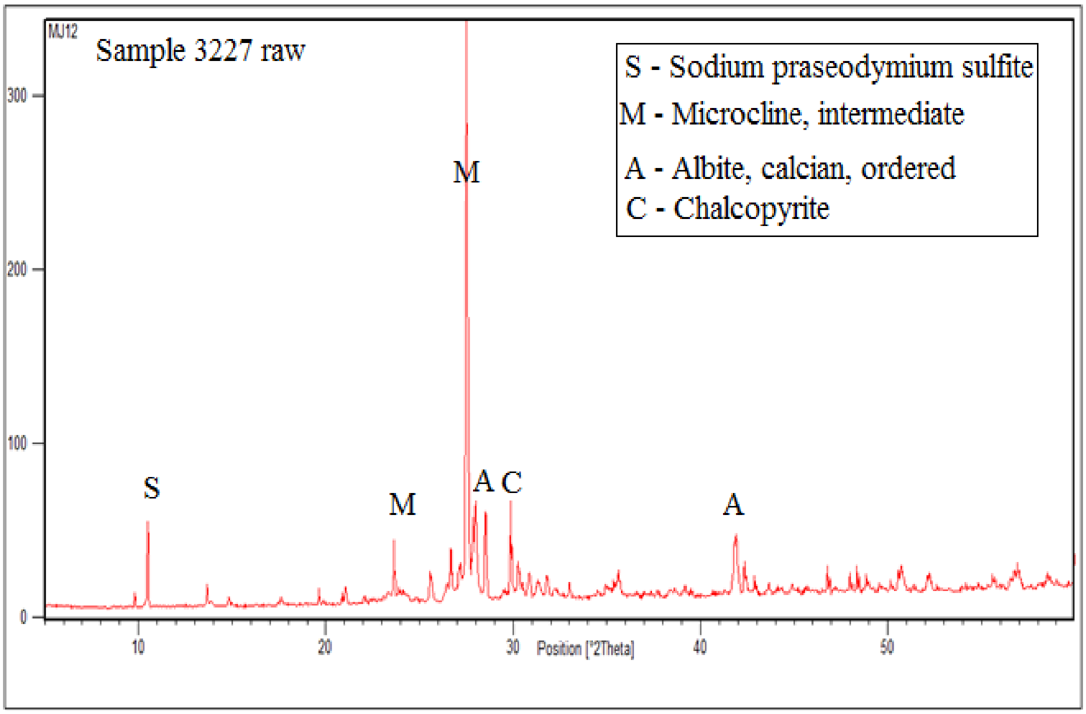
Appendix 1: The XRD Spectrum for Raw Ore Sample 3238



Appendix 2: The XRD Spectrum for Raw Ore Sample 3233



Appendix 3: The XRD Spectrum for Raw Ore Sample 3227



Appendix 4: The Elemental Analysis at level A and B Using AAS

Sample Code	SiO_2 Mean± SE	Al_2O_3 Mean± SE	K_2O Mean± SE	Na_2O Mean± SE	CaO Mean± SE	TiO_2 Mean± SE	MnO Mean± SE	Fe_2O_3 Mean± SE	CuO Mean± SE	MgO Mean± SE	LOI Mean± SE
3227 A	48.34± 0.01	8.42± 0.02	7.74± 0.07	5.22± 0.05	13.86± 0.06	0.32± 0.05	0.32± 0.05	5.27± 0.04	5.05± 0.01	2.12± 0.02	2.26± 0.03
3227 B	39.46± 0.02	5.63± 0.01	6.54± 0.04	8.50± 0.01	15.50± 0.03	0.46± 0.02	0.46± 0.01	12.55± 0.04	3.90± 0.02	2.03± 0.03	3.96± 0.06
3230 A	41.51± 0.08	8.13± 0.05	7.76± 0.05	12.85± 0.07	2.28± 0.02	0.41± 0.06	0.11± 0.02	3.82± 0.03	12.00± 0.01	5.81± 0.02	1.49± 0.04
3230 B	37.54± 0.01	6.28± 0.01	6.95± 0.01	13.85± 0.01	5.00± 0.03	0.67± 0.03	0.17± 0.02	4.37± 0.01	8.95± 0.08	6.91± 0.01	2.98± 0.05
3231 A	44.96± 0.13	5.47± 0.01	4.87± 0.02	6.08± 0.05	19.03± 0.07	0.46± 0.03	0.80± 0.02	7.58± 0.04	5.52± 0.02	3.73± 0.02	2.09± 0.04
3231 B	31.28± 0.01	7.14± 0.02	4.84± 0.01	5.85± 0.01	21.55± 0.03	0.37± 0.01	1.41± 0.02	8.93± 0.03	7.29± 0.01	3.55± 0.04	1.82± 0.06
3232 A	42.73± 0.08	11.47± 0.05	10.43± 0.03	3.87± 0.04	2.60± 0.01	1.13± 0.09	0.14± 0.01	17.60± 0.03	3.45± 0.02	5.55± 0.04	1.46± 0.01
3232 B	31.61± 0.01	9.28± 0.01	9.91± 0.01	1.05± 0.04	16.81± 0.02	1.86± 0.01	0.26± 0.01	21.08± 0.01	3.03± 0.62	3.17± 0.05	1.64± 0.02
3233 A	25.84± 0.05	9.17± 0.06	6.84± 0.01	3.69± 0.02	1.31± 0.01	0.91± 0.03	0.21± 0.03	40.92± 0.10	5.54± 0.03	3.14± 0.04	1.76± 0.05
3233 B	28.76± 0.01	11.90± 0.01	4.85± 0.03	8.84± 0.01	1.95± 0.01	1.14± 0.03	0.29± 0.01	24.55± 0.01	7.01± 0.05	2.88± 0.01	1.70± 0.02
3234 A	35.83± 0.06	3.59± 0.05	0.69± 0.02	12.5± 0.05	23.67± 0.06	0.64± 0.07	0.27± 0.07	13.10± 0.02	2.45± 0.02	4.12± 0.01	3.60± 0.01
3234 B	34.8± 0.02	2.84± 0.01	1.00± 0.01	8.39± 0.01	18.40± 0.01	0.45± 0.02	0.31± 0.01	19.85± 0.04	1.98± 0.05	5.14± 0.05	3.99± 0.07

Appendix 4: (Continuation)

Sample Code	**SiO_2 Mean± SE**	**Al_2O_3 Mean± SE**	**K_2O Mean± SE**	**Na_2O Mean± SE**	**CaO Mean± SE**	**TiO_2 Mean± SE**	**MnO Mean± SE**	**Fe_2O_3 Mean± SE**	**CuO Mean± SE**	**MgO Mean± SE**	**LOI Mean± SE**
3238 A	42.46± 0.04	10.75± 0.04	2.67± 0.03	13.05± 0.07	10.61± 0.03	1.71± 0.03	0.33± 0.03	10.06± 0.10	5.54± 0.01	1.93± 0.04	1.78± 0.02
3238 B	45.89± 0.01	7.24± 0.01	4.38± 0.05	17.75± 0.01	11.05± 0.05	1.58± 0.01	0.35± 0.01	5.46± 0.03	8.26± 0.02	3.63± 0.02	1.57± 0.03
3240 A	74.27± 0.09	3.33± 0.05	2.44± 0.05	9.03± 0.08	1.08± 0.01	0.39± 0.02	0.03± 0.01	1.56± 0.03	3.93± 0.02	1.03± 0.02	1.41± 0.01
3240 B	62.73± 0.01	5.46± 0.02	2.90± 0.01	12.92± 0.01	2.02± 0.04	0.52± 0.01	0.02± 0.01	2.49± 0.01	3.71± 0.02	1.03± 0.06	1.33± 0.02
3244 A	47.04± 0.06	14.73± 0.05	2.46± 0.04	16.37± 0.04	8.10± 0.04	0.18± 0.02	0.01± 0.01	0.04± 0.01	3.98± 0.01	4.23± 0.01	1.76± 0.02
3244 B	38.28± 0.01	8.95± 0.03	3.06± 0.05	16.91± 0.02	12.48± 0.02	0.38± 0.02	0.02± 0.01	0.03± 0.01	4.68± 0.01	2.99± 0.05	1.79± 0.06
3242 A	39.73± 0.04	7.65± 0.10	1.70± 0.01	5.24± 0.06	12.91± 0.02	1.06± 0.06	0.28± 0.02	20.26± 0.09	8.35± 0.01	3.22± 0.02	1.99± 0.03
3242 B	42.08± 0.03	4.26± 0.03	2.86± 0.02	2.93± 0.02	17.40± 0.02	1.17± 0.04	0.35± 0.01	12.47± 0.01	6.70± 0.02	3.06± 0.05	1.54± 0.04

Each value is Mean±SE of three replicates

Appendix 5: The Elemental Analysis at level A and B Using XRF

Sample Code	SiO_2 Mean± SE	Al_2O_3 Mean± SE	K_2O Mean± SE	Na_2O Mean± SE	CaO Mean± SE	TiO_2 Mean± SE	MnO Mean± SE	Fe_2O_3 Mean± SE	CuO Mean± SE	MgO Mean± SE
3227 A	48.34± 0.03	8.39± 0.02	7.76± 0.07	5.21± 0.02	13.85± 0.06	0.33± 0.04	0.25± 0.02	5.27± 0.03	5.06± 0.02	2.13± 0.01
3227 B	39.46± 0.03	5.58± 0.02	6.55± 0.03	8.48± 0.02	15.45± 0.02	0.49± 0.3	0.45± 0.03	12.43± 0.02	3.89± 0.01	2.04± 0.03
3230 A	41.58± 0.15	8.18± 0.04	7.76± 0.04	12.89± 0.03	2.28± 0.02	0.40± 0.03	0.11± 0.01	3.82± 0.04	12.07± 0.06	5.80± 0.04
3230 B	36.6± 0.01	6.24± 0.04	6.95± 0.02	13.84± 0.05	4.90± 0.03	0.68± 0.02	0.13± 0.05	4.35± 0.03	8.94± 0.03	6.92± 0.05
3231 A	45.22± 0.54	5.44± 0.02	4.87± 0.04	6.12± 0.01	19.03± 0.07	0.44± 0.02	0.83± 0.04	7.62± 0.04	5.54± 0.06	3.75± 0.01
3231 B	31.41± 0.02	7.13± 0.03	4.87± 0.07	5.83± 0.05	22.15± 0.02	0.35± 0.05	1.39± 0.06	8.87± 0.03	7.26± 0.01	2.59± 0.03
3232 A	42.75± 0.08	11.42± 0.04	10.49± 0.03	3.89± 0.02	2.60± 0.01	1.12± 0.13	0.14± 0.02	17.64± 0.03	3.40± 0.03	5.48± 0.07
3232 B	31.52± 0.05	9.26± 0.06	9.89± 0.03	1.09± 0.03	16.59± 0.05	1.88± 0.04	0.22± 0.03	20.9± 0.06	3.01± 0.05	4.23± 0.08
3233 A	25.85± 0.04	9.19± 0.03	6.81± 0.02	3.68± 0.03	1.33± 0.01	0.90± 0.04	0.23± 0.04	40.97± 0.04	5.50± 0.02	3.16± 0.01
3233 B	28.8± 0.03	11.91± 0.05	4.82± 0.02	8.83± 0.04	1.92± 0.08	1.15± 0.04	0.29± 0.07	24.55± 0.03	6.99± 0.02	2.86± 0.07
3234 A	35.87± 0.08	3.59± 0.03	0.69± 0.02	12.13± 0.06	23.67± 0.06	0.61± 0.04	0.20± 0.04	13.09± 0.05	2.41± 0.02	4.16± 0.03
3234 B	34.3± 0.06	2.85± 0.04	1.04± 0.03	8.37± 0.02	18.4± 0.06	0.46± 0.02	0.36± 0.05	19.82± 0.03	1.97± 0.05	5.13± 0.03

Appendix 5: (Continuation)

Sample Code	**SiO$_2$ Mean± SE**	**Al$_2$O$_3$ Mean± SE**	**K$_2$O Mean± SE**	**Na$_2$O Mean± SE**	**CaO Mean± SE**	**TiO$_2$ Mean± SE**	**MnO Mean± SE**	**Fe$_2$O$_3$ Mean± SE**	**CuO Mean± SE**	**MgO Mean± SE**
3238 A	42.47± 0.09	10.78± 0.01	2.71± 0.04	13.08± 0.08	10.61± 0.03	1.71± 0.02	0.52± 0.33	10.07± 0.09	5.51± 0.03	1.84± 0.02
3238 B	44.9± 0.03	7.24± 0.94	4.13± 0.04	16.95± 0.03	11.17± 0.08	1.56± 0.03	0.33± 0.02	5.44± 0.06	8.25± 0.02	3.61± 0.04
3240A	74.28± 0.02	3.23± 0.02	2.43± 0.01	9.04± 0.08	1.08± 0.02	0.42± 0.05	0.06± 0.02	1.55± 0.02	4.05± 0.07	1.11± 0.03
3240 B	62.8± 0.02	5.45± 0.06	2.97± 0.04	13.93± 0.07	2.0± 0.07	0.54± 0.04	0.04± 0.12	2.49± 0.05	3.70± 0.02	0.99± 0.03
3244 A	47.09± 0.06	14.70± 0.03	2.49± 0.01	16.37± 0.04	8.10± 0.04	0.18± 0.03	0.06± 0.02	0.04± 0.01	4.05± 0.09	4.29± 0.04
3244 B	38.3± 0.05	8.94± 0.10	3.09± 0.02	16.92± 0.09	11.95± 0.05	0.36± 0.18	0.06± 0.06	0.07± 0.04	4.69± 0.12	3.03± 0.07
3242 A	39.70± 0.09	7.68± 0.02	1.69± 0.03	5.12± 0.54	13.91± 0.02	1.05± 0.11	0.29± 0.01	20.41± 0.04	8.33± 0.03	3.19± 0.02
3242 B	42.1± 0.05	4.25± 0.08	2.97± 0.02	2.84± 0.01	17.39± 0.05	1.16± 0.07	0.42± 0.04	12.50± 0.08	6.68± 0.04	3.10± 0.03

Each value is Mean±SE of three replicates

Appendix 6: Magnetic Separated Sample after Reduction of Samples at Level A Using Biomass

Sample Code	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	CuO
3227	9.57	4.29	10.94	4.74	5.04	7.2	0.01	0.48	48.56	7.35
3232	29.81	10.67	0.87	2.57	1.28	8.9	0.02	0.02	42.85	1.55
3234	8.49	11.84	19.73	3.92	8.33	4.28	0.06	0.59	40.61	1.18
3230	27.26	6.92	2.02	0.94	3.82	5.87	0.03	0.25	38.41	14.91
3238	18.24	8.78	19.02	2.92	0.82	0.74	0.02	0.11	48.75	3.15
3231	21.82	2.48	12.49	1.73	4.88	5.61	0.04	0.46	44.91	7.20
3233	21.63	4.74	0.84	0.43	4.29	3.52	0.07	0.32	54.92	8.16
3240	27.28	5.67	1.85	0.84	4.83	2.64	0.02	0.56	52.54	1.51
3244	19.21	12.23	5.95	1.49	3.82	1.64	0.08	0.73	47.49	6.03
3242	21.18	3.69	7.19	3.73	6.17	5.13	0.04	0.03	43.94	9.65

Appendix 7: Non-Magnetic Separated Sample after Reduction Using Biomass

Sample Code	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	CuO
3227	56.05	6.88	14.25	3.92	3.87	3.21	1.33	0.37	3.79	4.43
3232	51.06	9.35	14.82	3.09	6.11	14.4	1.42	0.04	6.15	4.38
3234	42.38	13.64	20.59	3.11	4.33	3.8	1.02	0.12	5.78	6.29
3230	48.41	5.48	11.83	8.9	3.29	6.2	1.12	0.71	3.26	6.26
3238	44.92	6.84	17.45	5.55	4.1	2.92	2.11	0.12	5.03	2.75
3231	43.93	7.69	10.6	2.83	3.94	2.21	1.35	0.03	4.81	4.76
3233	48.39	14.22	4.61	3.77	5.21	3.98	1.61	0.66	8.52	2.99
3240	48.44	19.32	8.56	2.44	3.82	2.81	1.10	0.45	4.95	5.16
3244	49.47	9.84	16.82	5.87	7.32	3.99	0.62	0.46	4.28	3.40
3242	43.29	6.96	13.32	2.23	6.21	4.85	2.23	0.64	5.47	6.20

Appendix 8: The Summary of the Mean Elemental Analysis in Raw, Concentrate and in Tailing after Separation Using Biomass

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	CuO
Mean of raw samples	44.23±	8.20±	9.50±	3.49±	8.70±	4.70±	0.77±	0.25±	12.02±	5.58±
(level A) AAS	3.90	1.12	2.50	0.49	1.45	1.03	0.16	0.07	3.84	0.87
Confidence Level (95.0%)	8.824	2.54	5.658	1.097	3.276	2.328	0.370	0.16	8.678	1.58
Mean of the tailing samples	47.63±	10.02±	13.29±	4.17±	4.82±	4.84±	1.84±	0.36±	5.20±	4.66±
	1.31	1.39	1.47	0.65	0.42	1.12	0.24	0.08	0.46	0.34
Confidence Level (95.0%)	2.971	3.137	3.316	1.474	0.947	2.536	0.549	0.19	1.044	0.763
Mean of the magnetic concentrate	20.44±	7.13±	8.09±	2.33±	4.33±	4.55±	0.04±	0.36±	46.30±	7.58±
	2.24	1.12	2.28	0.47	0.69	0.80	0.01	0.08	1.63	1.11
Confidence Level (95.0%)	5.071	2.535	5.16	1.053	1.556	1.798	0.017	0.177	3.692	2.502

Appendix 9: The Magnetic Separated Sample after Reduction of Ore - Laterite Mixture Using Biomass

Sample Code	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	CuO
3227	23.72	11.73	8.94	2.64	3.11	2.05	0.02	0.29	42.8	6.76
3232	17.66	11.77	3.74	1.94	3.61	4.91	0.01	0.48	52.9	2.63
3234	18.5	8.62	9.6	8.65	0.75	0.51	0.03	1.1	48.1	3.46
3230	19.45	9.43	2.98	3.89	1.72	2.34	0.02	0.28	49.3	13.03
3238	13.7	17.18	4.45	0.95	1.96	9.4	0.04	0.9	45.7	3.63
3231	11.71	5.93	7.54	3.39	4.71	5.91	0.03	0.05	53.7	6.21
3233	8.32	9.32	11.94	2.83	5.39	7.03	0.04	0.71	48.3	6.73
3240	14.61	10.74	12.56	3.71	5.22	3.41	0.02	0.49	47.5	4.21
3244	18.39	6.98	4.21	2.37	5.77	6.32	0.03	0.56	48.5	6.41
3242	17.37	12.42	5.85	1.93	2.43	4.21	0.02	0.85	47.8	8.56

Appendix 10: Non-Magnetic Separated Sample after Reduction of Ore - Laterite Mixture Using Biomass

Sample Code	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	CuO
3227	56.22	13.57	12.84	5.17	7.5	8.22	1.43	0.03	2.45	1.46
3232	45.98	17.08	1.08	3.88	4.21	3.97	1.78	0.46	6.94	3.95
3234	57.36	16.05	5.96	7.12	4.71	3.93	1.42	0.29	4.23	1.05
3230	48.09	8.59	13.1	4.22	9.21	8.32	1.62	0.96	5.83	6.01
3238	49.26	15.74	10.69	8.11	4.82	9.43	2.48	0.95	5.91	6.49
3231	56.14	11.32	15.49	13.4	1.18	5.51	1.48	1.12	10.9	4.59
3233	38.47	14.45	21.85	7.21	5.99	6.43	2.31	0.95	8.46	4.03
3240	56.29	19.49	2.93	1.16	2.11	4.3	2.18	0.9	10.9	3.54
3244	55.22	15.48	5.39	4.19	8.81	5.93	0.97	0.54	2.15	2.56
3242	47.38	6.44	21.74	5.21	6.83	9.12	2.28	0.69	6.83	6.39

Appendix 11: Statistical Comparison of the Mean of Raw, Tailing and Concentrate after Reduction of Ore Laterite Mixture Using Biomass

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	CuO
Mean of raw samples (level A) AAS	44.23± 3.90	8.20± 1.12	9.50± 2.50	3.49± 0.49	8.70± 1.45	4.70± 1.03	0.77± 0.16	0.25± 0.07	12.02± 3.84	5.58± 0.87
Confidence Level (95.00%)	8.824	2.54	5.658	1.097	3.276	2.328	0.339	0.16	8.678	1.58
Mean of ore, laterite & biomass concentrate	16.34± 1.38	10.41± 1.01	7.18± 1.10	3.23± 0.65	3.47± 0.55	4.61± 0.84	0.03± 0.04	0.57± 0.10	48.46± 0.10	6.16± 0.77
Confidence Level (95.0%)	3.123	2.272	2.482	1.506	1.252	1.902	0.007	0.231	2.25	1.745
Mean of ore, laterite & biomass tailing	51.04± 1.96	13.82± 1.26	11.11± 2.31	5.97± 1.04	5.54± 0.84	6.52± 0.67	2.10± 0.20	0.69± 0.11	6.46± 0.97	4.01± 0.49
Confidence Level (95.0%)	4.438	2.849	5.232	2.356	1.902	1.525	0.463	0.251	2.187	1.108

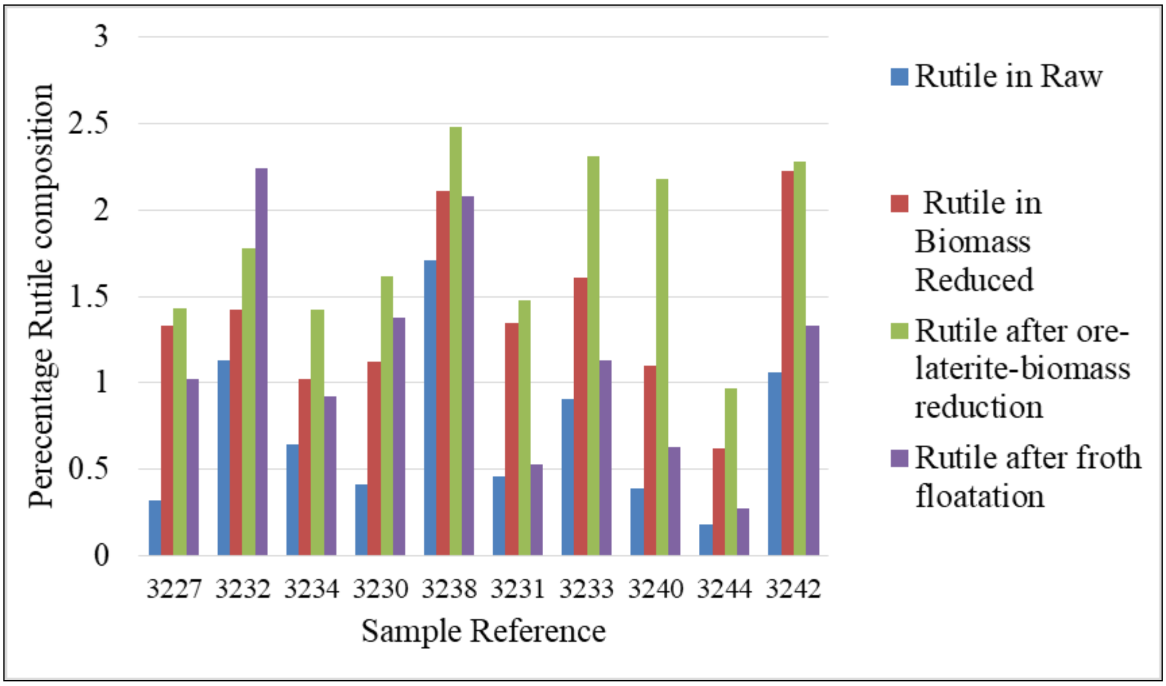
Appendix 12: The Chemical Composition of the Samples at Level A after Concentration Using Froth Flotation Method

Sample Code	SiO_2	Al_2O_3	K_2O	CaO	Na_2O	TiO_2	MnO	Fe_2O_3	CuO	MgO
3227	8.01	9.22	2.71	11.09	1.12	1.02	0.32	6.21	10.91	5.31
3230	19.06	11.61	6.09	1.46	2.53	1.38	0.17	9.93	2.60	3.44
3231	13.61	9.13	4.5	4.87	4.23	0.53	0.4	6.13	1.41	5.39
3232	5.41	7.1	8.23	1.51	2.6	2.24	0.19	18.12	1.16	8.1
3233	14.23	8.56	6.87	6.45	11.13	1.13	0.21	13.51	2.15	5.92
3234	4.65	4.28	2.52	7.94	9.82	0.92	0.19	12.08	0.93	7.31
3238	6.16	11.32	2.77	3.66	7.66	2.08	0.22	6.05	2.68	4.89
3240	8.16	4.01	1.78	0.18	2.01	0.63	0.04	2.03	0.53	4.58
3244	6.99	16.7	1.43	5.1	8.1	0.27	0.16	0.88	0.93	1.02
3242	13.98	11.07	0.99	8.02	5.02	1.33	0.29	18.28	8.86	0.48

Appendix 13: Mean Chemical Composition after Concentration Using Froth Flotation Method

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	Cu	CuO
Mean of raw samples (level A) AAS	44.23± 3.90	8.20± 1.12	9.50± 2.50	3.49± 0.49	8.70± 1.45	4.70± 1.03	0.77± 0.16	0.25± 0.07	12.02± 3.84	4.47± 0.7	5.58± 0.87
Confidence Level - 95.0%	8.824	2.54	5.658	1.097	3.276	2.328	0.339	0.16	8.678	1.58	1.58
Mean after froth flotation	10.03± 1.52	9.30± 1.18	15.03± 1.09	4.64± 0.77	15.42± 1.12	7.79± 0.79	1.15± 0.20	0.22± 0.03	19.32± 1.93	2.59± 1.16	3.23± 1.15
Confidence Level (95.0%)	3.453	2.675	2.463	1.747	2.525	1.788	0.455	0.071	4.385	2.589	2.591

Appendix 14: Rutile Composition in Raw, Ore - Biomass, Ore - Laterite – biomass and Froth floatation Concentrated Methods



Appendix 15: A Publication on Copper Extraction by Wet Chemical Method

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Abstract

In many countries, there occurs large deposits of copper and no locally established copper based industries. This is because known methods for extraction are expensive. In this study, alternative and viable method for extraction of copper from their respective ores has been investigated. The method involves reduction of copper (II) ions from mild acidic leachate by chlorine treated solution prepared from chicken dropping and at temperature range of 60 to 70°C. Ore samples were pulverized to 250 micro millimetres and leached with hydrochloric acid to obtain leachate containing copper ions. The dissolved copper was reduced to zero valence, and the reduced metal obtained by filtration. After analysis using XRFS, the metal purity was found to range between 60 and 80% depending on the ore used. In another experiment, chicken waste solution was used to extract copper from the ore. The copper (II) ions obtained in the solution was reduced by bubbling chlorine gas at temperature range of 60 to 70°C to obtain 13 percent pure metal. The results obtained have shown to have great potential for production of copper at low cost.

Keywords: hydrazones; copper extraction; chicken waste solution; zero valence; chicken dung.

1.0 Introductio*n*

Kenya is well endowed with bulk of mineral resources some of which are yet to be exploited (Republic of Kenya, 2001). Among these resources, copper is found in several minerals with varied elemental composition. Examples of such composition occur as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), cuprite oxide (Cu_2O), and malachite ($Cu_2CO_3(OH)_2$) among many other minerals (Earnshaw and Greenwood, 1997). Malachite and sulphides are the major deposits in Kenya, with elemental composition of 2.3 % Cu found at Macalder in South Nyanza-Kenya (Ogola, 1987). According to DuBois and Walsh (1970), 4 - 6 % Cu mineral deposits have been reported at Kitere near Kisii and 3 to 4.55 % Cu at Kipkomo near Kapenguria. More copper minerals have also been identified near Voi Hill and Maungu with a sample from the best mineralized part of the outcrop assaying at 8.2 %. More deposits containing chalcopyrite minerals have also been identified in Tharaka assaying 0.35 - 5 % copper Dubios and Walsh, 1970). Despite the presence of such rich copper deposits, their extraction has not been exploited for economic growth.

Currently the cost of extraction of copper is by pyrometallurgical process that involves use of electricity as well as coal. The use of fossil fuels in extraction produces carbon (IV) oxide gas which results to global warming. The other method used is solvent extraction followed by electro-winning (SX-EW). This method is applied in Zambia, Democratic Republic of Congo and in Uganda (Wills, 2011; Yager, 2013; Kasese Cobalt Company Ltd., 2007). The pyrometallurgical process involves thermal treatment of minerals and metallurgical ores and concentrates (after froth flotation) to bring about physical and chemical transformations of minerals. This produces saleable products such as pure metals, or intermediate compounds or alloys, which are suitable as feed for further processing (Adalbert, 2005).The methods are capital intensive and require suitable technologies.

To reduce this cost, the use of reducing agent has been investigated. This involves reducing copper ions using suitable and selective reducing agents. This can be achieved when copper compounds are dissolved to form copper (II) ions. Hydrazones are simple and suitable reducing agents in wet chemical form. They can be prepared by interacting ammonia or urea with chlorine in basic media (O'Neill *et al.*, 1984; Adams and Brown, 1941; Bourdauducq and Schirmann, 2002). The formation of these product is as shown in equations 1 and 2.

$$2NH_{3(g)} \xrightarrow{NaOCl\ 70^{o}C} H_2NNH_{2(aq)} + H_2O_{(l)} + NaCl_{(aq)} \tag{1}$$

$$(H_2N)_2CO_{(aq)} + NaOCl_{(aq)} \xrightarrow{2NaOH} N_2H_{4(aq)} + H_2O_{(l)} + NaCl_{(aq)} + Na_2CO_{3(aq)} \tag{2}$$

Hydrazine produced was found to react further with alkanones and hydrazones to form other forms of hydrazones which are also strong reducing agents as shown by equations 3 and 4. (Day and Whiting, 1988).

$$(CH_3)_2CO_{(aq)} + N_2H_{4(aq)} \rightarrow 2H_2O_{(l)} + [(CH_3)_2CN]_{2(aq)} \qquad 3$$

$$[(CH_3)_2CN]_{2(aq)} + N_2H_{4(aq)} \xrightarrow{100\ ^oC} (CH_3)_2CNNH_{2(aq)} \qquad 4$$

The reduction potential of hydrazine in basic environment occurs as shown in equation 5 below.

$$N_2H_{4(aq)} + 4OH^-_{(aq)} \longrightarrow N_{2(g)} + 4H_2O_{(l)} + 4e^- \quad E^0 = +1.15V \qquad 5$$

This shows that hydrazine can effectively be employed in reduction of various metal cations to the elemental state. This was reported by Chen and Lim (2002) while investigating the recovery of precious metals of silver and copper in a synthesized wastewater in batch reactors. In their study, they used hydrazine as the reducing agent as shown by reactions 6 and 7 below (Chen and Lim, 2002).

$$2Cu^{2+}_{(aq)} + N_2H_{4(aq)} \rightarrow 2Cu_{(s)} + N_{2(g)} + 4H^+_{(aq)} \qquad 6$$

$$Cu^{2+}_{(aq)} + 2N_2H_{4(aq)} + 2OH^-_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + N_{2(g)} + 2NH_{3(g)} + 2H_2O_{(l)} \qquad 7$$

In this study uric acid, amine and amide compounds obtained from decomposing chicken droppings or wastes (also known as biomass) were used to prepare the reducing agent. The chlorinated chicken waste solution in alkaline media produced compounds that reduced copper ions to zero valence. Those compounds also formed complexes with copper but latter reduced the metal.

2.0 Methodology

2.1 Materials and reagents

All reagents were of analytical grade and Millipore water was used to make all the solutions in this study unless otherwise stated. Chicken dung was obtained from poultry farmers in Thika, Kenya.

2.2 Sampling

Copper ore samples were obtained from Maragwa location and Kamwathu sub-location, Tharaka North Sub - County of Tharaka Nithi County at locations $0^{o}18$’S$38^{o}8$’E and $0^{o}21$’S$38^{o}11$’E respectively. Random sampling was done from ten quarries which were within one to two kilometres apart from each other. A mattock was used to dig and break the rocks and a shovel was used to scoop out the soil and rocks. A kilogram of mineral samples was collected from a depth of 30 cm and another one collected at one meter depth. The samples were crushed using a hammer and later pulverized to 250 micro millimetres using a ball mill.

2.3 Mineralogical analysis using XRD

A sample, 30 g of pulverized ore was put into sample holders. They were then loaded for analysis of minerals using data collector software. Results of analysis of minerals present in each sample were given using Bruker D8 Advance Diffractometer. The XRD spectra obtained from the analysis before treatment was used to determine mineralogical composition of rock samples.

2.4 Elemental analysis using XRF

Elemental composition of solid samples was done using the X-ray florescence spectrophotometer model S1Titan form Bruker. This was carried out in accordance to the test method D-6376 (ASTM, 2007). The analyser was calibrated using standards from Sigma Aldrich. Ground samples to 250 micron were each placed in the XRF cup. The powder was irradiated with an X-ray beam. The fluorescent characteristic X-rays of the elements present were detected by the spectrometer. The measured X-ray intensities were directly proportional to the concentration of the range of elements present. The results were recorded in percentage elemental composition. All samples were analysed in triplicates. These analyses were conducted in the XRF Laboratory of the ministry of mining in Nairobi, Kenya.

2.5 Leaching of copper from its ores

A sample, 200.0 g, of the ore was weighed into a one litre beaker and 500.0 ml of 2.0 M HCl was added. The mixture was left to react for one hour. The resultant solution was filtered and the residue was washed at least two times using distilled water. The filtrate was transferred into one litre volumetric flask and the content made to the mark using distilled water to make about 1.0 litre leach solution.

2.6 Preparation for chicken waste solution

A mass of one kilogram of chicken defecate was put into a desiccator. To this, 2.0 litres of water was added and the mixture stirred for 5 minutes to ensure a uniform mixture. The content was covered and left to dissolve the amino compounds. The functional groups of the extracted compounds were monitored after every three days for 15 days using FTIR Spectrophotometry. The content was filtered using 300 micron sieve to obtain the chicken waste solution.

2.7 Chemical characterization for chicken waste solution using the Fourier Transform Infrared (FTIR) Spectrophotometry

Qualitative analysis for the chicken waste solution was done using the FTIR Spectrophotometry model Alpha 1005 4238 from Bruker. The procedure was carried out in accordance to the test method D 7624-10 (ASTM, 2010). The instrument was initialized and calibrated by conducting a background scan. The resulting background spectrum was compared to a reference spectrum provided in the manufactures manual. The hydrazine hydrates solution was injected into an FTIR liquid cell for measurement as a standard. In the same manner, a scan for chicken waste before and after chlorination was obtained and spectra were used to compare with that of hydrazine hydrate. A comparison of the absorption bands obtained in the spectrum of the sample chicken waste with that of the hydrazine hydrate was used for data interpretation.

2.8 Optimisation studies on reduction of copper ions from leachate using chlorinated chicken waste solution.

2.8.1 The pH optimisation

A solution of 100 ml of chicken waste solution was put into 200 ml beaker. The pH and the temperature were recorded. To this solution, 30 ml of the ore leachate was added and chlorine gas bubbled in it for six minutes with constant stirring. While stirring, chicken waste solution was slowly added until no further precipitate was observed to occur. The chlorine flow rate was measured using a gas flow meter model 270134.003 from TA Instruments. The flow was regulated using a compressed air cylinder regulator to the appropriate flow range. The residue formed was filtered and dried in an oven at 40 ^{o}C and then the percentage copper present was later determined using XRF. The procedure was repeated by varying the pH from 7.0 to 12.7 using 1.0 M NaOH.

2.8.2 Chlorine bubbling time optimisation

After obtaining the optimal pH, the chlorination period was varied from one to six minute before addition of the leachate and later four minutes after addition of leachate. All experiments were done at optimal pH while maintaining all other parameters constant. The content of copper present was later determined.

2.8.3 Temperature optimisation

After establishing the optimal pH and the suitable chlorine content, the procedure was again repeated while holding pH constant at 11.0 and chlorine bubbling time at three minutes but varied the temperature between 28 ^{o}C to 90 ^{o}C at intervals of 5 ^{o}C and then 10 ^{o}C. In each case, the precipitate formed was filtered and dried in an oven at 40 ^{o}C and the content of copper determined.

2.9 In situ extraction and reduction of copper

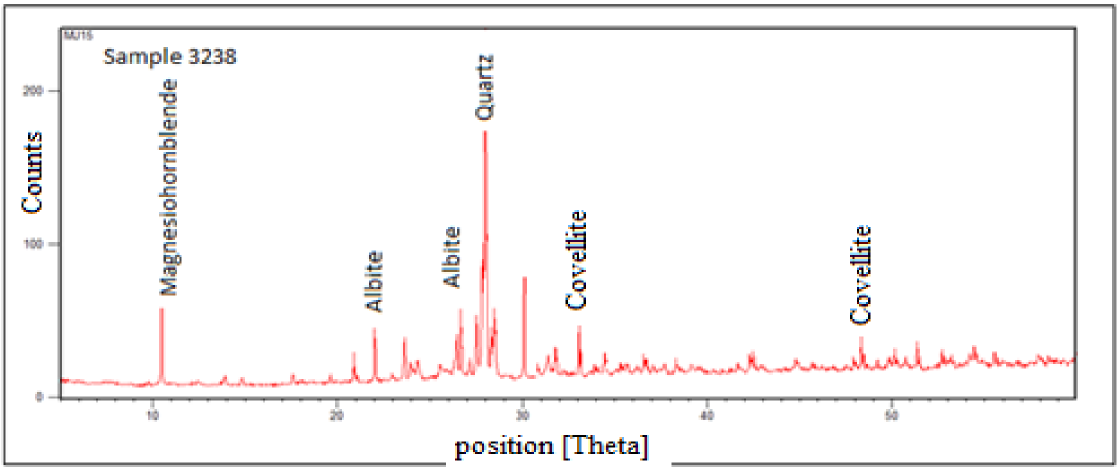
A 100 ml solution of chicken waste was put in a 250-ml beaker. To that, 1.0 g of the ore was added and the content stirred for 20 minutes. The content was filtered using 300 micronsieve. The filtrate was allowed to stand for 5 minute for any fine particles to settle and decant. More of chicken waste solution was added to make a volume of 200 ml and the pH adjusted to 11.0. The mixture was heated at 70 ^{o}C and then bubbling chlorine gas for three minutes. The content was cooled and filtered using whatman filter paper number 4 and the residue dried in an oven at 40 ^{o}C. The procedure was repeated using different masses of 2 to 10 g at intervals of 2.0 g but maintained previously obtained optimal parameters and the content of copper determined.

The procedure was repeated holding temperature at 70 ^{o}C, mass of the ore at 6 g and chlorine bubbling time at three minutes but varying time for stirring using the magnetic stirrer from one to sixteen minutes at intervals of two minute. The content was cooled and filtered using whatman filter paper number 4 and the residue dried in an oven at 40 ^{o}C.

3.0 Results and discussion

3.1 Mineralogical Analysis Using XRD

A mineralogical analysis of the ore was carried out and the results obtained were as presented in Figures 1 below.



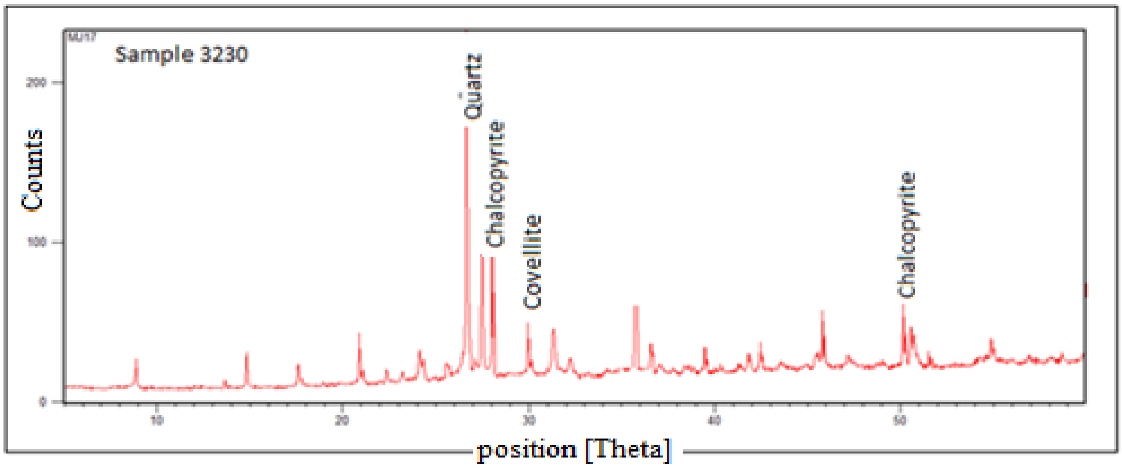


Figure 1: Mineralogical analysis of sample 3238 and 3230

The results show that copper minerals in Tharaka Nithi County exist mainly as chalcopyrite at angle theta 29.5, 49.0, and 58.0. Some few deposits have indicated presence of covellite at angle theta 33.0, 29.5 and 48.0. Other rich minerals are silica inform of quartz angle theta 37.0, albite at angle theta 38.0, 22.0 and 26.5, and hematite minerals at angle theta 33.0.

3.2 Elemental analysis using XRF

The results of elemental analysis from selected ten deposits are given in table 1.

Table 1: Elemental analysis of some selected copper deposits in Tharaka Nithi County.

Sample reference	**SiO_2**	**Al_2O_3**	**K_2O**	**Na_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**Cu**	**CuO**	**MgO**
3227	48.34± 0.03	8.39± 0.02	7.76± 0.07	5.21± 0.02	13.85± 0.06	0.63± 0.04	0.25± 0.02	5.27± 0.03	4.04± 0.02	5.06± 0.02	2.13± 0.01
3230	41.48± 0.15	8.18± 0.04	7.76± 0.04	12.89± 0.03	2.28± 0.02	1.00± 0.03	0.11± 0.01	3.82± 0.04	9.66± 0.05	12.07± 0.06	5.80± 0.04
3231	45.22± 0.54	5.44± 0.02	4.87± 0.04	6.12± 0.01	19.03± 0.07	0.44± 0.02	0.83± 0.04	7.62± 0.04	4.43± 0.05	5.54± 0.06	3.75± 0.01
3232	42.75± 0.08	11.42± 0.04	10.49± 0.03	3.89± 0.02	2.60± 0.01	2.12± 0.13	0.14± 0.02	17.64± 0.03	2.72± 0.02	3.40± 0.03	5.48± 0.07
3233	25.85± 0.04	9.19± 0.03	6.81± 0.02	3.68± 0.03	1.33± 0.01	0.90± 0.04	0.23± 0.04	40.97± 0.04	4.40± 0.02	5.50± 0.02	3.16± 0.01
3234	35.87± 0.08	3.59± 0.03	0.69± 0.02	12.13± 0.06	23.67± 0.06	0.61± 0.04	0.20± 0.04	13.09± 0.05	1.93± 0.02	2.41± 0.02	4.16± 0.03
3238	42.47± 0.09	10.78± 0.01	2.71± 0.04	13.08± 0.08	10.61± 0.03	1.71± 0.02	0.52± 0.33	10.07± 0.09	4.40± 0.02	5.51± 0.03	1.84± 0.02
3240	74.28± 0.12	3.23± 0.02	2.43± 0.01	9.04± 0.08	1.08± 0.02	0.42± 0.05	0.06± 0.02	1.55± 0.02	3.24± 0.06	4.05± 0.07	1.11± 0.03
3244	47.09± 0.06	14.70± 0.03	2.49± 0.01	16.37± 0.04	8.10± 0.04	0.18± 0.03	0.06± 0.02	0.04± 0.01	3.24± 0.07	4.05± 0.09	4.29± 0.04
3242	39.70± 0.09	7.68± 0.02	1.69± 0.03	5.12± 0.54	13.91± 0.02	1.05± 0.11	0.29± 0.01	20.41± 0.04	6.66± 0.03	8.33± 0.03	3.19± 0.02

The results shows that copper content ranges between 1 and 9%. Such content are better than some of the ores mined in other countries. An example is from Democratic Republic of Congo where ores grade between 2.68 and 2.96% (Engineering & Mining Journal, 2014; Yager, 2013). In Chile copper deposits ranges 0.4 - 1.0% (Kuck, 2014) while in South Africa copper deposits grades between 0.49 and 0.56% (Groves & Vielreicher, 2001). Botswana is another country in Africa that mine copper from ores with average composition between 1.3 and 1.5% copper (Discovery Metals Ltd., 2012). In Zambia all the mines have average composition of 0.5 to 2.3 per cent copper (Haglund, 2013). This shows that minerals in Tharaka Nithi with a composition that vary between 1.93 to 9.66% are more viable for commercial extraction.

3.3 Synthesized hydrazine from the chicken waste solution

The product obtained after chlorination of the chicken waste solution was analysed and the spectra obtained is given in Figure 2.

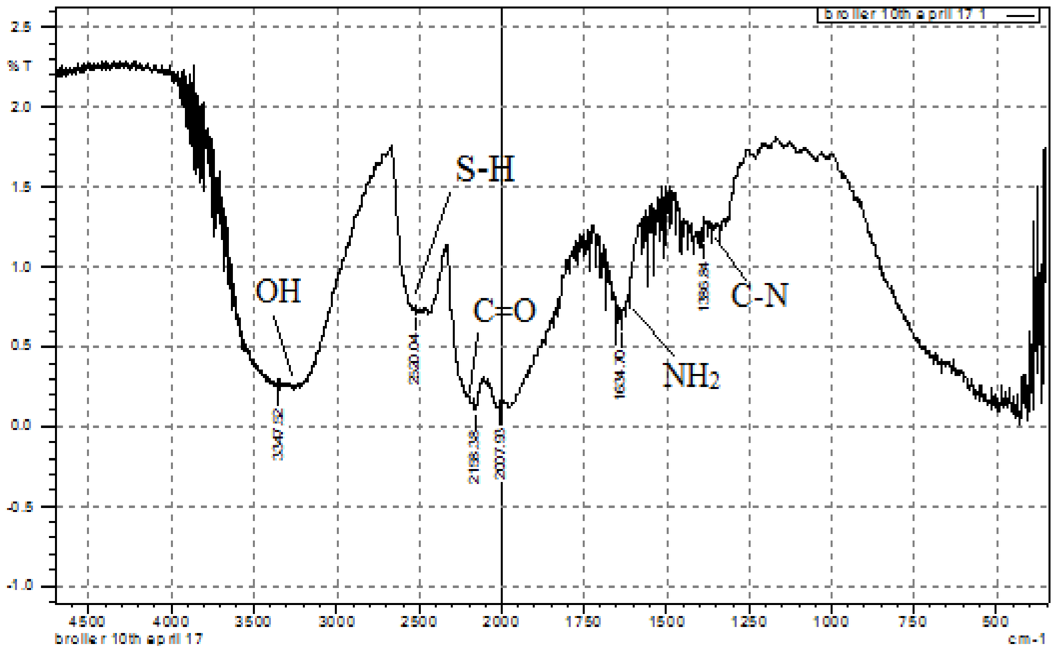


Figure 2: Spectrum of the chlorinated chicken waste solution

The results show that chicken waste contain OH group due to the bands between 3000 and 3500 cm^{-1}, SH group at 2500 cm^{-1}, carbonyl group stretching at 2000 and 2200 cm^{-1}, NH_2 group stretching at 1634 cm^{-1}, and CN group is found at 1334 cm^{-1}. C=O and NH_2 groups are found in amines and amides compounds. These compounds are potential sources for making hydrazones when suitable oxidizing agents are used. For the sake of comparison, AR grade hydrazine hydrate was analysed using FTIR and spectra given in figure 3.

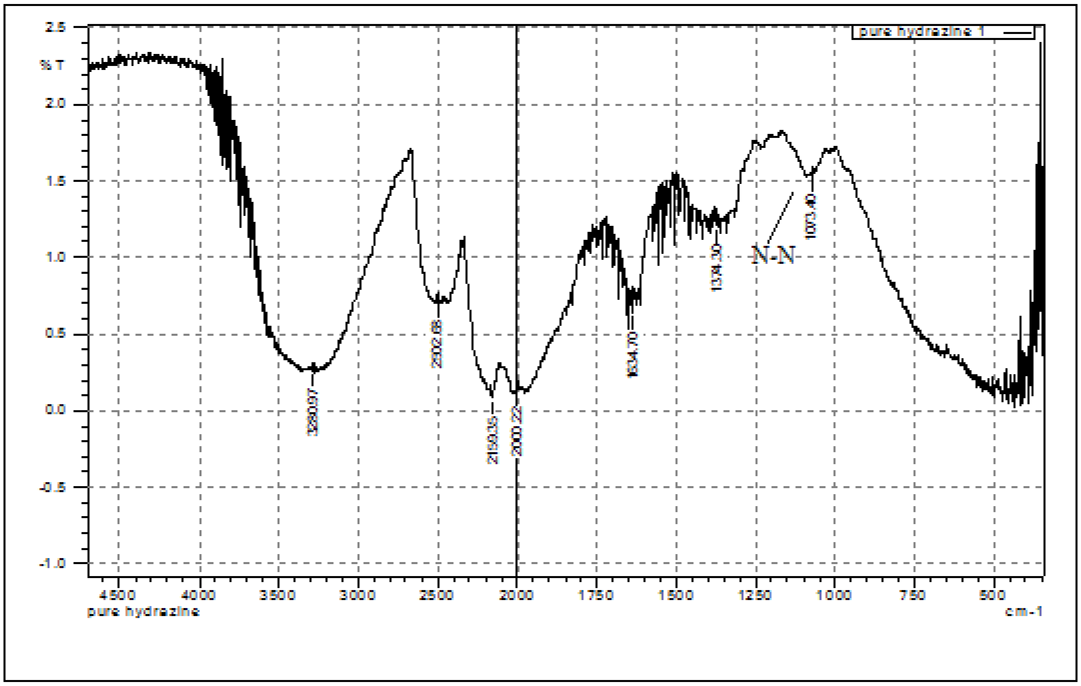


Figure 3: Spectrum of the AR grade hydrazine solution

Results show that hydrazine contained all functional groups found in chicken waste except N-N stretch found at 1090 – 1020 cm^{-1}. After chlorination of chicken waste in alkaline media the spectra obtained was given in figure 4 below.

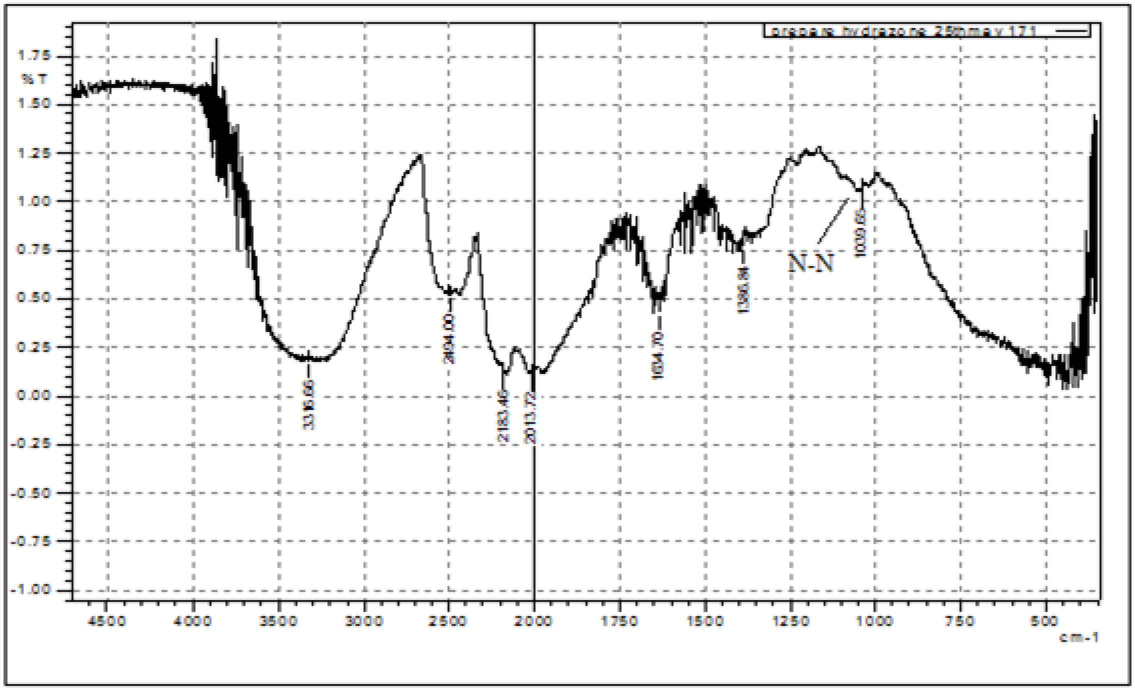


Figure 4: Spectrum of prepared hydrazine in chicken waste solution

The results obtained show the emergence of a band at 1090 cm^{-1}. This could be due to induced vibration excitation of N-N covalent bonds as reported by Giguère and Liu (1952). This shows that a reducing agent either symmetrical or unsymmetrical hydrazine was produced (O'Neill *et al.*, 1984). This product is prepared after chlorine gas reacts with sodium hydroxide as given in equation 8 (Earnshaw and Greenwood, 1979).

$$Cl_{2(g)} + 2NaOH_{(aq)} \xrightarrow{70\ ^{0}C} NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(l)} \qquad 8$$

The produced sodium hypochlorite oxidizes amines and amides to hydrazones as previously given in equations 1, 2 and 3. The other possible products are given by equation 9 below (Bourdauducq and Schirmann, 2002; Day and Whiting, 1988).

$$2RNH_2 \xrightarrow{2NaOCl\ \ 70^{0}C} RHNNRH \qquad 9$$

3.3.1 Optimized Results

3.3.1.1 Optimized pH of chicken waste solution

Results of pH optimization are as presented graphically in Figure 5.

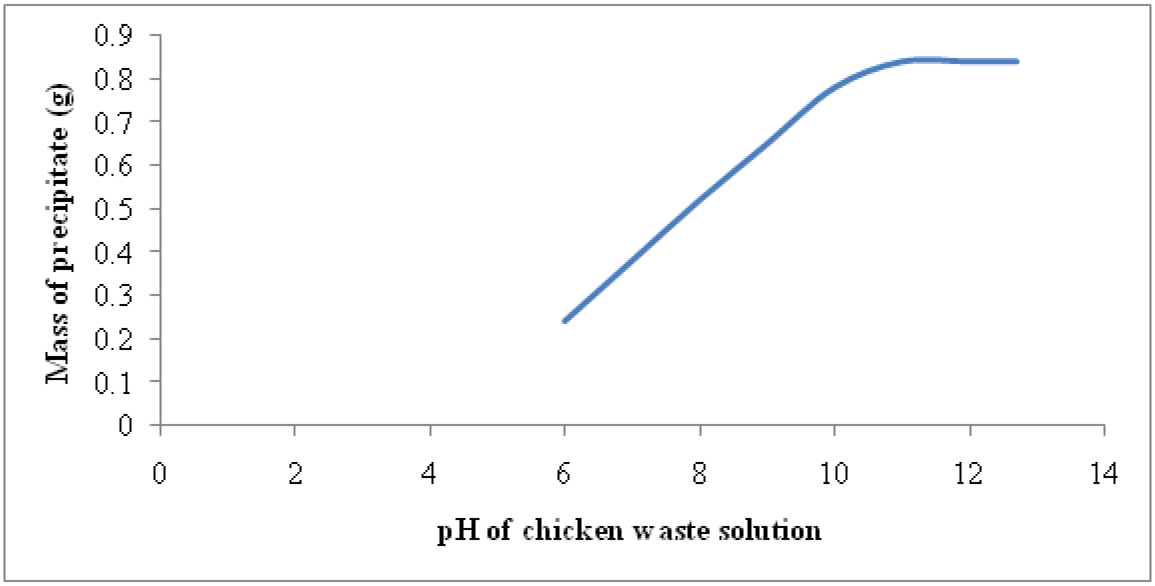


Figure 5: Relationship between pH of chicken waste solution and mass of precipitate produced.

The results show that at strongly acidic environment, no copper was produced as any reduced metal was dissolved by the acid. The emergence of precipitation started at a pH of 6.0 and increased with increase in pH up to plateau after pH 11.0. At the region between pH of 6.-11.0, it is the region where there was sodium hydroxide available forming sodium hypochlorite. The sodium hypochlorite produced oxidises amines forming hydrazones which is a strong reducing agent. The resulting hydrazones were responsible for the reduction process. Thus the reduction was found to be best in strongly basic media.

3.3.1.2 Optimized time for chlorination of chicken waste solution

The appropriate time for chlorination of chicken waste solution was investigated and the results obtained presented in Figure 6.

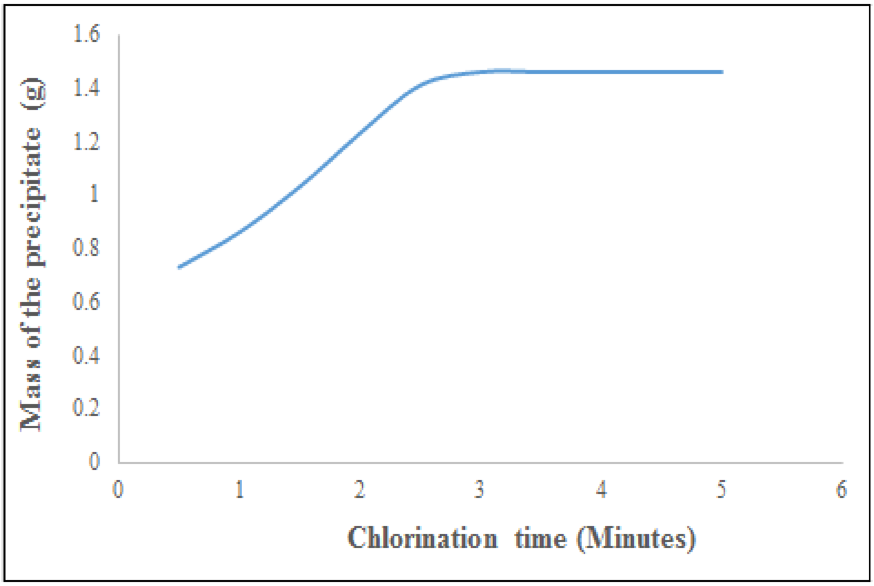


Figure 6: Chlorination time versus mass of the precipitate produced

The results show that bubbling chlorine gas into the chicken waste for three minutes was sufficient for the formation of required hydrazones to reduce the copper ions in solution. After that interaction period, the mass of the product remains constant because all the copper ions have been depleted.

3.3.1.3 Optimized temperature for the formation of hydrazones from chicken waste solution

Hydrazones are temperature sensitive compounds. The temperature of the chlorination process was therefore monitored and the results obtained are presented in Figure 7.

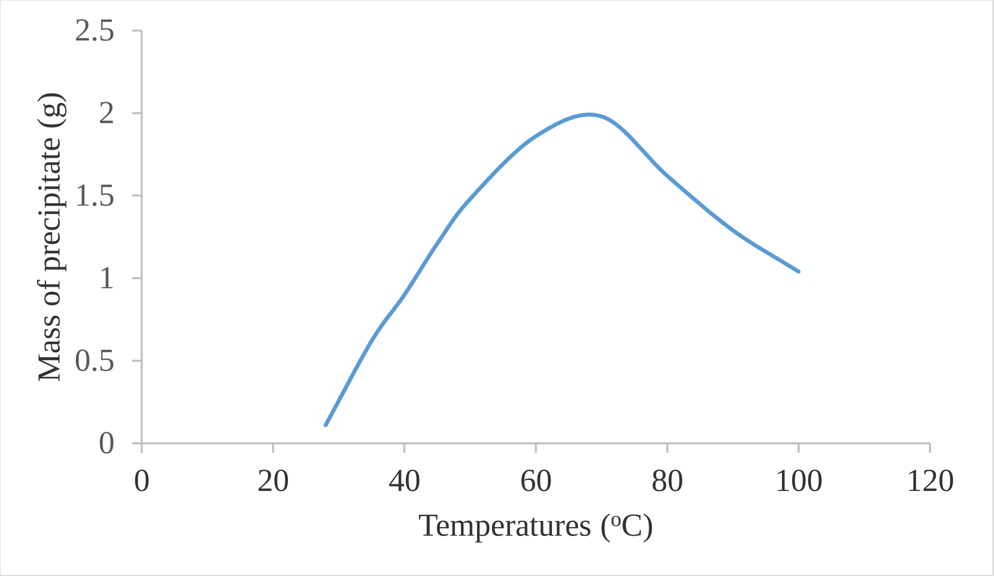


Figure 7: Appropriate temperature for the formation of hydrazine

The results show that as temperatures increases to 70 ˚C. Kinetic energy of the particles increases which increases collision of particles hence formation of hydrazones. Temperatures above 70 ˚C lead to decreased precipitate formation. This shows that the amino compounds present in chicken dung gets denatured at temperature above 80 ˚C hence affecting the formation of hydrazine.

3.3.2 Optimal masses for insitu reduction of the ore using chicken waste solution

Copper from varying masses of the ore was extracted and reduced in-situ. The results obtained was presented in Figure 8.

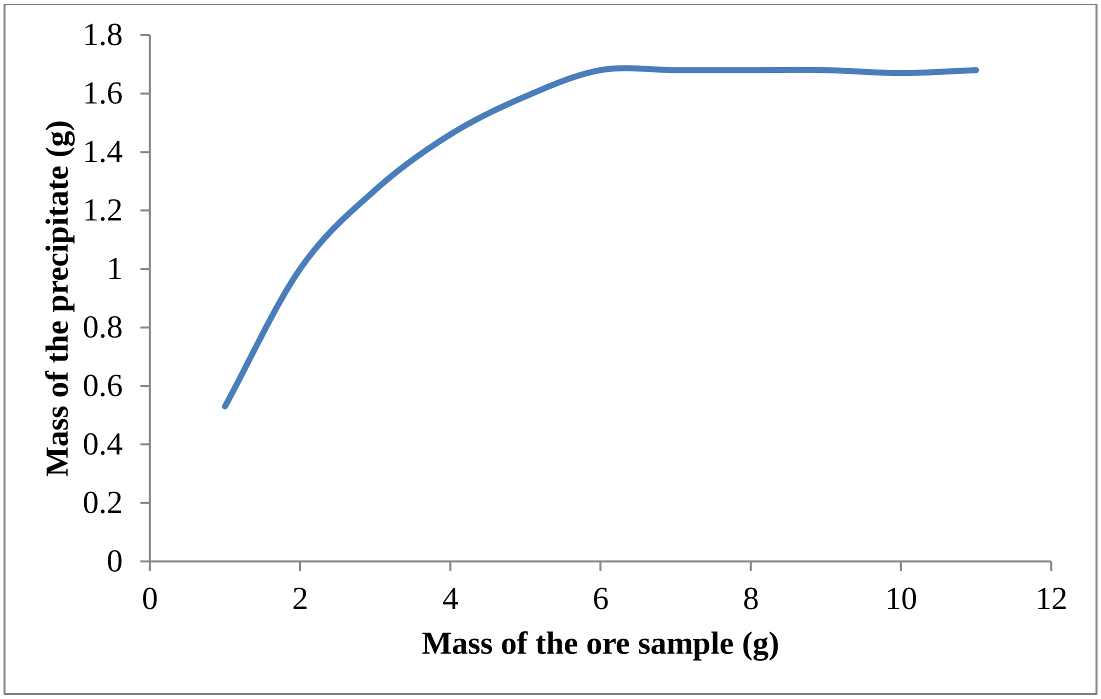


Figure 8: A curve of mass of the ore used in extraction against mass of the precipitate produced.

The results show that the amines and uric acids in chicken waste can complex copper ions from ores instead of leaching the ore with acid. Therefore the copper ions obtained from 6.0 g of the ore were later oxidized by *insitu* prepared hydrazones species. However the mass of the ore used varied depending with the composition of copper in the ore.

3.4. Kinetics of extraction and insitu reduction of copper using chicken waste solution

After establishing that about 6.0 g was a suitable mass for stoichiometric reduction of the copper ions, this study investigated the rate of reduction and the results obtained were given in Figure 9.

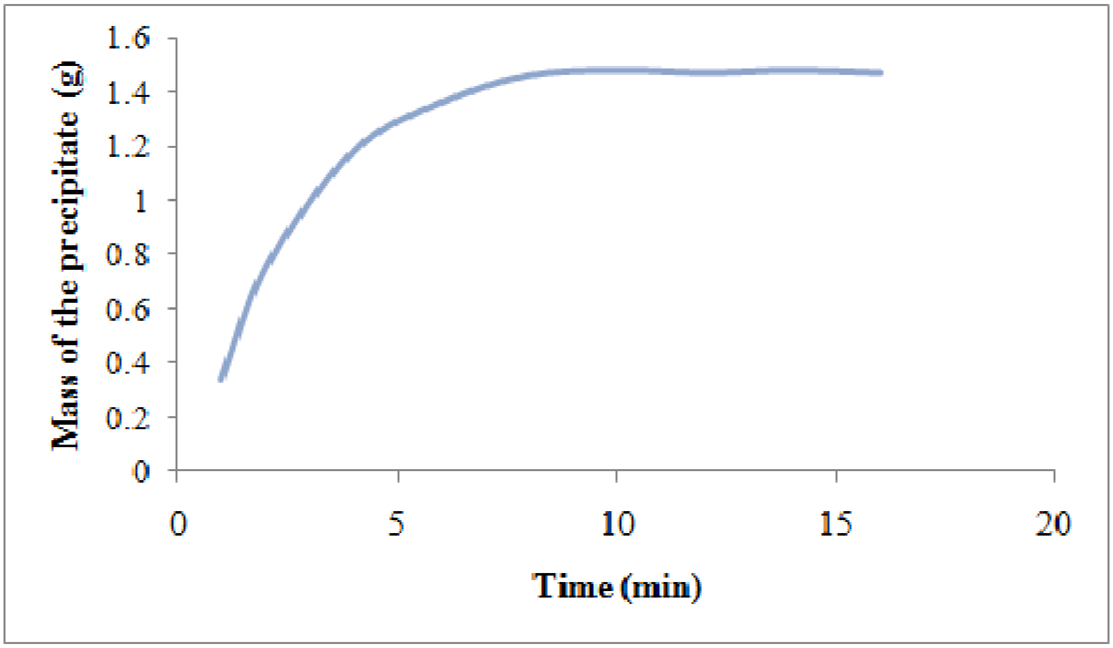


Figure 9: Time required for complexation of copper against the mass of precipitate produced.

The results show that about eight minutes was enough for 100 ml chicken waste solution to complex copper into ions from 6 grams of the ore sample and subsequently reduce copper to zero valence as shown in equations 10 and 11 below (Chen and Lim, 2002).

$$2Cu^{2+}_{(aq)} + N_2H_{4(aq)} \longrightarrow 2Cu_{(s)} + N_{2(g)} + 4H^{+}_{(aq)} \qquad 10$$

$$Cu^{2+}_{(aq)} + 2N_2H_{4(aq)} + 2OH^{-}_{(aq)} \longrightarrow Cu_{(s)} + N_{2(g)} + 2NH_{3(g)} + 2H_2O_{(l)} \qquad 11$$

After optimization of the various parameters, the method was applied for extraction of copper from different acid leached ores and the results obtained presented in Table 2.

Table 2: Percentage copper extracted from leachate using chlorinated chicken waste

Sample Code	Trial 1 (gms)	Trial 2 (gms)	Trial 3 (gms)	Average (gms)	% Extract	% copper purity using XRF
3227	1.82	1.69	1.76	1.76	29.33	64.4
3230	3.55	3.54	3.70	3.60	59.93	62.47
3232	1.94	1.84	1.88	1.89	31.47	74.88
3234	1.68	1.62	1.63	1.64	27.40	85.22
3238	1.82	1.87	1.91	1.87	31.13	71.0
3240	1.60	1.45	1.50	1.52	25.27	65.46
3244	1.49	1.33	1.42	1.41	23.53	79.07
3242	3.08	3.02	3.01	3.04	50.67	67.08
3233	1.96	1.98	1.93	1.96	32.60	73.47
3231	2.75	2.71	2.82	2.76	46.00	57.16

The results show that high percentage of copper was first obtained from digested ore using acid and then reduced to zero valence using chlorinated chicken waste solution. The leachate had less contamination of alumina, phosphorous, calcium and silica. That is why all copper produced was having high purity above 60 % copper. The *insitu* extraction procedure was also applied for extraction of copper and the results obtained are presented in Table 3.

Table 3: Results of *insitu* extraction and reduction of copper using chicken waste solution

Sample Code	Trial 1(gms)	Trial 2 (gms)	Trial 3 (gms)	Average (gms)	% Extract	% copper purity using XRF
3227	1.63	1.57	1.59	1.60	26.62	10.61
3230	1.83	1.79	1.84	1.82	30.32	12.25
3232	1.97	2.08	2.01	2.02	33.64	4.15
3234	2.11	1.97	2.07	2.05	34.16	5.78
3238	2.91	2.88	2.82	2.87	47.83	9.08
3240	1.82	1.76	1.79	1.79	29.86	5.78
3244	1.65	1.67	1.71	1.68	27.93	9.10
3242	2.21	2.16	2.18	2.18	36.39	12.93
3233	1.52	1.49	1.47	1.49	24.88	12.08
3231	1.51	1.43	1.49	1.48	24.60	10.82

From the experiment, percentage copper extracted using *insitu* extraction and reduction method was low. This occured because some of the hydrazones acted as a ligand to extract the copper from ore into solution to make it available for reduction. However, copper extracted from this method was found to have a high percentage impurity compared to the acid leached. This may be due to the fact that oxides of aluminium and silicon did not dissolve during the insitu/reduction method. The low percentage purity of copper was also attributed by formation of amine mesoporous silica nanoparticle (amine-MSN) with formula ($Si_rO_xC_yNHz$) (Batista, *et al.,* 2016). This interaction between silica and amines introduces impurities to copper extracted. Equally amines formed complex with phosphorous pentoxide, CaO and Fe hence introducing impurities to the copper extracts. Although the % extract was low, the purity of copper was high. This proves that chicken waste can produce a purer quality of extracted copper but at lower content.

4.0 Conclusion

The study successfully converted leachate from chicken waste into hydrazones by treating with chlorine and applied it for the extraction of copper from its ore. The results obtained confirmed that the resultant has potential application for reduction of copper in its ore to zero valence to produced copper with 60 – 85 % purity with less cost of inputs. The method was investigated in a laboratory scale can be up scaled to produce copper for industrial use.

5.0 Acknowledgements

In this study I acknowledge the immense support from my three supervisors, and more so to Mwangi Waweru of Kenyatta University where almost all work was done. I also acknowledge department of mines and geology in the ministry of mines and natural resources for allowing me to use their laboratories. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Appendix 16: A publication on monitoring the extent of extraction method of copper by chicken dung leachate using aluminium electrode as an indicator

(Heliyon Journal, https://doi.org/10.1016/j.heliyon.2019.e02921)

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Abstract

Copper is found in several minerals in the earth's crust with varying the elemental and mineralogical composition. Several techniques of extraction have been investigated all in the effort of obtaining a cheaper and viable method. This paper reports on further works done on copper extraction using a wet chemical method. According to the method, reduction of copper (II) ions using hydrazones from chlorinated chicken waste leachate was stoichiometrically driven. The chicken dung leachate used was an impure bio-material in which the concentration could not be determined. It was, therefore, difficult to quantify the stoichiometric ratios of species in that reaction. This paper reports on a method of monitoring the extent of copper reduction by chlorinated chicken dung leachate using an aluminum electrode as an indicator. Mineral rocks were obtained from Maragwa Location in Tharaka Nithi County in Kenya. The samples were ground into a fine powder of 250 micro millimetres. The samples were then subjected to mineralogical analysis using X-ray diffraction (XRD). Chemical analysis was done using atomic absorption spectroscopy (AAS) and X-ray fluorescence spectroscopy (XRFS). Ground samples were leached using 1.0 M hydrochloric acid. The resulting leachate was treated with chicken dung leachate prepared from chicken dung in which chlorine gas was bubbled at a constant temperature of 28°C. The pH of the resultant chicken dung leachate was adjusted from 4 to 12 using 1.0 M sodium hydroxide and then used as an electrolyte. An electrochemical cell was set up consisting of aluminum and graphite rods. The aluminum electrode was found not to corrode at pH above 11 while it was able to displace available copper ions. This property of the aluminum electrode was used to monitor when all copper ions were displaced. The recovered copper was analyzed using XRFS. The copper recovery rate from the samples ranged from 7.0 to 20.0 at level A and 7.4 to 26.8% at level B with a purity range of 84.9 level A to 88.6% level B. An overall positive potential in the reduction process confirmed the greater the tendency of copper reduction without an external source of electricity. The corrosion of the aluminium electrode in the process was not observed and therefore does not require frequent replacement. Therefore, a large scale extraction process needs to be investigated.

Key Words: Chicken Dung; Chicken Waste; Copper Extraction; Copper Reduction; Hydrazones; Aluminium electrode.

1.0 Introduction

Copper metal has an industrial and economic application such conduction of electricity to power industries and the making of currency coins [1]. It is obtained from its ore by reduction using a hydrometallurgical process that involves the use of electricity as well as fossil fuel. The reduction process is expensive and contributes to global warming [2]. The recovery of metallic copper from the copper leach solution by the cementation process using aluminum disc has been reported by Ahmet and co-workers (2012) [4]. In their study, the leaching of malachite was done using acetic acid. In their results, they observed that the cementation rate increased with increasing mass of the ore. The rate was also affected by temperature in a direct proportion and inversely proportional to the pH of the solution [4]. The extraction of copper by a wet chemical method has also been reported by Kugeria and co-workers. In their method, the electrolyte was made using a strongly alkaline media of chlorine-treated chicken dung leachate (chicken waste leachate) [5]. In that study, the complexation of copper (II) in a basic aqueous environment at a suitable temperature was optimized and subsequent reduction of the metal ion was achieved. The reduction process was stoichiometrically driven with a reaction ratio of chlorinated chicken dung leachate to copper leachate which was 100ml: 30ml respectively. The copper metal obtained depended on the concentrations of the *insitu* prepared hydrazones in chicken dung leachate. However, the hydrazones were formed from a biomaterial whose concentration could not be verified. This, therefore, could not enable a calculation of the species reduced. But, aluminum is known to reduce copper in solution [4]. The equation 1 below shows the reduction process.

$$3\mathrm{Cu}^{2+}_{(aq)} + 2\mathrm{Al}_{(s)} \Leftrightarrow 3\mathrm{Cu}_{(s)} + 2\mathrm{Al}^{3+}_{(aq)} \qquad (1)$$

The equilibrium constant for the equation can be expressed as shown in equation 2 below.

$$K_c = \frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Cu}^{2+}]^3} \qquad (2)$$

The K value determines the direction of the reaction. Thus, if less than one the reaction will move to the left and if the K value is greater than one the reaction will move to the right. The magnitude will, therefore, be dependent on the concentration of the reacting species. When the copper (II) ions have been depleted in the solution, K_c will be infinitely high.

In the redox process shown in equation 1, there exist two half-cells due to both reduction and oxidation reactions that involve a transfer of electrons as shown in equations 3 and 4.

$$Cu^{2+} + 2e \Leftrightarrow Cu \qquad E = +0.34\ V \qquad (3)$$

$$Al \Leftrightarrow Al^{3+} + 3e \qquad E = +1.67\ V \qquad (4)$$

In an ideal situation and considering a standard cell given in equations 3 and 4, the resultant potential between the cathode and anode is +2.01 V if the concentrations are unit based on equation 5 shown below. Equation (3) relates the content of species involved with the electrode potential, E, of each half-reaction and its standard electrode potential, E^{e} [7].

$$E = E^{0} - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]} \qquad (5)$$

The higher the difference in the electro potential the higher the tendency of electron transfers. This results in a spontaneous heterogeneous reaction taking place in the galvanic cell. Due to the different potentials between the solutions, the migration of electrons occurs which leads to the generation of electrical energy. This leads to a different electrochemical potential, E, being developed that is associated with the chemical reactions in the respective cell. The amount of chemical change is proportional to the electricity generated as demonstrated by Nernst equation 5 [6]. Therefore the potential difference of the cell can give a measure of the number of species involved in the reaction as shown in equation 5.

This study exploited that property to investigate the number of copper ions in solution by measuring the change in potential across an electrochemical cell. The cell was made of chlorinated chicken dung leachate as an electrolyte. In the study, therefore, the aluminum electrode was used to detect when all copper (II) ions were reduced by the hydrazones in the chlorinated chicken dung leachate and none is available to oxidize aluminum. In that case, it was expected that there would be no copper ions to interact with the aluminum electrode thus no cementing. In this study unlike the work done by Ahmet and co-workers, where the aluminum disc was being corroded [4], it was observed that the corrosion of aluminum rod was minimal due to the pH of the reaction chamber. This factor reduces the cost of depletion of aluminum.

The oxide of aluminum is known to offer a protective oxide layer that creates a kinetic barrier that inhibits oxidation of aluminum. In aggressive environments that contain anions such as chloride, Cl^-, the thin oxide film is broken down and enables oxidation [8]. Aluminum oxide being amphoteric, the stable protective layer of the oxide occurs at a pH range of 7.0 to 9.0. The oxide has been found to deteriorate in chloride environments at pH region below 7 and greater than 9 [9]. On the other hand, when copper ions are introduced in the environment containing the hydrazones reducing agents, they are converted to zero-valent. [10] & [5]

The study explored the reaction chamber is maintained at a working pH above 12.0 of chlorinated chicken dung leachate and using aluminum and graphite rods as electrodes. The study involved dispersing the copper ions in a chlorinated chicken dung leachate in which sodium hypochlorite had been formed in situ. This introduces chloride radicals that inhibit the formation of the aluminum oxide layer on the aluminum rod during the reduction of copper ions formed by hydrazones. Hydrazones are simple and suitable for reducing agents in a wet chemical form. Therefore, they can be prepared by interacting ammonia, urea or chicken dung leachate with chlorine in basic media as given by equations 6 and 7 [11], [12], [13] & [5].

$$2NH_{3(g)} + NaOCl_{(aq)} \longrightarrow H_2NNH_{2(aq)} + H_2O_{(l)} + NaCl_{(aq)} \qquad (6)$$

$$(H_2N)_2CO_{(aq)} + NaOCl_{(aq)} \xrightarrow{2NaOH} N_2H_{4\,(aq)} + H_2O_{(l)} + NaCl_{(aq)} + Na_2CO_{3(aq)}$$

(7)

Hydrazine produced in equations 6 and 7 is found to react further with alkanones and hydrazones to form other forms of hydrazones which are also strong reducing agents as shown in equations 8 and 9 [14].

$$2(CH_3)_2CO_{(aq)} + N_2H_{4(aq)} \rightarrow 2H_2O_{(l)} + [(CH_3)_2CN]_{2\,(aq)} \qquad (8)$$

$$\left[\left(CH_3\right)_2CN\right]_{2(aq)} + N_2H_{4(aq)} \xrightarrow{100^oC} \left[\left(CH_3\right)_2CHNNH_2\right]_{2(aq)} \qquad (9)$$

The reduction potential of hydrazine in a basic environment occurs as shown in equation 10.

$$N_2H_{4(aq)} + 4OH^-_{(aq)} \longrightarrow N_{2(g)} + 4H_2O_{(l)} + 4e^- \qquad E^0 = +1.15V \qquad (10)$$

Hydrazones are known to reduce some metal ions to elemental state as shown by equation 11 [7] & [5].

$$Cu^{2+}_{(aq)} + 2N_2H_{4(aq)} + 2OH^-_{(aq)} \longrightarrow Cu_{(s)} + N_{2(g)} + 2NH_{3(g)} + 2H_2O_{(l)} \qquad (11)$$

Nitrogen in chicken dung is found in the form of amide bound protein, amino acids, or other forms of organic compound [15], [16], [17] & [5]. In this study, amide and amino acid compounds were obtained from decomposed chicken dung. The dung was used to prepare the electrolyte as a reducing agent for copper ions in an electrochemical cell and aluminum rod acted as an indicator for the redox process.

2.0 Materials and Methods

Analytical grade sodium hydroxide, hydrochloric acid, hydrazine, chlorine gas, starch, nitric acid, boric acid, and deionized water were supplied by Kobian (K) Ltd, an outlet of Sigma Aldrich Company. These chemicals were used to make all the solutions used in this study. Aluminum was procured from East African Cables Company. Chicken dung was obtained randomly from local poultry farmers from Thika in Kenya. Mineral rocks were obtained from Maragwa location in Tharaka North Sub - County in Tharaka Nithi County at locations 0°18'S38°8'E and 0°21'S38°11'E from three quarries which were about 1.5 kilometers from each other. The three quarries were coded as 3230, 3234 and 3238. From each place, one kilogram of mineral rock was collected at a depth of 30 cm and 100 cm below the ground surface level respectively. The samples were packed in plastic bags labeled 3230A, 3234A, and 3238A. Another set of samples was obtained at about 100 cm depth (level B) and labeled as 3230B, 3234B and 3238B. The samples were then transported for analysis. The ore samples from each site were dried at 105 °C for 9 hours in an oven. The dry samples were pulverized to 250 micro millimeters size and used for XRD, AAS and XRFS analysis.

3.1 Mineralogical and Chemical Analysis

Mineralogical analysis of the samples was carried out using X-ray diffraction (XRD) and chemical composition was carried out using atomic absorption spectroscopy (AAS) and X-ray fluorescence spectroscopy [18]&[5].

3.2 Copper leachate

To obtain copper leachate, 100.0 ml of 1.0 M of HCl was added into a 200-ml beaker containing 5.0 g of the mineral sample. The content was stirred and left to react for 3 hours. The samples were filtered using Whatman filter paper number 110 mm. The residue was washed using distilled water and the filtrate transferred into a 100 ml volumetric flask and made to the mark using distilled water [5].

3.3 Preparation of chicken dung leachate

1 kg of chicken dung was placed in a desiccator. 2000 ml of water added and stirred for 5 minutes to ensure a uniform mixture was achieved. The content was covered and left to equilibrate for 15 days. The contents were filtered using 300-micron sieve to obtain the chicken dung leachate. To 100 ml of chicken dung leachate, chlorine gas was bubbled into at a flow rate of 0.5 - 0.7cm^3 per second for three minutes to form chlorinated chicken dung leachate [5].

3.4 Characterization of chicken dung leachate

The chicken dung leachate was characterized using the FT-IR spectrophotometer model Alpha 1005 4238 from Bruker. The instrument was initialized and calibrated by conducting a background scan. The resulting background spectrum was compared to a reference spectrum provided in the manufactures manual. The hydrazine hydrate solution was injected into a liquid cell for analysis the same manner samples of chicken waste leachate were done. A comparison of the absorption bands obtained in the spectra of the sample chicken waste with that of the hydrazine hydrate was used for data interpretation.

3.5 Reduction of copper

100 ml of copper leachate solution was introduced into a 500-ml beaker (cell 1) containing 100 ml of chlorinated chicken dung leachate solution. The initial pH and temperature of the resulting solution were taken. The content was allowed to react until all copper ions were reduced. At the same time, a second cell containing 100 ml of the chlorinated chicken dung leachate was done. A clean aluminum electrode of the thickness of 0.4 cm was weighed and introduced into cell 1 and then connected to a digital multimeter (model 6000 Counts TRMS from Neoteck Company). The meter was then externally connected to a graphite electrode in cell 2 using a copper wire. The two cells were then connected using another copper wire with two graphite electrodes in each cell as shown in Figure 1. The reaction was monitored until no further displacement of copper on the electrode was observed. The copper obtained was filtered and dried in the oven at 40°C. The dry extract was weighed and the percentage calculated from the original mass of the ore. The copper extract was later analyzed using XRFS for the percentage purity. The aluminum rod was reweighed after every experiment and results recorded.

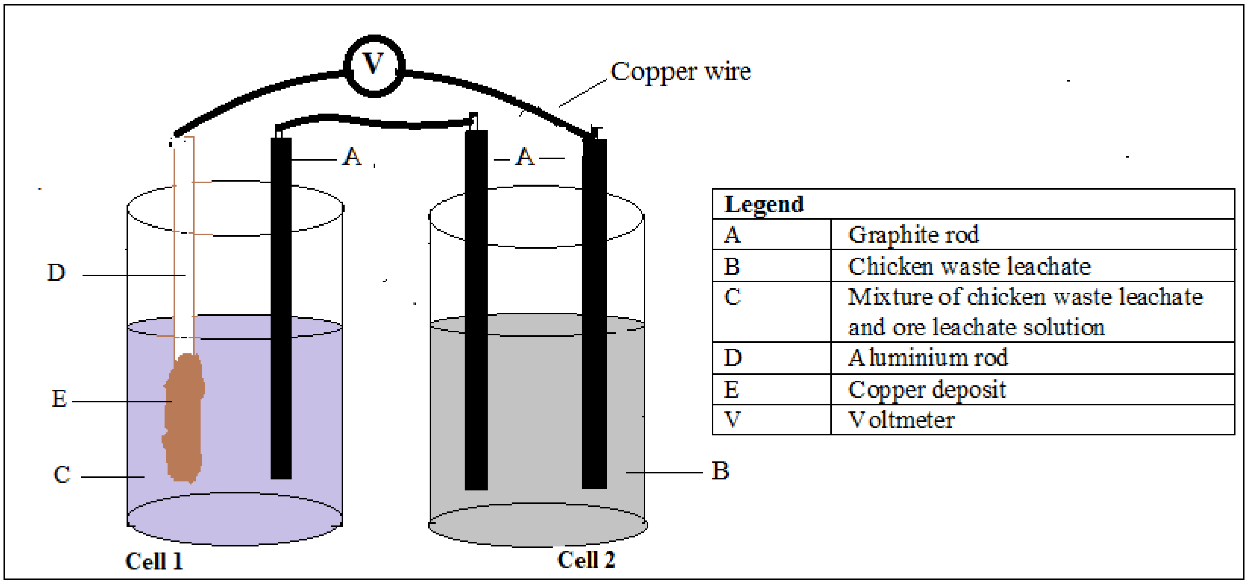

Figure 1: Diagrammatical presentation of an electrochemical cell

3.6 The pH optimization

The procedure 2.5 was repeated by adjusting the pH values in both cells from 4.0 to 14.0 using 1.0 M NaOH at an interval of 2. The temperature of the solutions was maintained at room temperature of 28^oC during the reaction. The resulting precipitates obtained were filtered and dried in the oven at 40^oC and later analyzed using XRFS.

3.7 Temperature optimization

Procedure 2.5 was repeated while varying the temperature from 30 to 70^oC at an interval of 10. The pH was maintained at the optimized value of 12.0. The resulting copper precipitates at every varied temperature were filtered and dried in the oven at 40^oC and later analyzed using XRFS. The aluminum rod was reweighed at the end of every experiment and the difference obtained was recorded.

3.8 Rates of copper ions reduction

Procedure 2.7 was repeated by measuring the change in potential against the time taken. The volume of the chicken dung leachate used remained as 100 ml. The pH was maintained at 12. The voltage produced by the cell was recorded for 150 minutes at an interval of 25 minutes. The copper produced at every time interval was filtered and dried in the oven at 40^oC and later analyzed using XRFS.

4.0 Results and Discussion

4.1 Mineralogical and Chemical Composition

The results for mineralogical analysis are as presented in Figure 2.

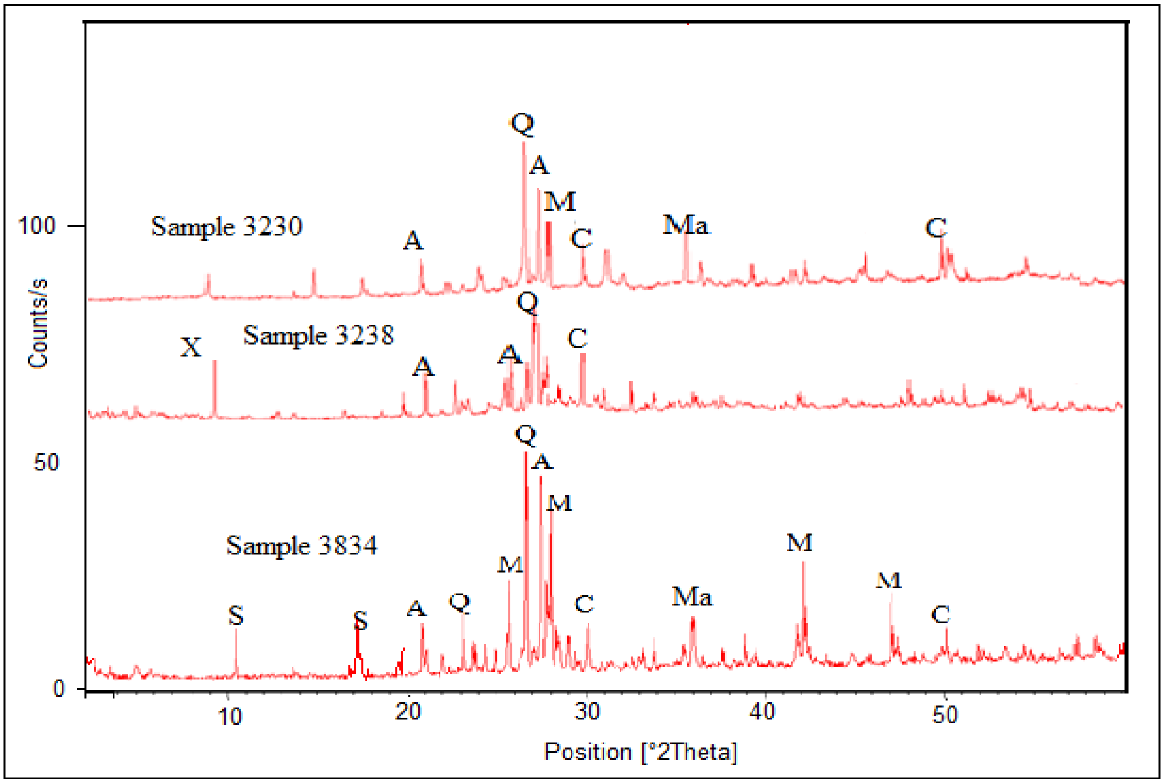

Figure 2: Minerals found in sample 3234, 3238 and 3230.

From figure 2; A- represent Albite, C – Chalcopyrite, Q – Quartz, M – Microcline, Ma – Magnetite, X – Magnesiohornblende, S – Sodium praseodymium sulphite.

The results show that the deposits contain chalcopyrite mineral ($CuFeS_2$), as evidenced by a peak at an angle 2θ of 30° and 50°), albite (angle 2θ of 27.5 °, 21 °, and 24.5°) and quartz (angle 2θ of 27.0 ° and 23.0 °) However various mineral deposits have different mineralogical composition. For instance, Magnetite (angle 2θ of 35.5 °, 63° and 43.5 °) and microcline (angle 2θ of 27.5 °, 42.0 °, and 50.5 °) were found in sample 3834 and 3230. Sodium praseodymium sulfite mineral (angle 2θ of 10.5 °, 17.5 °, and 19.8 °) was only found in sample 3834. This shows that mineral deposits in Tharaka North Sub County have varied mineral composition. Chemical composition was carried out on the samples and the results given in Tables 1 and 2. Statistical analysis of the two methods was done and the results given in table 3.

Table 1: Chemical composition of the mineral ores at level A and B analyzed using AAS

Oxides Sample Reference	SiO_2 Mean± SE	Al_2O_3 Mean± SE	K_2O Mean± SE	Na_2O Mean± SE	CaO Mean± SE	TiO_2 Mean± SE	MnO Mean± SE	Fe_2O_3 Mean± SE	Cu Mean± SE	CuO Mean ± SE	MgO Mean± SE
3230 A	41.53	8.16	7.69	12.81	2.28	1.00	0.11	3.81	9.60	12.00	5.81
3230 B	37.53	6.28	6.95	13.75	5.00	0.98	0.17	4.39	7.16	8.95	6.91
3234 A	35.86	3.56	0.69	12.15	23.67	0.66	0.27	13.13	1.96	2.45	4.12
3234 B	34.84	2.84	1.00	8.39	18.4	0.45	0.31	19.80	1.58	1.97	5.14
3238 A	42.44	10.79	2.68	13.15	10.63	1.70	0.33	10.06	4.43	5.54	1.93
3238 B	45.86	7.26	4.38	17.75	11.05	1.58	0.35	5.46	6.61	8.26	3.67

Table 2: Chemical composition of the mineral ores at level A and B analyzed using XRFS

Oxides Sample Reference	SiO_2 Mean ±SE	Al_2O_3 Mean ±SE	K_2O Mean ±SE	Na_2O Mean ±SE	CaO Mean ±SE	TiO_2 Mean ±SE	MnO Mean ±SE	Fe_2O_3 Mean ±SE	Cu Mean ±SE	CuO Mean ±SE	MgO Mean ±SE
3230 A	41.58	8.18	7.76	12.89	2.28	1.01	0.11	3.82	9.66	12.07	5.85
3230 B	36.6	6.24	6.95	13.84	4.90	0.96	0.13	4.35	7.19	8.94	6.89
3234 A	35.87	3.59	0.69	12.13	23.67	0.61	0.20	13.09	1.93	2.41	4.16
3234 B	34.3	2.85	1.04	8.37	18.4	0.46	0.36	19.82	1.59	1.97	5.17
3238 A	42.47	10.78	2.71	13.08	10.61	1.71	0.52	10.07	4.40	5.51	1.84
3238 B	44.9	7.24	4.13	16.95	11.17	1.56	0.33	5.44	6.60	8.25	3.61

Table 3: Statistical analysis of the means of AAS and XRFS methods at 95% confidence level

	SiO_2 Mean ±SE	**Al_2O_3 Mean ±SE**	**K_2O Mean ±SE**	**Na_2O Mean ±SE**	**CaO Mean ±SE**	**TiO_2 Mean ±SE**	**MnO Mean ±SE**	**Fe_2O_3 Mean ±SE**	**Cu Mean ±SE**	**CuO Mean ±SE**	**MgO Mean ±SE**
Mean using AAS	39.67± 1.75^a	6.48± 1.21^a	3.89± 1.21^a	13.0± 1.23^a	11.84± 3.28^a	1.06± 0.20^a	0.25± 0.04^a	9.45± 2.55^a	5.22± 1.28^a	6.52± 1.6^a	4.59± 0.71^a
P-Value using AAS	4.498	3.103	3.116	3.153	8.43	0.519	0.1	6.55	3.298	4.123	1.836
Mean Using XRFS	39.28± 1.74^a	6.48± 1.2^a	3.88± 1.21^a	12.87± 1.13^a	11.83± 3.29^a	1.05± 0.20^a	0.28± 0.06^a	9.43± 2.55^a	5.23± 1.29^a	6.53± 1.62^a	4.59± 0.73^a
P-Value Using XRFS	4.468	3.091	3.118	2.909	8.454	0.523	0.165	6.552	3.324	4.152	1.872

The values of the mean given with superscript "a" against each column show that there is no significant difference in results obtained using AAS and XRFS methods. This shows that any of the two methods can be used for the analysis of the samples. The p-values obtained from the two methods show no significant difference in mineralogical composition from the three quarries ($p>0.05$ at 95% confidence level). The results show well-distributed minerals in all quarries and their composition varies with the depth geologically. The percentage composition of Cu in samples 3230 3234 and 3238 ranges from about 2 and 10%. These compositions are better than those from the ores mined from other countries. For instance, Chile is one of the largest copper producers from ores containing 0.4 - 1.0 percent copper [19]. In Zambia, all copper mines contain an average ore composition of 0.5 to 2.3 percent copper [22]. In East Africa**,** copper mining has been going on in Uganda since the 1950s to 1980s from ores with compositions ranging between 0.48 to 2.0 percent Cu [20]. From this observation, it implies that ores from Tharaka Nithi County are viable for economic extraction. Since these copper deposits are yet to be exploited economically, this study investigated a possible alternative method for the extraction of these minerals. The method investigated was the one that could minimize impurities of silica, alumina, iron, and calcium which are the dominant impurities in the ore.

4.2 Synthesized hydrazones

The chicken waste samples were studied to show the presence of the various functional groups. The results from FTIR-characterization of the unchlorinated and chlorinated chicken waste leachate were as presented in figure 3 [5].

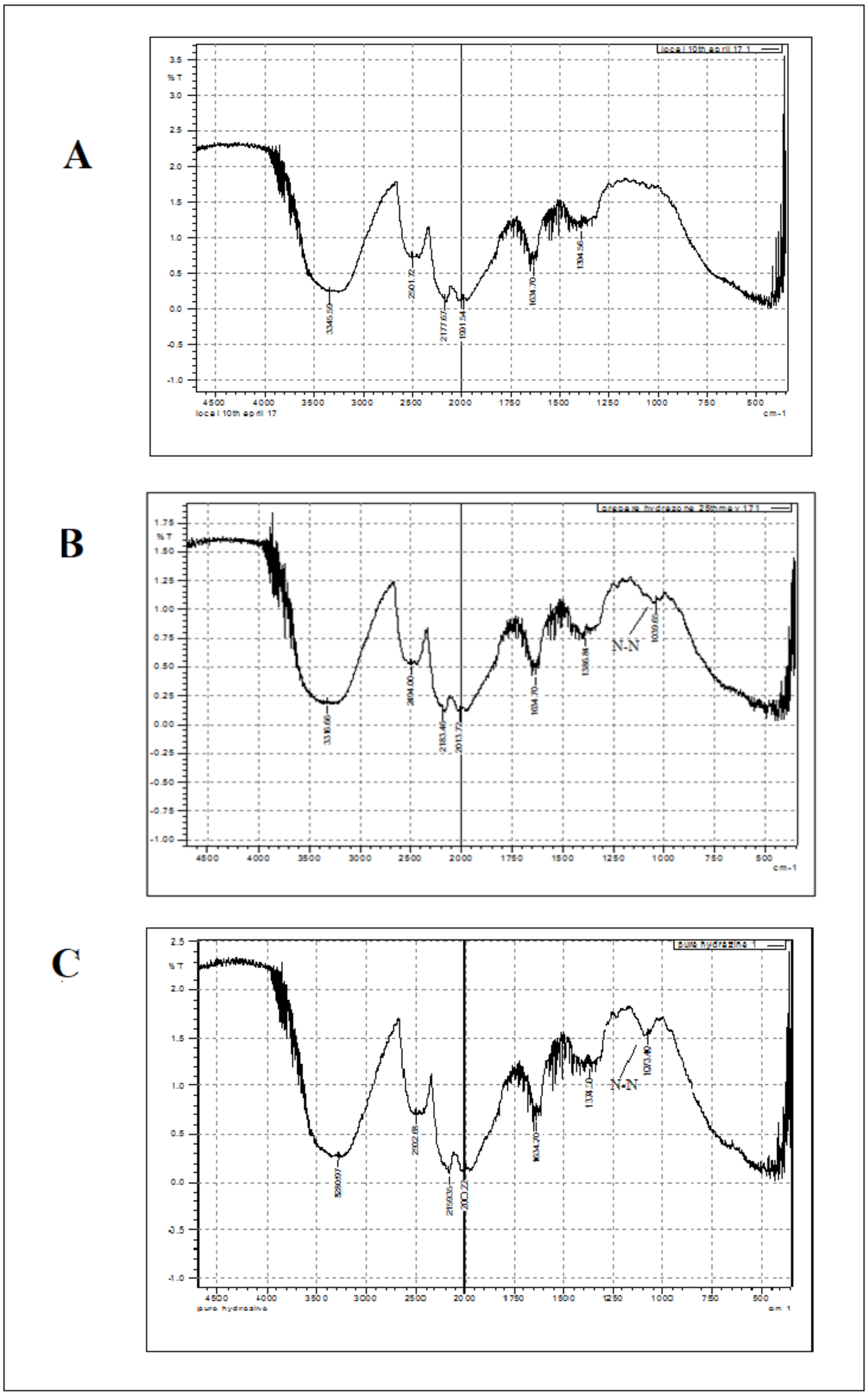

Figure 3: FTIR Spectra (A) before and (B) after chlorination and (C) hydrazine samples

The results show that before chlorination, the chicken waste samples contain OH, 1°&2°NH (amines), and C-H groups due to the bands found within the range from 3000 and 3500 cm^{-1}, SH group at 2494.9 cm^{-1}, carbonyl group stretching at 1634 cm^{-1}, CN triple bond stretch at 2100 cm^{-1}, and CH group are found at 1355 cm^{-1}. The spectra show that the same functional groups were found in pure hydrazine hydrate solution that was available in the chlorinated sample solutions. Before chlorination, the spectrum of chicken waste has no peak at around 1090 – 1020 cm^{-1}. However, after chlorination, a signal appeared at 1080.16 cm^{-1}, at the same position as that found in the hydrazine sample. The emergence of that band at 1080.16 cm^{-1} could be due to induced vibration excitation of N-N covalent bonds [21]&[5]. This shows that a reducing agent either symmetrical or unsymmetrical hydrazones were produced [13]. Since C=O and NH_2 groups are found in amines and amides compounds, then the same compounds are found in chicken waste solution. These compounds are potential sources for making hydrazones when reacted with suitable oxidizing agents as shown in equation 12 [3]&[5].

$$Cl_{2(g)} + 2NaOH_{(aq)} \xrightarrow{70°C} NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(l)} \quad (12)$$

The produced sodium hypochlorite oxidizes amines and amides to hydrazones as given in equation 13[12] [14]&[5].

$$2NH_{3(g)} \xrightarrow{NaOCl} H_2NNH_{2(aq)} + NaCl_{(aq)} + H_2O_{(l)}. \quad (13)$$

4.3 Copper Reduction and Oxidation of Aluminium

The results on the effect of pH on the relationship between the reduced copper and sacrificed aluminum are presented in figure 4.

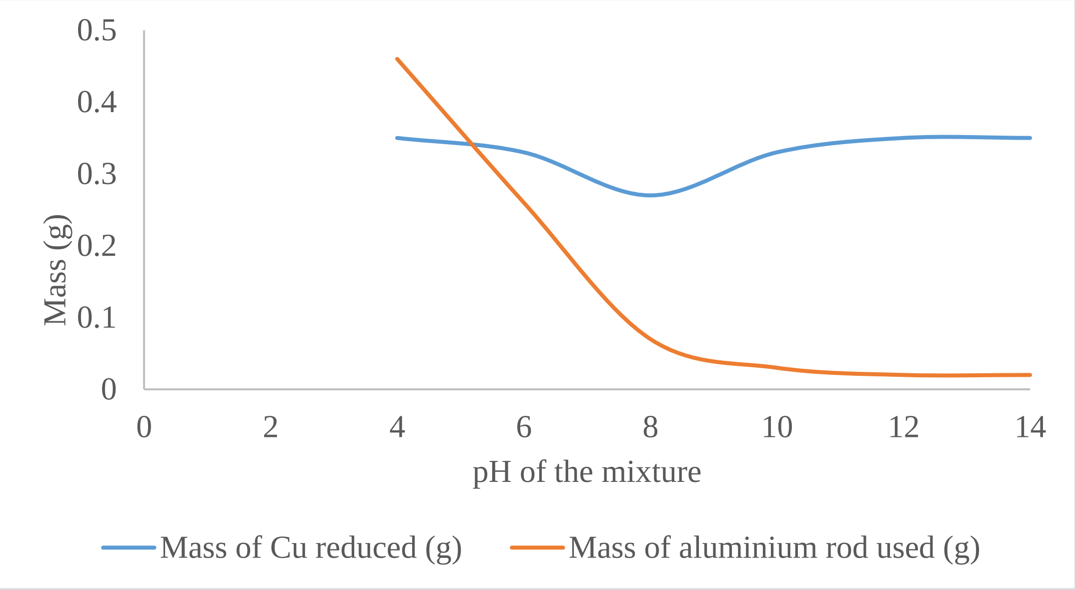

Figure 4: Effect of pH on the reduction of copper and oxidation of aluminum

The results show that at pH values 6.5 - 9.0, there was a decrease in the mass of copper obtained. This is because, at that pH environment, the oxide of aluminum on the aluminum electrode is stable thus reducing its deterioration. Also, there were no significant hydrazones produced for the reduction of copper ions. The mass of aluminum sacrificed is high in a strongly acidic environment due to both displacements of copper and hydrogen ions in solution. At pH values below 6.5, the copper reduction is as a result of oxidation of aluminum. Even when all copper ions have been reduced, aluminum continues to undergo oxidation. This is due to the presence of hydrogen ions in the solution. This explains why aluminum corrodes at low pH and the rate of corrosion decreases with an increase with the pH. Above the pH value of 11, all the copper ions are reduced by hydrazones as shown in equation 14.

$$N_2H_2R_{2(aq)} + 4OH^-_{(aq)} + 2Cu^{2+}_{(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)} + 2ROH_{(aq)} + 2Cu_{(s)} \tag{14}$$

From figure 4, there is little or no corrosion of aluminum electrode yet displacement of copper occurs on the electrode as shown in equations 15 and 16.

$$Al_{(s)} \rightarrow Al^{2+}_{(aq)} + 3e^- \tag{15}$$

$$Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \tag{16}$$

Oxidation of hydrazones in the alkaline environment is known to occur as shown in equation 8. Therefore the produced hydrazones in cell 2 will occur the same way thus providing with electrons that recharge the oxidized aluminum electrode as shown by equations 17 and 18 [5], [10] & [11].

$$N_2H_2R_{2(aq)} + 4OH^-_{(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)} + 2ROH_{(aq)} + 4e^- \tag{17}$$

(Where R is an alkyl group or halogen group)

$$Al^{3+}{}_{(aq)} + 3e \rightarrow Al_{(s)} \tag{18}$$

This explains why the aluminum electrode does not corrode. This property of the aluminum electrode makes it an indicator of the presence of copper ions during the redox process. Other reactions that occur in the electrodes are as follows; the hydroxide ions in cell 1 migrate to the graphite electrode where they undergo oxidation on as shown in equation 19.

$$4OH^{-}_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^{-} \quad (19)$$

The produced electrons flow to the next graphite electrode (cell 2), where they reduce available hydrogen ions from the solution to hydrogen gas as shown in equation 20.

$$4H^{-}_{(aq)} + 4e^{-} \rightarrow 2H_{2(g)} \quad (20)$$

The produced hydrogen gas is immediately oxidized to water by sodium hypochlorite in the electrolyte, equation 21.

$$H_{2(g)} + NaOCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \quad (21)$$

The graphite bridge was created to ensure a balanced flow of ions in chicken waste solution, as well as that of electrons in the cells.

4.4 Effect of temperature on the reduction of copper

The effect of temperature at the optimal pH value of 12.0 was investigated and the results obtained recorded in figure 5.

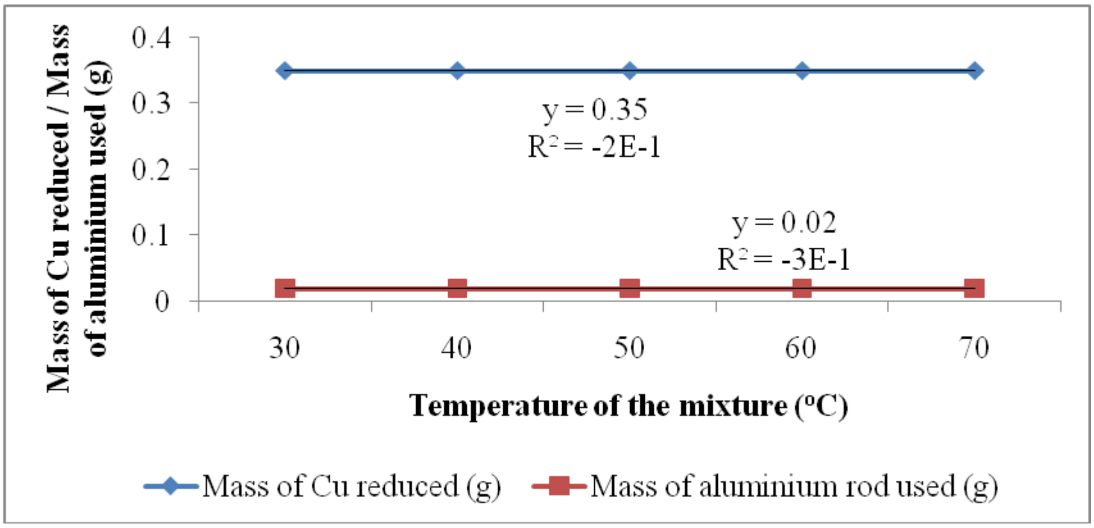

Figure 5: Relationship between temperatures, copper reduced and mass of used aluminum

The results of the regression analysis from the two curves show that r^2 is less than 0. The reaction shows that change in temperature of chlorinated chicken dung leachate has no effect on the reduction of copper ions and oxidation of aluminum at a pH greater than 12. The hydrazones in the chicken dung leachate react with all copper (II) at a given temperature to zero valences. An increase in temperature though increases the collision energy of hydrazones with copper (II), the total mass of copper produced remains the same. An increase in temperature did not influence an aluminum electrode.

4.5 Relationship between rates of copper ions reduction with potential

The relationship between the rates of copper ion reduction against the potential produced by the reaction was investigated and results given in figure 6. In the same figure 6, a plot of the amount of copper produced with time was given.

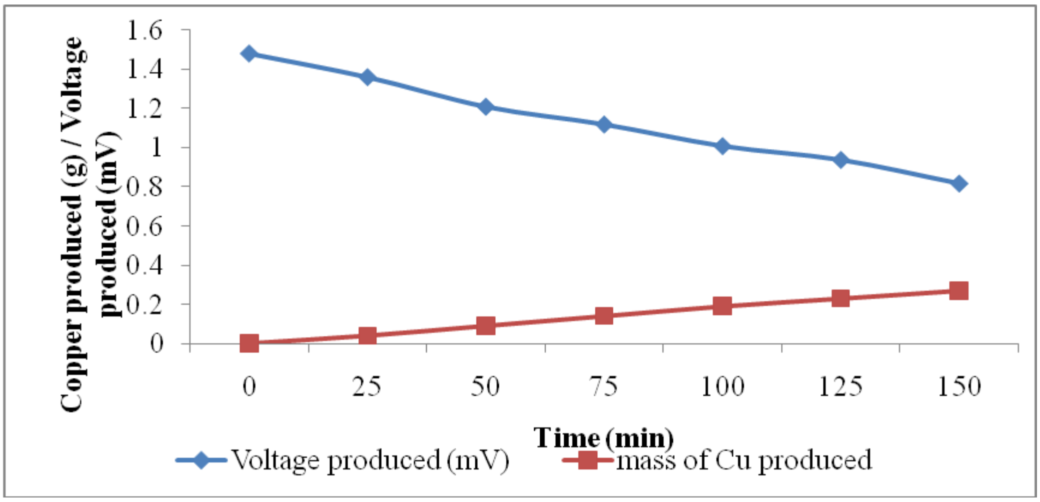

Figure 6: Effects of potential on time.

Based on figure 6, the time taken for the complete reduction of Cu ions by hydrazones in the leachate mixture is inversely proportional to the potential produced by the reaction. This follows the first-order reaction where there is a decrease in the concentration of copper ions in the chicken dung leachate with an increase in time as shown in equation 22.

$$\text{Rate} = {}^{-\,d[A]}\!\big/_{dt} = k[A] \qquad (22)$$

The "rate" is the reaction rate (in units of molar/time) and *k* is the reaction rate coefficient (in units of 1/time) [24]. The potential obtained also decreases with a decrease in the concentration of copper ions with time. In other words, the higher the concentration of copper ions in solution, the higher the potential produced during the redox process. Since in the cementation process, the reduction of copper ions and oxidation of aluminum metal occurs as given by equations 1 and 2 above, the high positive potential difference creates a spontaneous redox reaction. Therefore the chlorinated amine and uric acid in chicken waste produced a current that was used to recharge the number of electrons used from aluminum during the oxidation process. The change of potential with the concentration of copper ions can be explained by equations 23, 24 and 25.

$$E - E^0 = \frac{RT}{nF} \mathrm{InQ} \Rightarrow \Delta E = \frac{RT}{nF} \mathrm{InQ} \tag{23}$$

The equation can be written as $\Delta E = \frac{RT}{nF} \mathrm{In} \frac{\mathrm{Reduced}}{\mathrm{Oxidised}}$ (24)

For this case

$$\Delta E = \frac{RT}{nF} \mathrm{In} \frac{\left[Cu^{2+}(aq)\right]}{\left[Cu^0(s)\right]} \Rightarrow \Delta E = \frac{RT}{nF} \mathrm{In}\left[Cu^{2+}(aq)\right] \tag{25}$$

This implies that as the electro process continues, the value of ΔE proportionally decreases with a decrease in Cu^{2+} ions in Cell 1(Figure 6). Eventually, when ΔE=0, no more copper ions are available for the reduction and there was no copper displacement observed on the aluminum electrode. In this method of copper extraction, the aluminum electrode becomes a suitable method of determining when all copper ions are reduced. After optimization, reduction of copper ions from the mixture of ore leachate and chlorinated chicken dung leachate was done on samples 3234, 3238 and 3230. The aluminum electrode was used to monitor when all copper ions were displaced from the leachate mixture. The results obtained are given in figure 7. The results of the statistical mean extract for both level A and B are given in table 4.

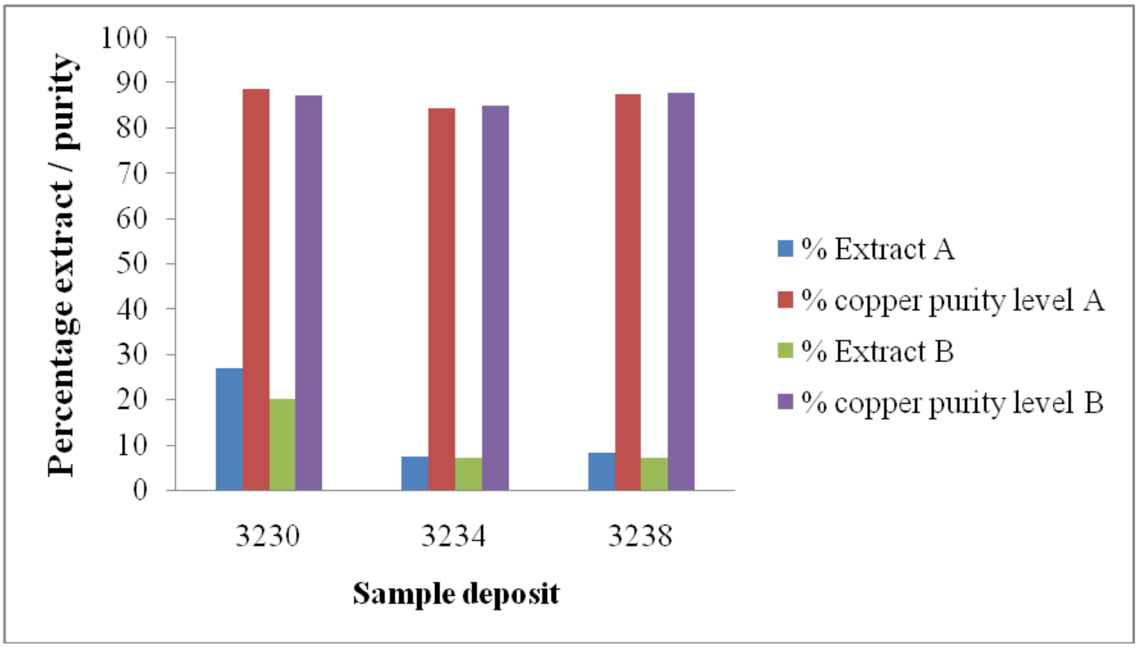

Figure 7: Percentage extract and purity of reduced copper

Table 4: Mean copper extract in both level A and B

	Mean±SE	**P-Value**
% Extract level A	0.56±0.37	0.6312
% Extract level B	0.71±0.51	0.5999

From the table, P-value was greater than 0.05. This shows that the amount of copper extract at level A and B did not differ significantly. The copper extract from the three ores ranged from 7.0 to 20.0% at level A and 7.4 to 26.8% at level B with purity range from 84.9% level A to 88.6% level B. The results show that the method of monitoring using aluminum electrode could be viable for copper extraction from ores.

5.0 Conclusion

The monitoring of copper ions reduction by hydrazones in chlorinated chicken dung leachate using an aluminum electrode was successful. In the study, there was minimal corrosion of the aluminum electrode. Therefore, further investigations on large scale production should be done for economic extraction. This will minimize the cost of using electricity for electrolysis as well as buying aluminum metal for replacement. The preparation of the chlorinated chicken dung leachate on large scale and mixing with copper leachate using the investigated ratios can be adopted and used for copper extraction from ores.

6.0 Acknowledgment

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